MAY 25 1990

DOE/PC/79817--7

DE91 005872

DIRECT CONVERSION OF METHANE TO C₂'s AND LIQUID FUELS

Seventh Quarterly Technical Progress Report for the Period April 1 - June 30, 1989

March 12, 1990

By Barbara Knight Warren; Kenneth D. Campbell;
J. L. Matherne; N. E. Kinkade
Contributions by P. H. Tate

Work Performed Under DOE Contract Number DE-AC22-87PC79817

Prepared for U. S. Department of Energy
Assistant Secretary for Fossil Energy

Industrial Chemicals Division

Solvents and Coatings Materials Division

**Union Carbide Chemical and Plastics Company Inc.
South Charleston Technical Center
South Charleston, West Virginia 25303**

Patent cleared by Chicago OPC on April 16, 1990

This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U.S. Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Chief Office of Patent Counsel, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

DOE-CH Form 383 (Rev. 6-78)

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This Report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PATENT STATUS

This Technical Report is being transmitted in advance of DOE patent clearance and no further dissemination or publication shall be made of the Report without prior approval of the DOE Patent Counsel.

Patent cleared by Chicago OPC on April 16, 1990

CONTENTS

I.	Contract Objectives	1
II.	Abstract.....	2
III.	Schedule	3
IV.	Organization	5
V.	Summary of Progress	6
VI.	Future Work	8
VII.	Technical and Experimental Results.....	9
VIII	References	83
IX.	Appendices	87
	A. Key to Tables	87
	B. Tables	89
	C. Figures	174
	D. Catalyst Compositions and Preparation Procedures	194
	E. Catalyst Preparation Procedures	195
	F. Detailed Experimental and Summary of Vapor Phase Reactions.....	202
	G. Selected Literature References, Catalysts for Methane Coupling Containing Alkaline Earth Metals.....	204
	H. Electron Microscopy and EDS Data.....	208

I. CONTRACT OBJECTIVES

Methane is expensive to transport, so it is often flared or reinjected¹. It is also a byproduct from coal gasification. Conversion of methane to liquid hydrocarbon transportation fuels in an energy efficient, economical process would represent important technology for extending natural hydrocarbon fuel reserves. One route from methane to liquid fuels involves the conversion of methane through light hydrocarbon gases rich in ethylene to liquid fuels. Other routes, including one through methanol, are considered less technologically feasible². The technological hurdle in the route through light hydrocarbon gases rich in ethylene is the direct conversion of methane to this ethylene-rich mixture. The light olefins may then, ideally, with little or no separation of products, be converted over molecular sieve catalysts to gasoline and distillates using Mobil's Olefins to Gasoline and Distillate (MOGD) Process³.

The objectives of the project are to discover and evaluate novel catalytic systems for the conversion of methane or by-product light hydrocarbon gases (from natural gas, Lurgi Dry Bottom Gasifiers, or Fischer-Tropsch processes) either indirectly (through intermediate light gases rich in C₂'s) or directly to liquid hydrocarbon fuels, and to evaluate, from an engineering perspective, different conceptualized schemes. The approach is to carry out catalyst testing on several specific classes of potential catalysts for the conversion of methane selectively to C₂ products, including metal oxide catalysts, catalysts containing metals in unusual oxidation states, and other novel catalysts and process ideas, and to provide appropriate engineering support to the catalyst design and testing effort. Promising catalysts and process ideas were to be further explored.

II. ABSTRACT

The behavior of alkaline earth/metal oxide/halide catalysts containing strontium was found to be different from the behavior of catalysts containing barium. This difference in behavior is consistent with differences in rates of transformations of alkaline earth compounds on the catalyst surface until steady-states of metal dispersion and concentrations of the various anions are reached. This explanation accounts for differences between barium and strontium catalysts and for differences among catalysts of one alkaline earth metal prepared with different anions. Electron microscopy results of fresh and used catalysts containing barium and strontium support this explanation.

Two approaches were pursued to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations. One approach was to eliminate or minimize the typical gas phase combustion chemistry and make more of the reaction occur on the surface of the catalyst by using silver. Another approach was to change the gas phase chemistry to depart from the typical combustion reaction network by using vapor-phase catalysts. Both approaches succeeded in demonstrating that these concepts to avoid the heterogeneous/homogeneous mechanism are viable. The surface contribution of the reaction was enhanced using catalysts containing silver and the vapor-phase conversion of methane to carbon oxides was inhibited by volatile metal salts.

The layered perovskite $K_2La_2Ti_3O_{10}$ was further studied. Higher than normal proportions of C_3 products were not observed in $Pd/X/\alpha$ -alumina catalysts, where X was not $SrCl_2$ or $BaCl_2$. Modifications of process and catalyst variables for $LaCaMnCoO_6$ catalysts (including doping with alkali metals) resulted in catalysts with superior performance to the parent catalyst. Results obtained with a literature catalyst Na_2CO_3/Pr_6O_{11} were better than those obtained with $NaCO_3/Pr$ -Ce oxide or Na_2CO_3/Ag -Pr-Ce oxide.

Two laboratory reactors were constructed and were used to investigate the effect of diluents, especially steam, and the effect of pressure.

Economic sensitivity studies were continued based on extrapolations of actual Union Carbide laboratory results from promising catalysts. Variables examined included reactor diluents (nitrogen, methane, and steam), methane to oxygen reactor feed ratio, and sequential feed versus co-feed process configurations.

The investments for methane and steam diluent cases and the sequential feed cases for methane coupling are all approximately equal to each other, differing by less than the $\pm 25\%$ investment accuracy. Nitrogen and steam diluent cases have higher cash cost and higher ROIAT's than either the methane diluent or the sequential feed case, due to the higher selectivity of these last two cases. The nitrogen and steam diluent cases have higher yields to C_2 's, so yield-to- C_2 's is not a good general indicator of overall process economics.

III. SCHEDULE

This program is planned as a 24-month research and development effort, from September 17, 1987 through September 16, 1989.

The contract work is composed of two tasks. Task 1 work involves the set-up of reactor equipment, the chemical investigation of novel and existing catalysts for the direct conversion of methane to light hydrocarbon gases rich in C_2 's (ethylene and ethane), and the integration of the conversion of methane to C_2 's with the conversion of C_2 's to liquid hydrocarbon fuels. Task 2 involves development of conceptual processes for converting methane to C_2 's and C_2 's to fuels, and engineering assistance to catalyst design and testing. Tasks 1 and 2 will proceed during the entire duration of the program.

In Task 1, methane coupling research on promoted metal oxide catalysts has continued with studies of alkaline earth/metal oxide catalysts, layered perovskites, catalysts containing solid solutions of Pr and Ce, bifunctional catalysts, and other complex and mixed metal oxides. Exploration of silver catalysts continued, and studies of vapor phase catalysts were initiated. Some control studies were also done, and a new laboratory reactor system was built in a third laboratory for process studies.

During the first year of Task 2, preliminary economics of a Comparison Case which uses established technologies for the conversion of methane to liquid fuels was completed to provide process performance targets (the minimum productivity and selectivity necessary) which any new catalyst must meet to be economically attractive. The economic evaluation of a hypothetical methane to ethylene case (Case 1) was reported, along with initial sensitivity studies of process variables on Case 1. Economic evaluations of several other examples of the conversion of methane directly to ethylene, based on laboratory results of a catalyst system identified in Task 1 as having potential, have been completed. These explore the effects of several major process variables on the economics of the process.

The economic evaluation of Case 2, the integration of the direct conversion of methane to C_2 's with the conversion of C_2 's to liquid hydrocarbon fuels, is complete.

During the first 15 months of the contract, the catalyst design, preparation, testing, and performance evaluation work under Task 1 was conducted by 1.8 full-time catalyst chemists and 2 full-time laboratory technicians (5 days/week, 1 shift/day) with additional part-time technical direction from the members of the technical management team and support from analytical and site services (maintenance) personnel. A third catalyst

chemist and a third laboratory technician joined the project last quarter and are pursuing process research on methane coupling.

Three engineers are involved in Task 2. Two of these are concerned mainly with process conceptualization, process integration, economic guidance, and input into the laboratory program on hydrocarbons, separations, equipment, and thermodynamics. The third is concerned with engineering assistance in the design of catalysts and reactor configurations, and in catalyst testing and interpretation of results. Thirteen man months of engineering support were planned for the duration of the contract.

IV. ORGANIZATION

Union Carbide's catalyst development, catalyst evaluation, and conceptual process design efforts for converting methane or by-product light hydrocarbon gases either indirectly or directly to liquid hydrocarbon fuels are being pursued by a group within the Solvents and Coatings Materials Division. During the initial portion of the contract, this group was part of the Engineering, Manufacturing and Technology Services Division.

The work is performed at Union Carbide's South Charleston Technical Center, South Charleston, West Virginia 25303.

Project Manager and Principal Investigator is Dr. Barbara Knight Warren.

Program Manager is Dr. Donald C. Best.

V. SUMMARY OF PROGRESS

TASK 1: Catalyst Design and Testing

Task 1 work involves the set-up of reactor equipment and the development and testing of catalysts for the direct conversion of methane to C_2 's (ethylene and ethane). Later in the contract, efforts to convert C_2 's to liquid fuels will be initiated.

In Task 1, methane coupling research on promoted metal oxide catalysts has continued with studies of alkaline earth/metal oxide catalysts, layered perovskites, catalysts containing Pr and Ce, bifunctional catalysts, and other complex and mixed metal oxides. Exploration of silver catalysts continued, and studies of vapor phase catalysts were initiated. Some control studies were done to determine the degree of enhancement of gas phase reactions by release of free radicals from the catalyst surface into the gas phase.

The behavior of alkaline earth/metal oxide/halide catalysts containing strontium was found to be different from the behavior of catalysts containing barium, which is consistent with differences in rates of transformations of alkaline earth compounds on the catalyst surface until steady-states of metal dispersion and concentrations of the various anions are reached. This explanation accounts for the observed differences between barium and strontium catalysts and for differences among catalysts of one alkaline earth metal prepared with different anions. Electron microscopy results of fresh and used catalysts containing barium and strontium support this possibility.

Two approaches were pursued to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations. One approach was to minimize or eliminate the typical gas phase combustion chemistry and make more of the reaction occur on the surface of the catalyst by using silver. Another approach was to change the gas phase chemistry to depart from the typical combustion reaction network by using vapor-phase catalysts. Both approaches succeeded in demonstrating that these concepts to avoid the heterogeneous/homogeneous mechanism are viable. The surface contribution of the methane coupling reaction was enhanced using catalysts containing silver and the vapor-phase conversion of methane to carbon oxides was inhibited by volatile metal salts.

The layered perovskite $K_2La_2Ti_3O_{10}$ was further studied. Higher than normal proportions of C_3 products were not observed in Pd/X/ α -alumina catalysts, where X was not $SrCl_2$ or $BaCl_2$. Modifications of process and catalyst variables for $LaCaMnCoO_6$

catalysts (including doping with alkali metals) resulted in catalysts with superior performance to the parent catalyst. Results obtained with a literature catalyst $\text{Na}_2\text{CO}_3/\text{Pr}_6\text{O}_{11}$ were better than those obtained with $\text{NaCO}_3/\text{Pr-Ce}$ oxide or $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ oxide.

Two laboratory reactors were constructed and were used to investigate the effect of diluents, especially steam, and the effect of pressure.

TASK 2: Process Conceptualization

Task 2 covers all of the engineering studies. It involves evaluation and development of conceptual processes for converting methane to C_2 's and C_2 's to fuels, and also includes engineering assistance to catalyst design and testing.

The Comparison Case consists of conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. The economic evaluations of the Comparison Case and of Case 1 (a hypothetical methane to ethylene case) were reported earlier^{4,5}.

Economic sensitivity studies were continued based on extrapolations of actual Union Carbide laboratory results from promising catalysts. Variables examined included reactor diluents (nitrogen, methane, and steam), methane to oxygen reactor feed ratio, and sequential feed versus the co-feed process configurations.

The investments for methane and steam diluent cases and the sequential feed cases for methane coupling are all approximately equal to each other, differing by less than the $\pm 25\%$ investment accuracy. Nitrogen and steam diluent cases have higher cash cost and higher ROIAT's than either the methane diluent or the sequential feed case, due to the higher selectivity of these last two cases. The nitrogen and steam diluent cases have higher yields to C_2 's, so yield-to- C_2 's is not a good general indicator of economics.

VI. FUTURE WORK

Future work until the end of the contract will include filing of patents, support work for patents, completion of laboratory work exploring classes of catalysts and process concepts reported, and completion of reporting requirements for Tasks 1 and 2. The contract completion date was extended from September 16, 1989 to December 31, 1989.

VII. TECHNICAL AND EXPERIMENTAL RESULTS

By B. K. Warren, K. D. Campbell, J. L. Matherne, and N. E. Kinkade

Contributions by P. H. Tate

TABLE OF CONTENTS

TASK 1: Catalyst Design and Testing	11
A. Introduction	11
1. Background.....	11
2. Approach.....	12
B. Experimental	13
1. BKW Laboratory	15
2. KLC Laboratory	20
3. NEK Laboratory.....	24
C. Results and Discussion.....	27
1. BKW Laboratory	27
a. Alkaline Earth Catalysts on Non-Alumina Supports.....	27
b. Vapor-Phase, Catalyst-Derived Free Radicals.....	41
c. Catalyst Surface Analyses.....	48
d. Avoiding the Heterogeneous/Homogeneous Mechanism.....	51
e. Silver Catalysts.....	52
f. Vapor Phase Catalysts.....	56
2. KDC Laboratory	60
3. NEK Laboratory.....	69
D. Summary	70
1. BKW Laboratory	70
2. KDC Laboratory	71
3. NEK Laboratory.....	72

TABLE OF CONTENTS (continued)

TASK 2: Process Conceptualization	72
A. Introduction	72
B. Results and Discussion.....	72
1. Nitrogen Diluent Cases.....	73
a. Process Description.....	73
b. Economics.....	74
2. Methane Diluent Cases.....	75
a. Process Description.....	75
b. Economics.....	76
3. Steam Diluent Cases.....	77
a. Process Description.....	77
b. Economics.....	78
4. Sequential Feed Cases.....	79
a. Process Description.....	79
b. Economics.....	80
5. Comparison of Different Cases.....	81
6. Support of Experimental Program.....	82
C. Summary	82
REFERENCES.....	83

VII. TECHNICAL AND EXPERIMENTAL RESULTS

TASK 1: Catalyst Design and Testing

INTRODUCTION:

Background

The mechanism proposed for the catalytic oxidative coupling of methane⁶⁻¹⁴ over metal oxides studied was discussed in previous Quarterly Reports and will be reviewed briefly here. It involves abstraction of hydrogen from methane by the catalyst to produce methyl radicals and surface hydroxyls, followed by release of the methyl radicals into the gas phase where they couple to form ethane. Methyl radicals can also be produced in the gas phase without a catalyst, by initiation on surfaces, by direct reaction with oxygen, or by cracking of higher hydrocarbon impurities in the methane. Ethane produced by catalyzed or uncatalyzed reactions may be converted to ethylene through known gas phase free radical chemistry. The sequence for the conversion of methane to ethylene is reviewed in Figure 1.

Figure 1. Methane to Ethylene Current Technology

This mechanism shows that much of the product distribution is dictated by gas phase chemistry, largely independent of catalyst, but dependent on the temperature and operating conditions. With this mechanism, one might at best approach C₂ yields of about 50% if certain reported models of the mechanism are correct¹⁵. Others^{16,17} have

proposed a yield barrier closer to 30%. Practically, literature results above a 30% yield to C₂'s are very rare, and these are probably transient results which cannot be maintained over practical periods of time.

Literature reports contain no data which indicates that the catalysts studied give stable, long-term performance. Rapid deactivation is shown in most cases. Recently, one catalyst was reported to run for over 100 hours with about a 14% C₂ yield¹⁸, but this yield is considered low, since there are many literature yields in the 18% yield range. A few metal oxide catalysts which are less volatile (e.g., Sm₂O₃¹⁹) undergo phase changes resulting in deactivation. Most frequently, catalysts lose critical components due to volatilization at the high temperatures used for methane oxidation. Catalysts containing alkali metals lose the metal salts, e.g., the lithium is lost from the Li/MgO catalyst.

The use of halides either as ingredients in methane coupling catalysts or as additives during the coupling process has become a topic of interest in recent literature. The literature and patent data relevant to halide addition, along with the conclusions presented by these sources, are summarized in Appendix G of the Fifth Quarterly Report⁴.

The reasoning for the use of halides is described in the Third²⁰, Fourth²¹, and Fifth⁴ Quarterly Reports. In these reports, stable catalyst systems were reported which exhibit high ethylene to ethane product ratios in the presence of optimum levels of added volatile chloride. Halide addition was shown^{4,21} to increase C₂ selectivity and C₂ yield through increases in the rates to C₂ products and a decrease in the rate to CO₂. Reported literature results with high ethylene to ethane product ratios are transient results (see Appendix G of the Fifth Quarterly Report⁴).

Approach

The plans at the beginning of this project were to explore simple catalyst systems which might be more active and/or stable than existing catalyst systems. Catalysts which might provide high (greater than 1) ethylene to ethane product ratios were of particular interest. Studies began with the exploration of a very simple NaCl on α -alumina catalyst (First²² and Second²³ Quarterly Reports) and proceeded in the following Quarterly Reports^{4,20,21} to alkaline earth chloride/metal oxide catalysts, which were shown to be less likely to volatilize than alkali chlorides. These alkaline earth chloride/metal oxide catalysts were shown^{4,5,20,21,23,24} to exhibit superior combinations of C₂ yields (18-24%), ethylene to ethane product ratios (2-10), and catalyst lifetimes (hundreds of hours) compared with literature catalysts.

Exploration of alkaline earth/metal oxide catalysts continued, both to understand what is unique about alkaline earth chloride/metal oxide catalysts, as well as to provide improved versions of these catalysts.

The layered perovskite, $K_2La_2Ti_3O_{10}$, was identified in the Third Quarterly Report²⁰ as a good methane coupling catalyst, and studies of this catalyst were continued to determine the long term stability of the catalyst, the effects of using methane as the diluent gas, and the effects of adding CO_2 or ethyl chloride (ECI) in the feed gas.

A study of the abilities of bifunctional catalysts to oxidatively couple methane initiated during the fourth quarter was continued. Experiments were carried out to see if the substitution of other halides for $SrCl_2$ in the $Pd(NO_3)_2/SrCl_2/\alpha$ -alumina catalyst would result in the high C_3 selectivities observed with $SrCl_2$, or enhance the catalytic results.

Oxygen carriers consisting of oxide solid solutions of praseodymium and cerium²⁵ (and these compounds with silver) were prepared and tested as methane coupling catalysts as reported in the Sixth Quarterly Report⁵. For undoped materials, high activities but low C_2 selectivities (<20%) were observed in the temperature range of 550 to 750 °C in the cofeed and sequential modes. In the Sixth Quarterly Report⁵, Na-doping (Na_2CO_3) of the catalysts resulted in decreased activities but enhanced C_2 selectivities in the cofeed mode. Further studies of interest on these materials were the effects of changing the reactant composition ($CH_4/O_2/N_2$ ratio) and the GHSV. For comparison, a literature catalyst, Na_2CO_3/Pr_6O_{11} , was made and tested.

Two tubular reactors were designed and constructed. These reactors are being used to study the effect of process conditions, specifically, the effect of diluents and pressures greater than 20 psig, on the methane coupling reaction in the presence of a barium on α -alumina catalyst.

EXPERIMENTAL:

Catalyst tests carried out under this contract are assigned notebook ID numbers which identify the appropriate researcher and the notebook reference of the experiment. Codes including KDC indicate that work is done in the KDC laboratory. Codes including BKW indicate that work is done in the BKW laboratory. Codes including the letters NEK indicate that work is done in the NEK laboratory. The laboratory reactor systems for BKW and KDC reactor systems are illustrated in Figure 1 of the Second Quarterly Report²³, Figure C1 of Appendix C, and Figure 4 of the Fourth Quarterly Report²¹, and

analytical procedures for these two laboratories are described in the Experimental Section, Tables 1-9, and Figures 3 and 4 of the Second Quarterly Report²³.

Linde oxygen, nitrogen, air, and ultra high-purity methane are used in all experiments unless noted otherwise. CP Grade ethyl chloride from Linde at 2% by volume is mixed in methane by Union Carbide's Automated Analytical Systems Gas Mixing Laboratory. Quartz wool is obtained from Alltech Company, and quartz chips are obtained from either National Scientific or Thomas Scientific.

The reactor systems for catalyst testing in KDC and BKW laboratories consist of gas feed-mix systems, steam feed systems, tubular reactors, Lindberg tube furnaces, liquid collection vessels, and gas analyzers connected directly to the product streams. The reactor system for the NEK laboratory is described below in the NEK Laboratory section. Reactions coded with BKW are run at about 11 psig (176 kPa). Reactions coded with KDC are usually run at 5 psig (135 kPa). Reactions coded with NEK are usually run at pressures of 3 to 20 psig (122 to 239 kPa).

In both KDC and BKW laboratories, the gas mixtures entering and exiting the reactor system are analyzed by gas chromatographic methods (vpc) using Hewlett-Packard Model HP-5880A gas chromatographs equipped with thermal conductivity detectors. Ultrapure helium is used for vpc analyses. Calibrations are done in the HP ESTD mode using calibration gases (Tables 5 and 9 of the Second Quarterly Report²³) prepared by Union Carbide's Automated Analytical Services group. Injections of calibration gases, product streams, and reactant streams are accomplished using a Valco valve with a fixed volume sample loop. Details of the analytical procedures may be found in the Experimental Section, Tables, and Figures of the Second Quarterly Report²³. In both KDC and BKW laboratories, the components analyzed include methane, oxygen, nitrogen, ethane, ethylene, propane, propene, carbon monoxide, and carbon dioxide. Analyses for C₄'s is not necessarily carried out unless there are large amounts of C₃'s. Carbon balance calculations indicate that other hydrocarbon products and oxygenates are not present in significant quantities; thus, analyses of heavier hydrocarbons and oxygenates are not performed during these screening experiments. However, analyses for heavier hydrocarbons and oxygenates will be carried out in the future by gas chromatography coupled with mass spectrometry.

The numbers from the ESTD mode from reactant streams are used as read from the vpc. The numbers as read from the vpc for product components are adjusted to correct for volume changes by multiplying by nitrogen in the reactants divided by nitrogen in the products. The Key in Appendix A shows how these numbers are used.

Pore size distributions were measured by the BET method with a Micromeritics ASAP-2400 instrument. Analyses of percentages of various elements were accomplished by ICP. Heavier hydrocarbons and oxygenates were analyzed by gas chromatography coupled with mass spectroscopy, and by gas chromatography coupled with ir. These were not present in significant amounts.

BKW Laboratory

For all BKW laboratory results described in the Results and Discussion Section below, or in Tables and Figures, Appendix D describes catalyst compositions for catalysts other than those used in the vapor phase experiments, and the Experimental Section and Appendix E describe catalyst preparation procedures. Appendix F described catalysts and details of conditions for vapor phase experiments. The key to abbreviations used in Tables or Figures, and to terms used in the Results and Discussion Section appears in Appendix A. Activity refers to methane conversion.

For those catalysts prepared from adding components, these are generally high purity (99.99+) components added by procedures described in Appendix E. Sources of materials are also described in Appendix E.

The main reactor system in the BKW laboratory (Figure 1 of the Second Quarterly Report²³) contains two parallel reactors which may be fed with a variety of gases. It consists of a gas feed system, two tubular microreactors (a steam feed system to one of these), two Lindberg tube furnaces, two liquid collection systems, an on-line gas analyzer with a stream selector, and a separate liquids analyzer. All the lines to the reactors are made of 1/8" and 1/4" SS tubing unless otherwise stated. The tubular reactors are operated outside the hood behind a safety shield.

All experiments this quarter in the BKW laboratory are done in the cofeed mode where methane and oxygen are simultaneously fed. The balance gas is nitrogen, and in some cases, ethyl chloride is fed in parts per million (from a mixed gas containing ethyl chloride and methane). Methane, oxygen, nitrogen, and other gases are fed through a feed system in which flow rates of gases are controlled by Brooks mass flow meters. System pressure is controlled with a Grove back pressure regulator. The Grove regulator sends excess gases to a vent in the hood. The system is designed so that gas ratios may be set independently by adjusting components flow rates. Pressures (controlled by GO Regulators after the reactors and collection pots), and flow rates may be easily and independently changed for each reactor. Relief valves are present between the gas regulators and the Brooks mass flow meters. A relief valve (vented to the hood) set at 25 psig is installed immediately before each quartz reactor so that the pressure in

the reactor cannot exceed 25 psig. Low flow switches after the reactors and before the liquid traps activate an emergency shut down system which passes nitrogen over the reactors and turns off heaters if there is a leak or plug in the reactor.

Two Lindberg Mini-Mite, model 55035 tube furnaces (800 watts, 115 volts, 1100 °C maximum operating temperature) are used for heating the tubular microreactors. The entire cylindrical heated chamber is comprised of two halves, with a split-hinge furnace design. Each half of the furnace is a composite unit of a high temperature ceramic fiber insulation, and a helically coiled alloy heating element. The furnaces are equipped with a chromel-alumel (type K) thermocouple (centrally positioned within the heated region) which is used to measure the temperature of the furnace. The heated region is 31 cm long and the hottest point is 2 cm above the center of this region. Athena temperature controllers are used to control the furnace temperatures. The temperature controllers have built-in overtemp devices which turn the furnace off when the operating temperature exceeds the set temperature by 80 °C.

Two cold traps, cooled with a circulating cooling fluid (50/50 mixture of propylene glycol and water) pumped through coiled copper tubing by a Haake A81 refrigeration unit, are used in parallel for each reactor so that one cold trap can be removed and sampled while the other one is collecting product. These traps are located after the reactor outlet (after the low flow switches) and before the reactor back pressure regulator. Another trap is present in the line after the back pressure regulator. This third trap is not cooled.

Compounds which are not trapped are analyzed on an HP 5880A vpc equipped with a thermal conductivity detector and column switching (including a molecular sieve column), utilizing four Valco valves and a 10-port stream selector, programmed to operate from the HP 5880A keyboard. Initial and final column temperatures of 85 °C and 170 °C are used for the analyses. Details of the analytical procedures may be found in the Experimental Section, Tables, and Figures of the Second Quarterly Report²³. Feed streams are periodically analyzed before, during, and after runs. Analyses of trapped liquids by gc-ms indicate only water. The water is acidic (<pH 3) by litmus paper. By ir, traces of carbonyls are detected.

Thermocouples, heating tape, and glass insulating tape are present on the steam feed system and lines before and after the reactors. Brooks mass flow meters are calibrated in place. Quartz tubing used in the construction of reactors is obtained from National Scientific Company.

A diagram of the reactor system used for vapor phase experiments is shown in Figure C1 of Appendix C. Catalysts are evaluated using a 77 cm long quartz reactor (Reactor V, Figure C2 of Appendix C) operated vertically and heated by two ovens stacked vertically, to provide two distinct temperature zones for the top and bottom portions of the reactor (see Figure C3 of Appendix C). The reactor system consists of a gas feed system, a liquid collection systems, an on-line gas outlet gas analyzer, and a separate liquids analyzer. Lines to the reactors are made of 1/8" and 1/4" SS tubing. Flexible stainless steel or polyethylene lines are used immediately after the reactor before a low flow switch. Lines to and from the reactor are connected by metal to quartz tubing to quartz O-ring connectors, which are connected to the quartz reactors. The reactor is operated outside of hoods behind a safety shield.

The quartz reactor is 77 cm long, constructed of 1.5 cm i. d. quartz tubing (1.7 cm o. d.). A 1.5 cm i. d., 1.7 cm o. d. quartz tube is attached to the outer tube from 4.5 cm below the top of the reactor to 39 cm below the top of the reactor. Oxygen and nitrogen enter the reactor through this inner tube and mix with methane in the upper part of the bottom reactor, 39 cm below the top of the reactor. Immediately below the point where the inner and outer tubes are joined, the methane inlet of the reactor is connected at a right angle to the reactor. It is constructed of 1.0 cm i. d. (1.2 cm o. d.) quartz tubing, with a quartz "O"-ring joint (0.9 cm i. d.). All quartz tubing used in the construction of the reactors is obtained from National Scientific Company. The "O"-ring joints are supplied by Quartz Scientific Inc. The joints are connected using FETFE "O"-rings obtained from Ace Glass Incorporated. The "O"-ring joints are supplied by Quartz Scientific Inc. The methane enters the methane inlet and proceeds between the inner and outer tubes to the point 39 cm below the top of the reactor, where it mixes with the oxygen and nitrogen mixture. A cup is constructed from 0.9 cm i.d., 1.1 cm o.d. quartz tubing which is 5.5 cm long. It is open at the upper end and closed at the lower end. The top of the cup is 16.5 cm below the top of the reactor, centered inside of the inner tube in the top part of the reactor, held (fused) by several small pieces of quartz. The cup holds metal compounds which are to be volatilized during experiments.

Oxygen and nitrogen are fed through Brooks mass flow meters to the top of the quartz reactor. Methane is fed through a Brooks mass flow meter to the top, side inlet of the reactor. When ethyl chloride is fed to the reaction mixture, it is added with the methane, using a 2% ethyl chloride and methane mixture. Reactor pressure is controlled by a GO Regulator after the reactor and liquid collection pots. Relief valves are present between the gas regulators and the Brooks mass flow meters. A relief valve (vented to

the hood) set at 273 kPa psig is located immediately before the quartz reactor so the pressure in the reactor can not exceed 273 kPa. The low flow switch after the reactor and before the liquid traps activates an emergency shut down system which passes nitrogen through the reactor and turns off heaters if there is a leak or plug in the reactor.

Two Research Inc. IR ovens, with approximately 1000 °C maximum operating temperature, are used for heating the tubular reactor. Each oven connects to its own phase angle power control (series 663), 240 volts, 25 amps, with line and load voltage regulation capability which is further connected to an Athena controller (Model 4000-S-E, 25 amp). Both controllers have their own overtemperature devices and are connected to additional overtemperature devices to shut off the furnaces when the operating temperature exceeds the set temperature by about 100 °C. Circulating cool tap water is supplied to both ovens when in use to cool lamp reflector bodies.

The two furnaces are equipped with chromel-alumel (type K) thermocouples which are used to measure the temperature of the furnaces. Temperature measurements can be inaccurate with direct ir-heating of the thermocouple, so the top part of the quartz reactor is surrounded by a 3.6 o.d., 3.4 i.d., 27 cm long stainless steel tub, and the bottom part of the reactor is surrounded by a 3.6 o.d., 3.4 i.d., 37 cm long tube. Athena temperature controllers are used to control the furnace temperatures. The temperature controllers have built-in overtemp devices which turn the furnace off when the operating temperature exceeds the set temperature by 80 °C.

Two cold traps are located after the reactor like those described above. Compounds which are not trapped are analyzed as described above.

In experiments where catalyst is used, the catalyst bed is formed in the reactor by placing quartz wool in the bottom portion of the inverted quartz reactor, followed by catalyst, then another plug of quartz wool, so the catalyst bed is centered in the bottom of the reactor when the reactor is correctly positioned. Metal compounds are placed in the cup in the quartz reactor. The tubular quartz reactor, surrounded by the two portions of 316 stainless steel sheath as described above, is positioned in the furnaces and connected to inlet and outlet connectors through O-ring connections. Controlling thermocouples (type K) and esd overtemp thermocouples are positioned at the center of each furnace between the stainless steel sheath and the quartz tubular reactor. The top oven (T. O.) center is 43.5 cm above the bottom of the reactor and bottom oven (B. O.) center is 13.4 cm above the bottom of the reactor. These thermocouples are connected to the temperature controllers (one for each furnace) and to overtemp shutdown devices. Another thermocouple for temperature measurement is placed at the center of the T. O. by the

controlling and overtemp thermocouples. Measurement thermocouples are measured and monitored by an Omega Microprocessor Controlled Temperature Indicator, Model 650/660.

Controlling thermocouples are calibrated to give the set temperatures of two measurement thermocouples placed inside the quartz tubing with a 160 sccm flow rate of nitrogen. This total flow rate is used for all experiments. The T. O. controlling thermocouple read the same temperature as the temperature reading of the measurement thermocouple placed along side the controlling thermocouple. The reactor is insulated at the reactor inlet and outlet ends and between the furnaces, in between the two stainless steel tubes, with fibrafax insulating material. Nitrogen is turned on to the reactor. Reaction gases are introduced to the reactor and may be analyzed before and/or after heating ovens. In most cases, the bottom oven is heated to the desired temperature, then the top oven is heated. Temperatures of both ovens are changed as needed. Outlet gases are analyzed at intervals using gas chromatography. After experiments, the reactant flow is terminated and the reactor is flushed with nitrogen while cooling. The reactor pressure is about 176 kPa and nitrogen is the diluent gas. The feed for all experiments contains $\text{CH}_4/\text{O}_2/\text{N}_2$ in a mole ratio of about 2/1/7.

Details of the vapor phase experiments are presented in Appendix F.

For all reactions in the BKW laboratory this quarter other than the vapor phase experiments, Reactor D was used. This is shown in Figure 3 of the Third Quarterly Report²⁰, and described in the Experimental Section of the Third²⁰ (and Fourth²¹ and Fifth⁴) Quarterly Reports. Reactor D is operated vertically as shown for another reactor in Figure 2 of the Second Quarterly Report²³. The center of the catalyst bed is 18.5 cm above the bottom of the oven, or 31.25 cm above the bottom of the reactor. When this point is heated to 802 °C under typical flow rates of gases, it is 800 °C at 2-2.5 cm above this point and 800 °C at 2 cm below this point. The temperature 5 cm below this point is 793 °C, and 10 cm below this point, it is 773 °C. 18.5 cm below this point (at the bottom of the heated portion of the reactor, the temperature is 645 °C. There is a significant temperature drop from the catalyst bed to the bottom of the reactor.

Catalysts for reactions coded BKW are not first preconditioned with oxygen. The reactors are filled with washed quartz chips above and below the catalyst bed; however, the capillary tubing in Reactors D and E is left empty. Quartz wool is used to separate the quartz chips from the catalyst bed and to hold the quartz chips in the reactor. Undiluted catalysts of varying mesh sizes are used except in cases where the catalyst is only available as a fine powder. In these cases, the catalyst is diluted with quartz chips.

Charged reactors are flushed with nitrogen during heating. After the experiment the reactant flow is terminated and the reactor is flushed with nitrogen while cooling. The reactor is cleaned between experiments by thoroughly rinsing with acid followed by distilled water. New reactors are frequently used to avoid using contaminated reactors.

KDC Laboratory

Substances tested for catalytic methane coupling activities this quarter included mixed and complex metal oxides, supported metal oxides, Pr-Ce oxides solid solutions, bifunctional catalysts, and literature catalysts.

Mixed and complex metal oxide catalysts, such as $A_2Ln_2Ti_3O_{10}$ layered perovskites, were prepared using a high temperature migration technique. The double perovskite, $LaCaMnCoO_6$, was prepared using a "liquid mix - citrate" technique.

In the high temperature migration technique²⁶ used to prepare $K_2La_2Ti_3O_{10}$, mixtures of metallic oxides and/or carbonates having the correct stoichiometric ratio of metals were ground to fine powders and placed in alumina crucibles. The crucibles were then heated in air to 1050 °C for 12 to 24 hours. The samples were then ground again, and the heating process was repeated. After three heating cycles, the samples were ground to powder and tested without further treatment.

In the liquid mix - citrate procedure used to prepare $LaCaMnCoO_6$ ²⁷, mixtures of $La(NO_3)_3$, $Co(NO_3)_2$, $MnCO_3$, and $CaCO_3$ having the correct stoichiometric ratios of metals were ground to fine powders and dissolved in saturated citric acid solution. Ethylene glycol was added to the citric solution (3%, v/v) and the solution was evaporated with constant stirring until a thick black syrup remained. This material was heated in air at 450 °C for 16 h to eliminate the organic material, then calcined in air at 550 °C (16 h) and 1000 °C (8 h). The resulting material was a homogeneous, dark powder.

Literature catalysts reported as oxygen carriers²⁵, Pr-Ce oxides solid solution and Ag-Pr-Ce oxides solid solution, were prepared using a coprecipitation method. In the method, two aqueous solutions were used. Solution one consisted of nitrates of praseodymium, cerium, and silver (if desired) in amounts needed to give the desired composition. Solution two contained ammonium carbonate in an amount sufficient to precipitate all the metals as carbonates. Solution one was then added dropwise to solution two with continuous stirring. The precipitate was separated by filtration and

washed with deionized water. The solid was then dried in a vacuum oven at 110-130 °C and calcined at 750 °C for 2 hours.

Alkali dopings of praseodymium oxide (Pr_6O_{11}), the double perovskite LaCaMnCoO_6 , and Pr-Ce oxide solid solutions were performed using a slurry technique. In the slurry technique, the required amounts of constituents needed to give the desired composition were added to 50-150 cc of distilled water. The mixture was evaporated with constant stirring until a thick slurry (paste) resulted. The paste was then dried in a vacuum oven at 110-130 °C. The alkali doped double perovskite was not calcined before testing. The alkali doped Pr_6O_{11} and Pr-Ce oxide solid solutions were calcined before testing at 800 °C for 2 hours.

Alkali or alkaline earth doped α -aluminas (Norton 5402, 30/60 mesh) were prepared using an incipient wetness technique. In the incipient wetness procedure, the amount of alkali or alkaline earth dopant required to give the desired metal loading was dissolved in a quantity of distilled water necessary to just wet the α -alumina (fill the void volume of the support). The α -alumina was then added to the solution and thoroughly mixed to insure even wetting. The resulting material was dried in a vacuum oven at 110-130 °C. It was used without calcining.

Materials referred to as bifunctional catalysts were prepared using a second incipient wetness step on the previously prepared alkali or alkaline earth doped α -aluminas. In the procedure, the amount of palladium nitrate [$\text{Pd}(\text{NO}_3)_2$] required to give the desired metal loading was dissolved in a quantity of distilled water necessary to just wet the alkali or alkaline earth doped α -alumina (fill the void volume of the support). The alkali or alkaline earth doped α -alumina was then added to the solution and thoroughly mixed to insure even wetting. The resulting material was dried in a vacuum oven at 110-130 °C. It was used without calcining.

The oxide conducting material, $(\text{Bi}_2\text{O}_3)_{0.85}(\text{La}_2\text{O}_3)_{0.15}$, was prepared using a coprecipitation technique²⁸. In the technique, 50 ml of 10% HNO_3 , 0.062 moles of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and 0.0109 moles of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were heated to 80 °C to dissolve the solids. Then the pH of the solution was adjusted from less than 1 to approximately 4 by the dropwise addition of concentrated NH_4OH . This resulted in the formation of a white solid. The liquid volume was reduced to about 20 cc by boiling and then dried in a vacuum oven. The resulting solid was calcined at 290 °C for 4 hours and 425 °C for 16 hours, ground to a fine powder, and calcined at 800 °C for 16 hours. The final product was a yellow solid.

The V_2O_5/MgO catalyst²⁹ was prepared by adding 16g of MgO to 1.03 liters of aqueous solution containing 0.5 wt% ammonium vanadate (NH_4VO_3) and 1 wt% ammonium hydroxide (NH_4OH) at 70 °C. The solution was evaporated to dryness at 70 °C using a purge of nitrogen. The resulting solid was calcined at 550 °C overnight.

Quartz reactors were used for all of the work this quarter in the KDC laboratory. These include Reactor A (Figure 5 of the Second Quarterly Report²³), Reactor B (described in the Experimental Section of the Third Quarterly Report²⁰), Reactor F (Figure 5 of the Fourth Quarterly Report²¹), Reactor G (Figure C1 of the Fifth Quarterly Report⁴), and Reactor H (Figure C2 of the Fifth Quarterly Report⁴). Reactors A, B, and F were used in the cofeed mode studies. Reactors G and H were used for sequential mode (pulse) studies.

Reactor B was used for most of the cofeed studies carried out in the KDC laboratory this quarter. It was constructed of 1.5 cm i.d. quartz tubing (1.7 cm o.d.) with a thermocouple well positioned along the center of the reactor of 0.3 cm i.d. quartz tubing (0.5 cm o.d.) enlarging to 1.3 cm o.d. at the outlet end (26.7 cm) of the thermocouple well. All quartz tubing used in the construction of the reactor was obtained from National Scientific Company. The thermocouple well extends through the catalyst bed (into the preheater region) which allows the temperatures of the preheater, catalyst bed and post-catalyst region to be monitored. The reactor had a length of 55.9 cm and the thermocouple well extended 33.0 cm into the reactor. The ends of the reactor are made up of quartz "O"-ring joints (1.5 cm i.d. at inlet ; 0.9 cm i.d. at outlet) which allows easy placement of the reactor in the system. The joints were connected using FETFE "O"-rings obtained from Ace Glass Incorporated. The "O"-ring joints were supplied by Quartz Scientific Inc.

The reactor was charged with catalyst by adding 20 to 40 mesh washed quartz chips around the enlarged thermocouple well (post-catalyst region), quartz wool, catalyst bed, quartz wool, and either a solid 1.3 cm o.d. quartz rod with 20 to 40 mesh washed quartz chips around the outside or 20 to 40 mesh washed quartz chips (preheater region).

Other cofeed reactors were filled with washed quartz chips above and below the catalyst bed. Quartz wool was used to separate quartz chips from the catalyst bed and to hold quartz chips in the reactor. The catalyst beds were composed of 0.25 - 5.00 grams of catalyst. For some experiments the catalyst was mixed with enough washed 20/40 mesh quartz chips to make a total volume of 4 cc. The quartz chips were obtained from National Scientific Company.

In cofeed studies, charged reactors were flushed with nitrogen during heating. The reactor temperature was raised to 450-500 °C and the catalyst was usually preconditioned with flowing air (100 cc/min) for 1 hour. After preconditioning, the air flow was terminated, the reactant flow was started, and the reactor temperature was raised to the desired value. Product stream analysis was carried out at timed intervals using gas chromatography. After the experiment, the reactant flow was terminated and the reactor was flushed with nitrogen while cooling. The reactor was cleaned between experiments by thoroughly rinsing with acid followed by distilled water.

Reaction conditions used for catalytic cofeed runs included:

temperature	200 - 850 °C
reactant flow rate	25 - 250 cc/min
weight of catalyst	0.25 - 30.00 grams
methane	5 - 90 molar%
methane/oxygen molar ratio	1.1 - 10
water	0 %
nitrogen	balance

Sequential mode studies were performed using one of the KDC reactor units modified such that product gases exiting the reactor could be collected in gas sampling bags. In a typical sequential experiment, Reactor G or H was charged with catalyst by adding quartz wool, catalyst, quartz wool, and 20 to 40 mesh washed quartz chips (preheater region).

Reaction conditions used for catalytic sequential runs included:

temperature	700 - 900 °C
conditioning air flow rate	100 - 250 cc/min
conditioning time	1 - 2 hours
methane flow rate	50 - 150 cc/min
weight of catalyst	2 - 20 grams
product collection times	0 - 2, 2 - 5, and 5 - 10 min

Charged reactors were flushed with air while the reactor temperature was raised to the desired value. Then, the catalyst was conditioned with flowing air (100-250 cc/min) for 1-2 hours. After conditioning, the air flow was stopped and the reactor was flushed

with nitrogen. Nitrogen flow was stopped, methane flow was initiated, and samples of gaseous product were collected immediately after exiting the reactor using gas sampling bags. The product samples were obtained during timed intervals. The reactor was then flushed with nitrogen, the reactor temperature was set to the desired value, the catalyst was conditioned with air, and the process was repeated. Collected samples were analyzed using the same GC analysis employed for the cofeed studies. After the experiment, the reactor was flushed with nitrogen while cooling. The reactor was cleaned between experiments by thoroughly rinsing with acid followed by distilled water.

In the KDC laboratory, oxygen conversions show a maximum of 95 to 96% due to the presence of argon in the feed air. The argon and oxygen components are not separated in the GC separation scheme. Carbon balance calculations indicate that other hydrocarbon products are not present in significant quantities; thus, analyses for heavier hydrocarbons and oxygenates are not performed during these screening experiments.

NEK Laboratory

The reactor system consists of a feed system, two tubular reactors in high temperature tubular furnaces, two liquid condensers, and on-line gas chromatographic analysis of each off-gas. The only common components of the two reactor systems are the feed gas cylinders, the check valves and safety relief valves, and the gas sampling system for the GC analysis. The rest of the system was constructed in duplicate and is identical, with the exception of the two different tubular furnaces. A schematic of the reactor system is shown in Figure C4 of Appendix C. Typical reaction conditions are:

temperature	500 - 850 °C
pressure	3-20 psig
total gas flow rate	250 to 1200 sccm
amount of catalyst	3 to 20 cc
methane	20-90%
oxygen	3-14%
water	0-85%
argon or helium	balance

Each reactor has its own gas feed system allowing different compositions to be fed to each reactor. The feed rate to each reactor is determined by the sum of the flow rates

of each of the feed gases and, if steam is co-fed, its feed rate, in ccm. Flow rates are determined by settings on calibrated Brooks mass flow metering valves. The feed rate of water to the vaporizer is determined from the Gilson liquid pump setting and the calibration graph for that pump.

The vaporizer consists of a 1/2" diameter stainless steel tube partially filled with glass beads and heated with heat tapes to a temperature about 20 °C above that required to produce steam at the reaction pressure.

During start-up, the feed system is isolated from the tubular reactors and all the feed gases are vented to the hood using a GO back pressure regulator to regulate the pressure in the feed system. The feed gas composition can be determined gas chromatographically (after diluting with inert and passing through a condenser, if the diluent is steam). The total flow rate can be measured with a bubble meter when there is no steam in the feed. Otherwise the flow measured is that of the feed gases, minus the steam, plus the diluent.

Once the feed has been analyzed and the furnace is at reaction temperature, the inert gas purging the reactor is replaced with the feed gas. If the feed gas composition is changed, the catalyst can be purged with argon or helium while the feed is analyzed, or the feed composition is calculated based on the Brooks meter settings and calibration. The later method was generally preferred and resulted in carbon mass balances of between 96 and 103%, which is not significantly different from those obtained using the gas chromatographically determined feed compositions.

Quartz reactors I and J were used in NEK laboratory. These were the same as Reactor B (described in the Experimental Section of the Third Quarterly Report²⁰) except that the overall length of Reactor I was 56 cm and of Reactor J was 61 cm. The reactors were constructed of 1.5 cm i.d. quartz tubing (1.7 cm o.d.) with a thermocouple well positioned along the center of the reactor. The thermocouple well was constructed from 3 mm i.d. quartz tubing (0.5 cm o.d.) which is enlarged to 1.3 cm o.d. at the outlet end (26.7 cm) of the thermocouple well. All of the quartz tubing used in the construction of the reactors was obtained from National Scientific Company. The thermocouple well runs the entire length of the catalyst bed. The ends of the reactors are made up of quartz "O"-ring joints (1.5 cm i.d. at inlet ; 0.9 cm i.d. at outlet) which allows easy placement of the reactor in the system. The joints were connected using FETFE "O"-rings obtained from Ace Glass Incorporated. The "O"-ring joints were supplied by Quartz Scientific Inc.

Each reactor was charged with catalyst by adding 20 to 40 mesh washed quartz chips around the enlarged thermocouple well (post-catalyst region), quartz wool, catalyst, quartz wool, and 20 to 40 mesh washed quartz chips (preheater region). The catalyst

beds in experiments coded with NEK were composed of 20 cc of catalyst, which was weighed prior to loading. The quartz chips were obtained from National Scientific Company. After loading the tubular reactors with catalyst they are placed horizontally into tubular furnaces. Two different solid shell tubular furnaces were used to allow comparison of their performance. Both are 1 1/4 inch i.d., solid shell tubular furnaces which are resistively heated with a variable pitch along a length of 18 inches. The one supplied by ThermPro Inc. also has 8 tapped shunts which allows the resistance to be varied by the addition of resistors. The other, supplied by CM Furnaces, Inc., does not have this capability; however, both companies claim that their furnace will provide a 6 inch section heated to $900\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

From the vaporizer to the furnace inlet and from the furnace outlet to the inlet of the condenser, everything, with the exception of the Heise pressure gauge in the gas feed system, which is connected through a water filled pigtail, is heated with heat tapes.

Thermocouples for temperature determination are positioned under the heat tapes at various locations, and inside the vaporizers and the tubular reactors. Three thermocouples are located along the length of the catalyst bed and the temperature reported is that of the thermocouple located at the center of the bed.

The steam diluent and liquid products are condensed at atmospheric pressure in a 2250 cc teflon-lined Hoke cylinder which is cooled to $5\text{ }^{\circ}\text{C}$ with methanol using a Cole Palmer circulating refrigerated bath. When steam is used as the diluent, the offgas is diluted with inert gas prior to entering the condenser. Thus, even if the conversion of the oxygen is low, the oxygen concentration in the gas exiting the condenser will be below the flammable limit. The condenser is drained at least once a day when steam is being fed and less frequently when it is not. The frequency of collection depends on whether the liquid samples are being collected for analysis or to prevent the condenser from overflowing.

Slip steams from the product gas and the feed gas from the reactors are sent to a stream select/gas sampling box and then to the vent. The positions of the four eight-port stream select valves and the one Valco 10 port gas sampling valve in the stream select/gas sampling box are controlled by Computer Automated Laboratory System (CALS) software on a Hewlett Packard computer. The gas sampling valve, shown in Figure C5 of Appendix C, is configured for injection of two, two-milliliter samples of one gas stream simultaneously onto two GC columns.

The product and feed gas samples are analyzed on two analytical columns, which are located in the oven of a Varian 3700 gas chromatograph equipped with a flame

ionization detector and a thermal conductivity detector. Both detectors are operated simultaneously with the signal outputs going through separate digimetries to the CALS. Ethylene, ethane, and propylene/propane (unresolved) in the sample are separated using a 10 ft. by 1/8" stainless steel Porapak R column with an argon or helium carrier gas and a flame ionization detector. C₄ hydrocarbons could be qualitatively detected. The carbon oxides, nitrogen, oxygen, hydrogen, methane, and water are analyzed with a thermal conductivity detector using a 10 ft. by 1/8" stainless steel column filled with Carbosieve S-II. Both columns are subjected to the same temperature program, starting at 50 °C for 10 minutes after injection, then heating at 30 °C/min to 200 °C and holding at that temperature for 16 minutes, for a total analysis time of 31 minutes. The response factors for all of the expected compounds were determined by calibrating with gas standards prior to the first run. These are updated periodically. The analytical procedures used are detailed in Tables B1 and B2 of Appendix B.

Nitrogen, cofed with ethyl chloride, is used as an internal standard to correct the mole percents in the product gas analysis for any volume contraction which may have occurred due to the reaction.

The catalysts used in NEK's laboratory were prepared by the slurry method described in the Experimental Section of the First Quarterly Report²².

RESULTS AND DISCUSSION:

BKW Laboratory

Alkaline Earth Catalysts on Non-Alumina Supports

In the literature, nearly all elements have been used or claimed for methane coupling catalysts. One patent in particular³⁰ claims an unusually large number of catalysts and components for "the oxidative conversion of organic compounds to other organic compounds," and includes two examples of methane oxidation to C₂'s. This patent and the literature do not distinguish among the many materials used and claimed, which, if any, material would provide a stable catalyst for the conversion of methane to ethylene which might be commercializable. Only two examples of the oxidation of methane are presented, and these exhibit low ethylene to ethane product ratios, and no evidence of a long catalyst lifetime for these is presented. A catalyst system which would provide a high ethylene to ethane product ratio would be more economical, from a

commercial point of view, than a similar one which would not provide a high ethylene to ethane ratio, since ethylene is more valuable as a raw material than ethane.

The approach to the discovery of stable catalysts is described in the Introduction Section above, and in previous Quarterly Reports^{20,21}. Methane coupling catalysts were discovered which provide hundreds of hours of stable operation in the oxidation of methane to C₂'s with high product ethylene to ethane product ratios (2.5-10 or more). These catalysts contain alkaline earth components and require the presence of halides, either as a catalyst component or as a periodic or continuous additive to the catalyst. Literature use of halides in methane coupling reactions was reviewed in Appendix G of the Fifth Quarterly Report⁴. Selected literature articles and patents describing the use of alkaline earth components in catalysts for methane coupling^{6,30-37} are reviewed in Appendix G of this report.

The study of alkaline earth/metal oxide halide catalysts for methane coupling was continued this quarter (summarized in Table B3 of Appendix B) with exploration of catalyst and process variables. A BaCl₂/α-Al₂O₃ catalyst (33-BKW-81) was compared with a BaCO₃/Al₂O₃ catalyst (33-BKW-74, see the Sixth Quarterly Report⁵) to see if the catalysts reached a common state of mixed anions and the same catalyst performance. Both catalysts were prepared with the same support and were prepared to contain the same amount of barium. Table 1 below (and Table B3 of Appendix B) shows that the chloride catalyst is not as active as the carbonate catalyst under similar process conditions, which results in a lower C₂ yield.

Table 1. BaCO₃/Al₂O₃ (33-BKW-74) and BaCl₂/Al₂O₃ (33-BKW-81) Catalysts

<u>Ref.</u>	<u>CH₄C</u>	<u>Sel</u>	<u>Yield</u>	<u>O₂C</u>	<u>=/-</u>	<u>CO₂/CO</u>	<u>Time, h</u>	<u>GHSV</u>	<u>ECl</u>
33-74	29.1	59.0	17.0	45	1.6	1.8	208	2233	4
33-74	40.8	47.8	19.3	77	3.0	1.8	332	1116	8
33-81	19.7	58.7	11.5	27	1.6	0.7	115	1067	4

Table headings, terms, and units are defined in Appendix A. CH₄C, Sel, Yield, and O₂C are in %, =/- represents the molar ethylene to ethane ratio in product, and CO₂/CO is the molar ratio. GHSV is in h⁻¹ and ECl is in ppm.

Analyses of these two catalysts by microscopy showed significant differences in distribution of the barium before and after reaction (see Catalyst Surface Analyses Section below). Larger clumps of barium were present before the reaction on the catalyst prepared with barium chloride than on the catalyst prepared with barium carbonate. After the reaction, the barium on the catalyst made with carbonate had further dispersed,

whereas the barium was still clumped up in the catalyst made from chloride. The different dispersions of barium could explain differences in the activity of these two catalysts. The catalyst for reaction 33-BKW-74 was reported⁵ to contain 3.1% barium before and after reaction (by ICP). The catalyst for reaction 33-BKW-81 was analyzed by ICP to contain 3.8% barium before reaction and 3.3% barium after reaction. EDS analyses (Table H1 of Appendix H) showed that the surface of the catalyst for reaction 33-BKW-74 contained 22 atom% barium before reaction and 15 atom% barium after reaction. The surface of the catalyst for 33-BKW-81 contained 6 atom% barium before and 11 atom% barium after reaction.

Alkaline earth catalysts on titania were shown in earlier quarterly reports to produce high ethylene to ethane product ratios. Two catalyst levels of barium carbonate (5 wt% and 17 wt%, see Appendix D) were explored for methane coupling on each of two kinds of titania supports (Norton and JM, see Appendices D and E) to determine the effects of catalyst loading and of the kind of titania support on catalyst performance. Table 2 presents results for the two catalysts on Norton supports (see also Table B3 of Appendix B). The highest selectivity/yield combination for the catalyst containing less barium (reaction 33-BKW-85) is compared with results for the catalyst containing more barium (33-BKW-91) at the same temperature (750 °C), space velocity (1579 h⁻¹), and the same levels of methane (10 vol%) and oxygen (5 vol%) in the feed gas. The catalyst with the higher loading of barium is more active and selective than the catalyst with less barium on this support.

Table 2. BaCO₃/TiO₂: 5% BaCO₃ (33-BKW-85, 101) and 17% BaCO₃ (33-BKW-91)

Ref.	Ba	CH ₄ C	Sel	Yield	O ₂ C	=/-	CO ₂ /CO	Time, h	GHSV	ECl
33-85	low	36.9	39.4	14.8	69	5.6	0.5	164	1579	200
33-91	high	39.8	42.1	17.2	68	5.9	0.4	69	1579	150
33-91	high	44.3	44.6	19.9	73	8.6	0.3	249	1579	300
33-101	low	23.9	51.0	12.2	36	3.9	0.2	249	1579	300

Table headings, terms, and units are defined in Appendix A. CH₄C, Sel, Yield, and O₂C are in %, =/- represents the molar ethylene to ethane ratio in product, and CO₂/CO is the molar ratio. GHSV is in h⁻¹ and ECl is in ppm.

Table 2 also shows that the highest yield obtained in reaction 33-BKW-85 was 14%. The catalyst for this reaction was used again in reaction 33-BKW-101. Table 2 above (and Table B3 of Appendix B) shows that although higher levels of ethyl chloride

were used, results for methane coupling were not significantly improved over those for reaction 33-BKW-85.

Table B3 of Appendix B and Figures C6 and C7 of Appendix C show results for methane coupling with a catalyst of 5% barium carbonate on Norton titania (33-BKW-85). The C_2 yield was not over 11% and the C_2 selectivity was not over 45% for a variety of process changes in methane to oxygen ratio, temperature, space velocity, and ethyl chloride level, until the ethyl chloride level was raised to 200 ppm. The time period between 134 and 185 hours of operation of this catalyst is presented in Figures C6 (C_2 selectivity, methane conversion, C_2 yield, and ethylene to ethane ratio) and Figure C7 (relative rates to products) of Appendix C. At a given methane to oxygen ratio, C_2 selectivity and ethylene to ethane ratio are higher at higher ethyl chloride levels (with levels of 47, 100, and 200 ppm ethyl chloride). A change in the volume percentages of methane and oxygen fed from 80% and 10%, respectively, to 10% and 5%, respectively, resulted in a drop in C_2 selectivity. The expected rise in methane conversion was observed and resulted in a significant increase in the C_2 yield.

Figures C8 and C9 of Appendix C compare methane conversions and C_2 selectivities (Figure C8 of Appendix C) and C_2 yields and ethylene to ethane ratios (Figure C9 of Appendix C) for barium carbonate catalysts on titania (33-BKW-85) and alpha-alumina (33-BKW-74, see the Sixth Quarterly Report⁵) supports under the same set of process changes. The reactions were run simultaneously, although the times for only reaction 33-BKW-88 are shown (the times for reaction 33-BKW-74 are those shown plus 317.1 hours since it had been on-stream for 317.1 hours when reaction 33-BKW-88 was begun). Figure C8 of Appendix C shows that both the magnitude of changes in conversion and selectivity and the direction of these changes are different for catalysts on alumina and titania supports containing the same amount of barium. The change in ethyl chloride level from 200 to 4 ppm results in an increase in conversion for the catalyst containing alumina, and a decrease in both selectivity and conversion for the catalyst containing titania. For both reactions, the change in concentrations of methane and oxygen fed to the reactors from 80 and 10%, respectively, to 10 and 5%, respectively, resulted in increased methane conversion (as a percentage of that fed) and decreased selectivity to C_2 's. Figure C9 of Appendix C shows that the ethylene to ethane ratio rises as the ethyl chloride level is raised and as the methane to oxygen ratio is lowered on the catalyst containing titania. On the catalyst containing alumina, changes in the ethylene to ethane ratio are lower for similar process changes. This shows that the ethylene to ethane

product ratio depends on the process variables, including the level of ethyl chloride in the reaction, and on the support.

The support used for the catalysts in reactions 33-BKW-114 and 115 was over 99.99+% pure titania. Figures C10 and C11 of Appendix C show similar patterns of reactivity and similar results for these two catalysts for the same sequence of changes in process variables (see Table B3 of Appendix B for the process changes). The difference in the amounts of barium on catalysts in reactions 33-BKW-114 and 115 has little effect on methane coupling results under the wide variety of conditions used. This is also shown below in Table 3, which presents results for two levels of BaCO₃ with each of the two types of titanium dioxide supports (some examples are repeated from Table 2 above). The level of BaCO₃ does not correlate with methane conversion or selectivity to C₂'s.

Table 3. BaCO₃/TiO₂ Catalysts with Different Types of Titania and Amounts of BaCO₃

<u>Ref.</u>	<u>CH₄C</u>	<u>Sel</u>	<u>Yield</u>	<u>O₂C</u>	<u>=/-</u>	<u>BaCO₃</u>	<u>Type^a</u>	<u>Time, h</u>	<u>GHSV</u>	<u>ECl</u>
33-85	36.9	39.4	14.8	69	5.6	5	N	164	1579	200
33-91	44.3	44.6	19.9	73	8.6	17	N	249	1579	300
33-101	23.9	51.0	12.2	36	3.9	5	N	249	1579	300
33-114	34.7	56.4	19.3	52	6.4	17	J	148	1548	500
33-115	37.1	50.5	18.6	60	7.4	5	J	146	1548	500

a. N is Norton (0.6 m²/g) and J is JM (0.82 m²/g) titania (see Appendices D and E).

Table headings, terms, and units are defined in Appendix A. CH₄C, Sel, Yield, and O₂C are in %, =/- represents the molar ethylene to ethane ratio in product, and CO₂/CO is the molar ratio. GHSV is in h⁻¹ and ECl is in ppm.

Figure 2 shows the relative rates to ethylene and ethane for different concentrations of ethyl chloride and ethyl bromide in the feed gas for reaction 33-BKW-114.

Figure 2. Rates to Ethylene and Ethane with Different Ethyl Bromide and Ethyl Chloride Levels, 33-BKW-114

Figure 3 shows the relative rates to carbon monoxide and carbon dioxide for different concentrations of ethyl halide (EX, X=Br or Cl) in the feed gas for this reaction.

Figure 3. Rates to Carbon Monoxide and Carbon Dioxide with Different Ethyl Bromide and Ethyl Chloride Levels, 33-BKW-114

The relative rates to ethylene increase as the amount of ethyl halide (EX) is increased. Figure 3 shows that the amount of carbon monoxide increases when the ethyl halide level is raised, but the increase for ethyl chloride is slight compared with that for ethyl bromide.

Under similar conditions, the rates to ethylene and carbon monoxide are higher with ethyl bromide than with ethyl chloride. The rates to total C_2 's (the sum of ethane and ethylene) are also higher under a given set of reaction conditions with ethyl bromide rather than ethyl chloride in the feed gas (see Figure 2). Ethylene is considered to result primarily from gas phase conversion of ethane to ethylene. Carbon monoxide is considered to be primarily from gas phase (non-catalytic) oxidation of methane or other gas phase products and intermediates. The higher rates to C_2 's, to carbon monoxide, and to ethylene in the presence of ethyl bromide (higher ethylene to ethane ratios) are consistent with the presence of higher concentrations of radicals in the gas phase when ethyl bromide is present. Since the C-Br bond is weaker than the C-Cl bond, it is possible that ethyl bromide reacts with the catalyst to release bromine radicals at a more rapid rate (in higher concentration) into the gas phase, or that homolytic dissociation of the C-Br bond occurs to a significant degree without catalysis. These radicals then initiate chain reactions which convert ethane to ethylene and methane to carbon monoxide, among other things.

A higher concentration of radicals in the gas phase would also be expected to result in higher rates of methane conversion, higher rates of product oxidation, and lower in selectivities (from faster oxidation of the higher concentration of products). Figure 4 below shows that the selectivity is higher under similar conditions with ethyl chloride rather than ethyl bromide in the feed gas [mainly from the exceptionally high rate to carbon monoxide in the presence of ethyl bromide (Figure 3 above)]. The C_2 yields are also higher with ethyl chloride (due to the higher selectivity), even though the actual rates to ethylene are higher with ethyl bromide (Figure 2 above).

With a $BaCO_3/TiO_2$ catalyst, ethylene to ethane ratios as high as 25 (32% selectivity to C_2 's, 51% methane conversion, 16.5% yield to C_2 's) were observed (33-BKW-91). Ethylene to ethane ratios were four times higher with ethyl bromide than with ethyl chloride (10 vs. 2.6 at 250 ppm and 5.7 vs. 1.4 at 50 ppm) with other conditions the same on a $BaCO_3/TiO_2$ catalyst (33-BKW-114, Table B3 of Appendix B). Selectivities were lower with bromide (36% vs. 65%).

Figure 4. Effect of Ethyl Halide Levels on C₂ Selectivity, C₂ Yield, and Ethylene/Ethane 33-BKW-114

Increases in space velocity at a given set of process conditions result in increased selectivity to C₂'s, decreased methane conversion, decreased ethylene to ethane product ratios, and decreased C₂ yields (see Table B3 of Appendix B and Figure C12 of Appendix C). Figure 5 below shows that relative amounts of carbon monoxide, carbon dioxide, and ethylene are lower at higher space velocities (lower residence times). The drop in the relative amount of CO in the product is large compared with drops in other products. A slight increase in the relative amount of ethane is observed at the higher space velocities.

Figure 5. Space Velocity Changes with $\text{BaCO}_3/\text{TiO}_2$ Catalyst with 500 ppm Ethyl Chloride, 33-BKW-114

As the space velocity is lowered, the residence time is greater, so the conversion of primary to secondary products occurs to a larger extent, and gas phase reactions become relatively more important (especially if chain branching reactions occur). Ethylene is a secondary product, and can be produced in the gas phase from ethane in the presence of radicals. The amount of ethane is therefore relatively less at lower space velocities, and the amount of ethylene is relatively more. Carbon dioxide is also a secondary product from oxidation of ethane and ethylene, presumed to result mainly from reactions on surfaces (catalyst and reactor packing and walls). At low conversions, a significant amount of the carbon dioxide is presumed to result from catalytic oxidation of methyl radical. As space velocity is decreased, more carbon dioxide is observed. Carbon monoxide is a known product of gas phase combustion of methane.

In Figure 6, the relative amounts of products in the reaction outlet are multiplied by the space velocity, to give relative rates to products. The actual rates to ethylene and ethane increase as space velocity is raised, whereas the rates to CO and CO₂ decrease as the space velocity is raised (for the three higher space velocities). Results at the lowest space velocity are inconsistent with trends observed at the three higher space velocities in Figures 5 and 6, in that rates are lower than those of the next higher space velocity. Two of several possible explanations for this are diffusional or mass transfer problems at the lowest space velocity, or since the lowest space velocity was at the end of the time period

for the data displayed, the lower rates could be due to catalyst deactivation (e.g., from non-optimum chloride levels - overchlorination).

Figure 6. Space Velocity Changes with $\text{BaCO}_3/\text{TiO}_2$ Catalyst with 500 ppm Ethyl Chloride

A physical mixture of BaCl_2 and BaCO_3 was melted, crushed, then used as a catalyst in reaction 33-BKW-121. At 750 °C and 2400 h⁻¹ GHSV, a C₂ selectivity of 70% was obtained at a methane conversion of 12% with no added ethyl chloride. Addition of ethyl chloride of levels up to 500 ppm did not result in improved activity or selectivity (see Table B3 of Appendix B).

Different amounts of chloride were explored for $\text{SrCO}_3/\text{Al}_2\text{O}_3$ (34-BKW-18) and $\text{SrCl}_2/\text{Al}_2\text{O}_3$ (34-BKW-19) catalysts. It appears that 500 ppm ethyl chloride may not be too much for the Ba/TiO_2 catalysts tested (see above, 31-BKW-46 in the Fourth Quarterly Report²¹ and 32-BKW-80 in the Fifth Quarterly Report⁴), but a level of 500 ppm ethyl chloride was too much for the $\text{SrCO}_3/\text{Al}_2\text{O}_3$ catalyst (Figure C13 of Appendix C and Table B3 of Appendix B), and even 50 ppm was too much for the $\text{SrCl}_2/\text{Al}_2\text{O}_3$ catalyst (Figure C14 of Appendix C and Table B3 of Appendix B).

The relative rates to products for the first part of reaction 34-BKW-18 are shown in Figure 7 below. Figure C15 of Appendix C shows the relative rates to products for the entire reaction.

Figure 7. $\text{SrCO}_3/\text{Al}_2\text{O}_3$ Catalyst

In the last few quarterly Reports^{4, 5, 21}, three roles of chloride were described.

1. When ethyl chloride is added in the feed gas to a barium catalyst, the rate to C_2 's rises to a constant level slowly. Removal of ethyl chloride results in a rapid loss in rate to C_2 's. The selectivity and activity increases are proposed to be from the halide on the catalyst reacting with and breaking up stable carbonates or other salts (aluminates, titanates, etc.) to allow the formation of active oxygen species on barium which can abstract hydrogen from methane to lead to C_2 's. This is a slow change for a deactivated catalyst. Figure 7 shows that the strontium carbonate catalyst does not show the same initial increase in the rate of C_2 production in the presence of halide as did a similar barium catalyst (see reaction 33-BKW-74, Figure 12 and Table B4 of the Sixth Quarterly Report⁵). This is consistent with the proposition that under similar reaction conditions, the strontium catalysts would have a lower requirement for chloride to catalyze decomposition of stable salts compared with barium catalysts. Strontium carbonate is less stable than barium carbonate³⁸, so this is reasonable.

2. With barium carbonate catalysts in the presence of ethyl chloride in the feed gas, the rate to carbon dioxide decreases slowly with addition of ethyl chloride and increases by removal of ethyl chloride^{4,5,21}. Apparently, the chloride also reacts with and destroys surface catalyst species which oxidize C₂'s or methyl radicals to carbon dioxide. Figure 7 shows that with the strontium carbonate catalyst, using 5 and 50 ppm ethyl chloride, the rate of carbon dioxide formation drops during a period of greater than 100 hours. Figure C15 of Appendix C shows that the rate to carbon dioxide rises when the level of ethyl chloride is changed from 500 to 5 ppm.
3. Increases in the ethylene to ethane product ratio from addition of ethyl chloride in the gas feed are consistent with gas phase, free radical reactions involving halide radicals produced on the catalyst surface and released into the gas phase, where free radical chain reactions occur. The changes in ethylene to ethane product ratios are fast when the level of ethyl chloride is changed, which would be expected from a gas phase reaction. Carbon monoxide is known to result from gas phase methane oxidation, and process changes on many alkaline earth/metal oxide catalysts which result in increased rates to CO generally result in higher ethylene to ethane ratios. Ethane is known to be converted in the gas phase to ethylene in the presence of halides³⁹. Figure 7 shows little change in the ethylene to ethane ratio with an increase from 5 to 50 ppm ethyl chloride on the strontium carbonate/alpha-alumina catalyst, but little change is expected at these low levels of chloride on a relatively non-acidic alumina support (see Appendix D of this Report and Table 4 of the Fourth Quarterly Report²¹ and the discussion about it).

Although catalysts containing strontium may not require chloride to form the active sites (since an initial increase in the rate of C₂ production was not observed for a catalyst with Sr, see 1. above), chloride is still required to lower the rate of carbon dioxide production to obtain good selectivities to C₂'s. It is also required to produce high ethylene to ethane ratios on supports where this is favored, e.g., titania.

Figure 8 shows the relative rates to products for the first part of a methane coupling reaction sequence over a SrCl₂/Al₂O₃ catalyst (34-BKW-19) under the same conditions (at the same time) as were used for the SrCO₃/Al₂O₃ catalyst in reaction 33-BKW-18 (Figure 7 above), except that the space velocity for the reaction over the chloride catalyst

was one-half of that used for the reaction over the carbonate catalyst, in order to compare results under similar methane conversions (since the chloride catalyst is less active). The same amounts of catalyst were used, with the same Sr loading. Results for the catalyst made with chloride differed significantly from those of the catalyst made with carbonate (see also Figures C13 and C15 of Appendix C). Rates to CO, CO₂, and ethylene rise and pass through maxima (at about 25, 60, and 45 hours, respectively), whereas the rate to ethane is fairly constant for about 40 hours, then rises only slightly for the next 25 hours.

Figure 8. SrCl₂/Al₂O₃ Catalyst

Figure C14 of Appendix C shows that the methane conversion goes through a maximum at a reaction time of about 60 hours on-stream. This catalyst initially contains a large amount of chloride. An explanation consistent with the observed results is that catalyst surface changes occur slowly over a period of hours. These surface changes lead to increased methane conversion through formation of additional sites, perhaps by dispersion of alkaline earth metal, and to an increase in the rate of release of chlorine radicals from the catalyst surface. These chlorine radicals then initiate free radical chain reactions, resulting in higher rates to CO and higher rates of conversion of ethane to ethylene. The rate of release of chlorine radicals and the concentration of radicals in the gas phase are proposed to go through maxima. If, as described above under 2., the reaction of chloride with the catalyst surface results in slow catalyst changes, poisoning sites which convert methane, products, and intermediates to carbon dioxide (see

discussion above), then loss of chloride from the catalyst should result in an increase in these sites and an increase in the rate to carbon dioxide. This is observed initially with reaction 34-BKW-19 (Figure 8 above).

The increase in sites which can oxidize methane, products, and intermediates to carbon dioxide on the catalyst surface can result in decreases in observed rates to CO and C₂'s, because these are further oxidized as they are produced. When the concentration of chloride on the catalyst is reduced to a level where the rate of release of chlorine radicals into the gas phase is lower, the rate of conversion of ethane to ethylene should be lower, resulting in lower ethylene to ethane ratios. This is observed in Figure 8, where the rate to ethane after 60 hours increases, while the rate to ethylene and the overall rate to all other products decreases.

Similar maxima are not normally observed for reactions of barium chloride on alumina (Figure 10 of the Third Quarterly Report²⁰, and Figure 12 of the Fourth Quarterly Report²¹). This could reflect differences in the rates of transformations of alkaline earth compounds on the catalyst surface to form a steady state of metal dispersion and steady states of the concentrations of various anions. In the case of the catalysts containing barium, the maximum rate of release of chlorine radicals from the catalyst surface could be at or soon after the start of reactions. Figure 12 of the Fourth Quarterly Report²¹ shows the highest ethylene to ethane ratio at the start of the reaction, which is consistent with this explanation.

Reactions 34-BKW-59 (SrCO₃/Al₂O₃ catalyst), 34-BKW-61 (BaCO₃/Al₂O₃ catalyst), and 34-BKW-63 (BaCO₃/Al₂O₃ catalyst) were run with 80% methane and 8% oxygen, which were conditions found to be favored in economic analyses of methane coupling processes (largely due to higher selectivities presumed to result from higher ratios, see Task 2 Discussion Section below). Selectivities were not that much higher than have been observed for reactions with 10% methane and 5% oxygen in the feed gas (typical reaction conditions). Results are presented in Table B3 of Appendix B. The space velocities and concentrations of ethyl chloride in the feed gas were not optimized for these process conditions and catalysts. The amount of ethyl chloride could have been far from the optimum amount, resulting in decreased selectivities and activities. Selectivities were lower for the Sr catalyst than for the Ba catalysts. No significant catalyst deactivation was observed for 70 hours on stream (after which, several process variable changes were made). The highest C₂ yield was 11.1% (reaction 34-BKW-61, 68% C₂ selectivity and 16.5% methane conversion). This was a transient result after an increase in space velocity, suggesting that the ethyl chloride level is not optimized.

Five grams of catalyst were used in reaction 34-BKW-63, whereas 2.5 g of the same catalyst were used in reaction 34-BKW-61. At 750 °C and 2820 h⁻¹ GHSV, with the same feed gas, results for the two reactions were similar (8% C₂ yield, 63-66% C₂ selectivity, 13% methane conversion).

Vapor-Phase, Catalyst-Derived Free Radicals

Gas phase reactions during methane coupling reactions with alkaline earth/metal oxide catalysts appear to be altered by presence of chloride in the starting catalyst or by addition of ethyl chloride (or other sources of volatile chloride) to the catalyzed methane coupling reactions (see the Fifth Quarterly Report⁴ and the section Alkaline Earth Catalysts on Non-Alumina Supports above). Higher ethylene to ethane ratios were observed in product compositions of methane coupling reactions which used alkaline earth/non-basic metal oxide supports, in the presence of chloride. This observation is consistent with the production of chlorine radicals on the catalyst surface which are released into the gas phase, with the conversion of ethane to ethylene in the gas phase, catalyzed by the chlorine radicals in the gas phase. Figure 9 below illustrates this and shows selected key gas phase and surface reactions. The conversion of ethane to ethylene in the gas phase catalyzed by chloride is a known reaction³⁹.

Figure 9. Role of Surface Generated Chlorine Radicals in Conversion of Ethane to Ethylene

The addition of volatile chloride to gas phase methane oxidation reactions²⁰ results in only small changes in methane conversion without catalysts, indicating that methane oxidation in the gas phase under reaction conditions used for catalyzed reactions is not affected to a large extent by ethyl chloride in the gas phase in the absence of catalysts. Reactions 33-BKW-130 and 33-BKW-131 in Table B4 of Appendix B show that in the reactor most commonly used (Reactor D), under typical conditions of 10% methane and 5% oxygen at 750 °C with flow rates of 80 or 160 ccm (typically used with 5 g of catalyst to give space velocities of 1000-3000 h⁻¹), methane conversions of over 5% are not observed with levels of ethyl chloride of from 0 to 150 ppm. Reaction 33-BKW-130 has a void space of 4.5 cc (between quartz chips) in the hottest part of the oven. Reactor 33-BKW-131 has quartz chips throughout the reactor (without any additional void spaces other than those present from the spaces among the quartz chips).

The concept of production of radicals on the catalyst surface and release of these into the gas phase was shown by Lunsford and coworkers⁶⁻⁹ (through the trapping of methyl radicals released from catalyst surfaces and the correlation of the rates of methyl radical production with rates of C₂ formation) to be important in the catalyzed oxidation of methane to ethane. Radicals of hydrocarbon fragments higher than methane have additional pathways of reaction available to them other than coupling (e.g., alkene

formation through loss of a hydrogen atom), so they do not have lifetimes comparable to methyl radicals. They therefore cannot be detected by the esr methods employed by Lunsford and coworkers.

Since higher hydrocarbon radicals could not be directly detected, H. H. Kung⁴⁰ developed an indirect method to indicate the presence of enhancement of gas phase reactions due to the presence of free radicals produced on catalyst surfaces and released into the gas phase. He applied this method to the oxidation of butane. This method to detect radical enhancement of gas phase reactions from release of radicals produced on catalysts into the gas phase was applied to determine if radical enhancement of gas phase reactions could be observed during methane oxidation over $\text{BaCO}_3/\text{Al}_2\text{O}_3$ catalysts in the presence and absence of added chloride.

Two reactions were run simultaneously in two reactors with the same amount of the same $\text{BaCO}_3/\alpha\text{-Al}_2\text{O}_3$ catalyst, already activated in a previous experiment (32-BKW-63). In one case (34-BKW-1, Figure C16 of Appendix C), the catalyst was placed after a 2.5 cc void space in the reactor. In the other case (34-BKW-2, Figure C17 of Appendix C), the catalyst was placed before the 2.5 cc void space in the reactor. Results and conditions used for these experiments are in Table B4 of Appendix B.

Reactions 33-BKW-130 and 131 show us that methane conversion in the void space before the catalyst in reaction 34-BKW-2 will be negligible, so differences in catalyst activity and selectivity to products between reactions 34-BKW-1 and 2 are due to the void space after the catalyst. The same reactions occur to the same extent in the catalysts in both reactions, but in the case with the void volume after the catalyst, gas phase reactions of products and intermediates may occur to a greater extent after the catalyst bed.

Thus, differences in the reactions are due to increased contributions of gas phase reactions in reaction 33-BKW-2, from oxidation of products or from reactions of radicals produced on the catalyst and released into the gas phase. These radicals may cause chain reactions. If one sees an increase in the rate to a product in reaction 33-BKW-2 compared with reaction 33-BKW-1, it is likely that this is due to a gas phase reaction.

The following reactions (Figure 10) may occur (without consideration of relative rates of reaction, or whether these reactions occur on the catalyst surface, in the gas phase, or both):

Figure 10. Some Reaction Steps Leading to Products during Methane Oxidation

CO_2 may come from methane, ethane, ethylene, or CO. Ethylene is produced from ethane. CO is produced from methane, ethane, or ethylene.

Figure 11 below compares relative rates of CO_2 production for reactions 34-BKW-1 (void space after catalyst) and 34-BKW-2 (void space before catalyst).

Figure 11. Relative Amounts of Carbon Dioxide Produced in Reactions 34-BKW-1 and 2

The rates to CO_2 are nearly the same for both reactions 34-BKW-1 and 2 for levels of 5 and 50 ppm of ECl and 50 ppm of EBr, under each of the same process conditions. This implies that no additional CO_2 is produced in reaction 33-BKW-2 from additional gas phase reactions, than is produced in reaction 33-BKW-1 over catalyst. This result is consistent with the formation of CO_2 from all sources on the catalyst surface, with little or no gas phase contribution to the rate determining step of oxidation of methane, intermediates, or products to CO_2 .

Figure 12 below compares relative rates of CO production for these two reactions. The rate of CO production under each set of process conditions is significantly higher in

Figure 12. Relative Amounts of Carbon Monoxide Produced in Reactions 34-BKW-1 and 2

reaction 33-BKW-2 than it is in reaction 33-BKW-1. This is consistent with the production of CO resulting from gas phase reactions, which is known in combustion chemistry. The increased amount of CO produced in 34-BKW-2 with the 2.5 cc void space after the catalyst (relative to 34-BKW-1) with 50 ppm ECl in the feed gas was more than the total amount of CO produced in an uncatalyzed 4.5 cc void space (34-BKW-130, see Table 4 below). This indicates that the increase in CO production results from reactions other than exclusively gas phase reactions of methane and oxygen (which in

reactions 33-BKW-130 and 131 were observed to occur to only a small extent under reaction conditions). Possibilities include production of radicals (e.g., chlorine) on the catalyst surface followed by release of these into the gas phase to initiate chain reactions. These chain reactions would be expected to produce CO from Reactions 3, 7, and 9 of Figure 10 above. More ethylene would be expected from Reaction 5 of Figure 10. An increase in the observed methane coupling reaction to ethane might also be observed due to additional gas phase oxidation of methane from the increased concentration of free radicals. The actual amount of ethane observed would be that expected from reaction 34-BKW-1 plus that from the increase in gas phase methane oxidation minus that lost from reaction 5 in Figure 10 above.

Table 4. Enhanced Gas Phase Reactions, 34-BKW-1 and 2 and 33-BKW-130 and 131

<u>Ref.</u>	<u>CO</u>	<u>CO₂</u>	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>CH₄</u>	<u>EX</u>	<u>X</u>	<u>Time, m</u>
34-BKW-1	0.7	1.2	0.4	0.2	31.7	0	0	235
34-BKW-2	0.9	1.3	0.5	0.2	34.5	0	0	270
34-BKW-1	0.6	0.6	0.3	0.2	24.6	50	Cl	1730
34-BKW-2	1.0	0.6	0.4	0.2	27.6	50	Cl	1695
34-BKW-1	1.3	1.3	0.4	0.1	35.2	50	Br	2640
34-BKW-2	1.7	1.3	0.5	0.1	37.8	50	Br	2685
33-BKW-130	0	0.002	0.001	0.01	1.3	0	0	170
33-BKW-131	0	0	0	0	0.8	0	0	195
33-BKW-130	0.09	0.002	0.01	0.03	2.6	50	Cl	1250
33-BKW-131	0.01	0.0004	0.006	0.01	1.2	50	Cl	1295
33-BKW-130	0.15	0.003	0.02	0.05	3.8	50	Br	3210
33-BKW-131	0.05	0.0006	0.008	0.03	2.2	50	Br	3190

Figure 13 shows the increase in methane conversion in reaction 34-BKW-2 with the void space after the reactor, compared to the reaction with the void space before the reactor, 34-BKW-1. Looking at Table 4, it may be seen that increases and decreases in ethylene and carbon dioxide levels roughly track changes in methane conversion. The amounts of CO with different amounts of ethyl halide in the feed gas in reaction 34-BKW-2 do not correlate with methane conversion. The amount of CO produced is higher with 50 ppm than it is with no ECl in the feed gas, even though methane conversion is less with 50 ppm ECl than it is without added ECl in the feed gas.

Figure 13. Relative Amounts of Methane Conversion in Reactions 34-BKW-1 and 2

As expected, the amounts of ethylene are higher in reaction 34-BKW-2 than 1, and the amounts of ethane are lower, due to conversion of ethane to ethylene in the gas phase after the catalyst bed in reaction 34-BKW-2 (Figure 14).

Figure 14. Relative Amounts of Ethane and Ethylene Produced in Reactions
34-BKW-1 and 2

An explanation consistent with observed results is that the catalyst generates radicals which are released into the gas phase to start chain reactions. Lunsford has shown that methyl radicals are released into the gas phase in this manner⁶⁻⁹. It is reasonable to expect chlorine radicals could also be released from the catalyst surface into the gas phase. Since thermolysis and/or oxidation of C_2 's can also initiate chain reactions, it is not known what portion of the enhancement in gas phase reactions is initiated by decomposition of C_2 's and what portion is initiated by free radicals lost from the catalyst surface. Experiments with added C_2 's would help clarify roles of gas and surface reactions.

Even in the absence of added volatile chloride, residual chloride on the catalyst surface could be released for a period of time from the catalyst into the gas phase.

Catalyst Surface Analyses

Appendix H presents Electron Microscopy results [Tables H1 through H5 of energy dispersive spectroscopy (EDS) results and Figures H1 through H14 of secondary electron

image (SEI) and backscattered electron image (BEI) pictures] from fresh and used alkaline earth/metal oxide catalysts. The weight and atom percents of Al, Si, Cl, and Ba for the surface of Ba/Al₂O₃ catalysts which were prepared with nitrate, carbonate, and chloride catalysts are presented in Table H1 of Appendix H for fresh and used catalysts. For catalysts made from nitrates and chlorides, the surface amount of barium increases during the reaction. For the catalyst prepared with barium carbonate, the surface amount of barium decreases during the reaction. The amount of surface barium detected for used chloride and carbonate catalysts is similar after reactions. Even when a catalyst is prepared with chloride, the surface amount of chloride detected by EDS is low (0.06%). Appendix D describes catalyst compositions. Ethyl chloride was used in reactions 33-BKW-49, 74, and 81, but the amounts of chloride on these used catalysts are low.

Figure H1 of Appendix H shows barium as light chips on darker chunks of alumina for the fresh BaCO₃/Al₂O₃ catalyst, 33-BKW-64A. After use in reaction 33-BKW-74, the used catalyst contains less surface barium visible by BEI, which is consistent with the EDS analyses. Figure H2 of Appendix H shows a better dispersion of barium on alumina on the fresh Ba(NO₃)₂/Al₂O₃ catalyst, 33-BKW-47B than on the carbonate catalyst. Very little distinct barium is visible in the used catalyst, 33-BKW-49, whereas by EDS it is present, suggesting that the barium is dispersed uniformly over alumina particles. Large, light areas of caked-looking barium are visible by BEI in a fresh BaCl₂/Al₂O₃ catalyst, 33-BKW-79A. The used catalyst, 33-BKW-81, looks the same as the fresh catalyst.

Table H2 of Appendix H shows that for BaCO₃/Al₂O₃ catalysts analyzed by microscopy, no chlorine was detected by EDS. Again, the amount of barium detected by EDS on the surface of the catalyst decreases with use of the catalyst. Figure H4 of Appendix H shows that in SEI pictures, barium is not distinct from aluminum in the fresh BaCO₃/Al₂O₃ catalyst (32-BKW-20I), but in BEI pictures chunks of barium (light) are present on the alumina (darker). Figure H5 of Appendix H shows lower magnifications of the fresh catalyst 32-BKW-20I, next to used catalyst 32-BKW-62. In the used catalyst, fewer particles of barium are visible by BEI, but rather the catalyst is mainly dark gray, suggesting either loss of barium, or dispersed barium on alumina. Figure H6 of Appendix H is a higher magnification of fresh and used catalysts, which better shows the loss or dispersion of barium.

Since ICP analyses of used barium catalysts showed no loss of barium, catalyst particle cross sections were examined by SEI, BEI, and EDS to determine if barium migrated into the catalyst during reaction over BaCO₃/Al₂O₃ catalysts. These showed by

EDS (Table H2 of Appendix H) that the barium concentration increases the middle of catalysts particles during methane coupling reactions. Although there appear, by BEI, to be fewer barium particles after reaction, EDS analyses clearly indicate the presence of barium, which must therefore be well dispersed on alumina, so not visible by BEI. Figure H7 of Appendix H shows that for a cross section of fresh catalyst 32-BKW-20I, the light particles of barium are concentrated on the outside of the sliced catalyst. For used catalyst 32-BKW-62, there is no concentration of barium on the outside of the catalyst. The barium in $\text{BaCO}_3/\text{Al}_2\text{O}_3$ catalysts appears to disperse into and throughout the catalyst in methane coupling reactions, whereas barium remains in clumps during methane coupling with $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts.

The surface concentration of Sr in a $\text{SrCO}_3/\text{Al}_2\text{O}_3$ catalyst is lower with used than with fresh catalysts, whereas the reverse is true for a $\text{SrCl}_2/\text{Al}_2\text{O}_3$ catalyst (Table H3 of Appendix H), just as was observed for $\text{BaCO}_3/\text{Al}_2\text{O}_3$ and $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts. The amounts of chlorine observed on used Sr catalysts in Table H3 of Appendix H are much higher than amounts observed for used barium catalysts in Tables H1 and H2 of Appendix H.

Figure H8 of Appendix H shows that for the $\text{SrCO}_3/\text{Al}_2\text{O}_3$ catalyst, surface Sr (light areas in BEI) remained in clumps during the methane coupling reaction. For the fresh $\text{SrCl}_2/\text{Al}_2\text{O}_3$ catalyst lighter areas of more concentrated, but relatively well dispersed Sr are observed by BEI in Figure H9 of Appendix H (34-BKW-16B). Patches of more concentrated Sr cannot be detected by BEI in the used catalyst (34-BKW-19).

Table H4 of Appendix H shows relatively little chloride on used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts from reactions 30-BKW-52 and 93. Figure H10 of Appendix H presents SEI pictures showing areas of EDS analyses for these two catalysts. Figure H11 of Appendix H displays the two used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts (30-BKW-93 and 30-BKW-52) in greater magnification. These SEI pictures show tiny (<1 micron) cotton-like particles clinging to the alumina particles. Figure H12 of Appendix H presents two SEI magnifications of the fresh catalyst (30-BKW-68D) for 30-BKW-93 (Figure H11 of Appendix H). The small, cotton-like particles are not present. Figure H13 of Appendix H shows by SEI the areas used for EDS analyses of fresh $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts 30-BKW-68C and 68D.

Catalysts 30-BKW-68C and D are on different alumina supports. Catalyst C uses Norton 5551 alumina, and catalyst D uses Norton 5502 alumina. The Norton 5502 support is more acidic and has a higher surface area (see Table 4 of the Fourth Quarterly Report²¹). The concentration of Ba on a fresh catalyst on this higher surface area support (Table H5 of Appendix H) is lower (2.7 wt%) than that on the Norton 5551 support (5.2

wt%), most likely due to the fact that the same amount of Ba is spread out over a larger surface.

Table H5 of Appendix H shows that area 6 of fresh catalyst 30-BKW-68C contained 26 atom% Ba and 16 atom% Cl, by EDS, whereas other areas contained as little as 1 atom% Ba or no chlorine. This suggests poor dispersion of barium, or clumps of barium, as Figure H3 of Appendix H confirms is present on fresh and used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts. Figure H14 of Appendix H shows clumps on the alumina particles on a fresh $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalyst (by SEI) which are presumed to be clumps of barium compounds.

A used CaCl_2 catalyst (31-BKW-13, Table H5 of Appendix H) had 1.09 wt% Ca on the surface by EDS compared with 0.88 wt% Ca on the fresh catalyst. Figure H15 of Appendix H shows SEI pictures of fresh and used $\text{CaCl}_2/\text{Al}_2\text{O}_3$ catalysts with spots marked which were used for EDS analyses (Table H5 of Appendix H).

In summary, fresh barium chloride and carbonate catalysts on alumina have different dispersions of barium. The barium in a carbonate catalyst moves from the surface into the particle as the reaction proceeds, and Ba clumps disappear as the barium disperses to more uniformly coat alumina particles. Barium on fresh catalysts prepared from barium chloride and alumina is in larger clumps than is the barium on fresh catalysts prepared from barium carbonate and alumina. The barium remains in clumps during methane oxidation reactions over $\text{BaCl}_2/\text{Al}_2\text{O}_3$ catalysts.

In contrast to the barium catalysts, strontium catalysts from SrCO_3 have larger Sr clumps which do not disperse well, whereas the SrCl_2 is dispersed fairly well on fresh catalysts, and it appears to spread out even more as the reaction proceeds.

The $\text{BaCO}_3/\text{Al}_2\text{O}_3$ catalyst used in reaction 32-BKW-62 was analyzed by XPS. No chlorine was found on the catalyst surface. Trace amounts (<0.10 atom%) of Ca, Ag, and N were detected. From XPS analysis, the top layer on the catalyst surface most likely is BaO with O^{2-} anion, mixed with a small amount of BaCO_3 . 6.4% Ba, 51.7% O, 21.9% C, and 19.9% Al are present.

Avoiding the Heterogeneous/Homogeneous Mechanism

The barium and strontium catalyst systems described above are thought to operate by the heterogeneous/homogeneous mechanism with creation of methyl radicals on the catalyst surface by hydrogen abstraction from methane, followed by release into the gas

phase of the methyl radical, then coupling of two methyl radicals to form ethane. The product distribution for this mechanism is largely dictated by the gas phase chemistry, as discussed in the Introduction Section. Two approaches are suggested to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations. One is to get away from the gas phase chemistry and make more of the reaction occur on the surface of the catalyst, at lower temperatures. The other is to change the gas phase chemistry to depart from the typical combustion reaction network.

Silver Catalysts

To increase the surface contribution of the reaction, one may increase the surface reaction rate relative to the reaction rates of gas phase reactions. This may be accomplished by increasing rates of reaction steps on the catalyst surface, or decreasing the rates of the gas phase reactions (operating at lower temperatures). Barium peroxide was reported⁴¹ to convert methane to C_2 's at temperatures below 400 °C. Certain other metals activate hydrocarbons unselectively at low temperatures (compared to the typical temperatures of 700-950 °C used for methane coupling), e.g., silver, platinum, and palladium.

In the Third Quarterly Report²⁰, catalysts were prepared containing silver, and selective methane coupling activity was obtained in the presence of other catalyst components, such as alkali and alkaline earth components, and in the presence of chloride, despite the presence of the unselective metal component. The catalysts can be operated at relatively low temperatures to effect methane coupling. Moreover, the use of the lower temperatures reduces the homogeneous reaction rates in favor of the heterogeneous reactions.

In the earlier work with silver-containing catalysts, chlorides (and alkali or alkaline earth components) were used since it was known that chlorides (and alkali or alkaline earth components) were important modifiers for silver catalysts in selective ethylene oxidation. It was thought that the presence of chloride could decrease total oxidation on silver for methane oxidation as it did for ethylene oxidation. (The details of why chloride works in this manner for ethylene oxidation are still not well understood). At the time this work was begun, there were few references to the use of silver in catalysts for methane conversion to C_2 's^{32,33}. In one of these references³³, halides of a large variety of metal cations are claimed for methane coupling, including silver. No examples showed low temperature operation of a silver catalyst for methane coupling selectively to

C₂'s. One reference⁴² reported modification of Pd and Pt with selective adsorption of Br and Cl to allow methane oxidation but suppress total oxidation.

A low temperature catalyst containing 9% silver, 5% barium chloride, and α -alumina (31-BKW-2, see the Third Quarterly Report²⁰) exhibited C₂ yields as high as 10% at 650 °C. Without the barium chloride (30-BKW-123), complete oxygen conversion occurred at temperatures of 400-500 °C, with methane converted only to carbon oxides²⁰. Examples of results are shown in Table 5. The two catalysts containing barium have different levels of barium and were prepared using different methods of silver deposition.

Table 5. Low Temperature Catalysts

<u>Catalyst*</u>	<u>Ref</u>	<u>°C</u>	<u>CH₄ Conv. %</u>	<u>C₂ Sel. %</u>	<u>C₂ Yield. %</u>	<u>GHSV</u>	<u>±</u>	<u>ECI</u>
Ag/ α -alumina	30-123	425	25	-	-	1636	-	50
Ag/ BaCl ₂ /Al ₂ O ₃	31-2	650	32	32	10	682	0.8	50
Ag/ BaCl ₂ /Al ₂ O ₃	34-63	670	17	25	4.5	1263	0.6	5

The catalyst with undoped silver resulted in methane oxidation to CO₂ at 425 °C, but it was necessary to raise the temperature to 650 °C for high methane conversions with the doped catalyst. Lower levels of dopants were of interest in hopes of obtaining activity at lower temperatures, but retaining or improving the C₂ selectivity observed at 650-700 °C. Catalysts with a variety of dopants were made and tested for methane coupling activity. Catalyst preparation methods for catalyst containing silver which were used this quarter are described in detail in Appendix E. With low levels of Pr (34-BKW-6 and 7), Bi (34-BKW-10), Ba (34-BKW-11,14), and K (34-BKW-15) dopants (see Appendices D and E), methane conversions were high, and C₂ selectivities were low, as they had been without dopants (see Table B5 of Appendix B). For example, in reaction 34-BKW-6, at 425 °C, 98% oxygen conversion and 26% methane conversion to carbon dioxide were observed using 10% methane and 5% oxygen, with a space velocity of 2341 h⁻¹. The catalyst for this reaction contained 0.1% praseodymium. Addition of 10 ppm of ethyl chloride in the feed gas to this reaction at 400 °C resulted in an initial increase in methane conversion from 15 to 16%, followed by a drop in methane conversion to 4%. No

significant amounts of C_2 products were produced with any of these catalysts under any conditions, even at 700 °C, where C_2 's are produced to some extent without catalysts in gas phase reactions. It is concluded that these silver catalysts with low levels of modifiers not only oxidize methane efficiently to CO_2 , but they also efficiently oxidize intermediates (e.g., radicals) and products (e.g., ethylene) of methane oxidation to CO_2 .

The catalysts for reactions 34-BKW-6, 7, 10, 11, 14, and 15 were made using a different method of silver deposition on alumina from the method used for preparing the silver catalysts reported in the Third Quarterly Report²⁰. Nitrates were used as dopants in place of chloride, and a different level of silver was used (see Appendices D and E).

Additional catalysts were prepared (34-BKW-36 and 45) with the same method of silver deposition, but with higher levels of dopant, using barium and calcium chlorides rather than nitrates. Unusually high C_3 selectivities (e.g., 18%, with C_2/C_3 product ratios of 1.4) were obtained with the $BaCl_2/Ag/\alpha$ -alumina catalyst. C_2/C_3 product ratios are normally around 15-20. Also, the C_3 product was all propane rather than propylene, which is usually observed for oxidative methane coupling. For example, Table 6 below shows that propylene ($C_3^=$) to propane (C_3^-) ratios are between 0.5 and 2 in reactions 32-BKW-135, with a Li/MgO catalyst, and propylene 33-BKW-6, with a Ba/Al_2O_3 catalyst, using 10% methane and 5% oxygen. In contrast, the catalyst with silver shows no propylene, but only propane as product. With the two catalysts without silver, the C_2/C_3 product ratios are 18-20, whereas almost as much propane as C_2 's is produced in reaction 34-BKW-36.

Table 6. C_3 Products

Ref	Cat.	T, °C	CH_4 C	C_2 Yield	C_2 Sel	$\equiv$	$C_3^=/C_3^-$	C_3 Sel	GHSV	Time, m	C_2/C_3	ECI
34-63	Ba/Ag/ Al_2O_3	670	17	4.5	25	0.6	0	18	1263	255	1.4	5
32-135	Li/MgO	720	36	19	52	1.1	1.4	2.9	9600	665	18.2	0
33-6	Ba/ Al_2O_3	750	39	20	52	2.4	0.7	2.6	2182	2590	20	10

Propylene is expected from the normal heterogeneous/homogeneous methane coupling mechanism. Propylene formation has been proposed to result from methyl radical reaction with ethylene in the gas phase^{43,44}. It is likely that the propane in

reaction 34-BKW-63 results from a mechanism other than the normal heterogeneous/homogeneous mechanism of methane coupling. Release of a significant amount of methyl radicals from the catalyst surface in the presence of product ethylene would result in some propylene. The absence of propylene therefore suggests that this does not occur. The presence of propane without propylene is consistent with a mechanism of conversion of methane to ethane followed by coupling of ethyl and methyl radicals, all on the catalyst surface. It is believed that these results demonstrate the principle of enhanced surface reaction during methane coupling.

Since these results were obtained, Matsushashi⁴⁵ reported that a Na/ZrO₂ catalyst gives C₃ hydrocarbons as the main products during the oxidative coupling of methane. Their catalyst produced more C₃ than C₂ products with the C₃ hydrocarbons being 77% propane and 23% propylene. Another reference³³ reports high C₃ and C₄ yields with bivalent metal halides [46.8% of the hydrocarbons (38.6% overall selectivity including carbon oxides) are butenes with BaBr₂/pumice and 24.1% of them (14.3% overall selectivity) are butenes with CaBr₂/MgO].

Silver catalysts were made containing lanthanum oxide, because one patent example³³ claimed a Ag/La₂O₃ (unsupported) catalyst among catalysts for methane conversion including Group IIA, IIIA, lanthanide series or mixtures of these components. It was desired to determine if the presence of La in catalysts containing silver would provide any advantage over silver catalysts not containing lanthanum. Results for methane coupling with catalysts containing silver with and without La are summarized in Table 7 below. The results show that C₂ selectivities and C₂ yields are similar for silver catalysts with and without La.

Table 7. Silver Catalysts for Methane Coupling

Ref.	Cat.	T, °C	CH ₄ C	C ₂ Yield	C ₂ Sel	±	GHSV	Time, m	ECI
34-36	Ba/Ag/Al ₂ O ₃	670	17	4.5	25	0.6	1263	205	5
34-37	Ba/La/Ag/Al ₂ O ₃	670	16	4.5	28	0.6	1263	290	5
34-44	Ba/La/Ag/Al ₂ O ₃	670	27	4.1	15	0.6	1263	325	5
34-50	Ba/Ag/Al ₂ O ₃	675	23	6.6	29	0.6	1171	235	5
		675	21	6.5	30	0.7	1171	4060	500
34-51	Ba/La/Ag/Al ₂ O ₃	675	27	7.2	27	0.6	1171	280	5
		675	27	8.2	30	0.8	1171	4105	500

Catalysts were prepared with barium chloride, using one method of silver deposition for catalysts in reactions 34-BKW-36, 37, and 44, and another method of silver deposition to prepare the catalysts used in reactions 34-BKW-50 and 51. These two types of silver catalysts contain different amounts of silver (see Appendices D and E). In reactions 34-BKW-50 and 51, 500 ppm ethyl chloride were added in the gas feed near the end of the runs (675 °C). The methane conversion, C₂ selectivity, and C₂ yield were rapidly rising when the runs were stopped. Higher C₂ yields might be expected from lined-out reactions with optimized ethyl chloride levels.

Vapor Phase Catalysts

The second approach, suggested to avoid the heterogeneous/homogeneous mechanism, is to change the gas phase chemistry to depart from the typical combustion reaction network. As an example, a volatile metal complex is oxidized to some state, for instance a superoxide, which abstracts a hydrogen atom from methane. The complex does not have as large a reservoir of oxygen to further oxidize the new methyl radical, as an oxidized surface would. Methyl radicals therefore couple in the gas phase rather than being further oxidized.

Alternately, volatile complexes could be used to quench the hydroperoxides which convert methane coupling intermediates and products to carbon oxides. Volatile catalysts could also be used to increase the rate of hydrogen abstraction and shift the gas phase reaction away from the typical heterogeneous/homogeneous product distribution, as halogen radicals were shown to do in producing higher ethylene to ethane ratios.

The reactor used for vapor phase catalyst studies is shown in Figure 15 (see also Figures C2 and C3 of Appendix C). Oxygen and nitrogen are introduced into the top of the reactor which is heated in the vaporizer zone by one oven. The catalyst or additive to be volatilized is in a quartz cup within the vaporizer zone. Methane is added so that it mixes with the oxygen/nitrogen/vapor phase catalyst mixture in a reactor heated by a second oven. In this way, reactions may be conducted with or without volatile catalysts present, since the vaporizer zone oven can be turned on or off as desired. When operating with vapor phase catalysts, the volatile catalyst components are trapped in the cool quartz chips located in the bottom of the reactor.

Figure 15. Vapor Phase Catalytic Reactor

Results are shown in Table 8. Methane conversion is decreased significantly by addition of volatile CsCl to a methane oxidation reaction in an empty, heated reactor space. Since the methane is essentially all converted to carbon oxides under these conditions, the volatile catalyst reduces the rate of homogeneous methane conversion to carbon oxides. This is shown for temperatures of 650 and 750 °C. The effect can be shown by either adding the vapor phase catalyst, which results in a drop in methane conversion, or by stopping volatile catalyst addition, which results in an increase in methane conversion, as shown in Table 8. Results for LiCl were similar to those obtained

with CsCl. Experimental conditions and results for all vapor phase catalysts are shown in Tables B6 and B7 of Appendix B.

Table 8. Vapor Phase CsCl Catalyst

<u>Vaporizer Zone T. °C</u>	<u>Reaction Zone T. °C</u>	<u>CH₄ Conv., %</u>
196	650	5
600	650	0.8
650	750	4
226	750	15

The discovery of the effect of volatile metal/salts on the homogeneous CH₄ conversion was studied in the presence of a catalyst. Catalyst conditions and volatile chloride levels were not optimized, but results in Table 9 show an increase in selectivity to C₂'s and a decrease in CO₂ formation upon addition of volatile catalyst to a methane coupling reaction over a used BaCO₃/Cl/α-Al₂O₃ catalyst. This is interpreted as a reduction in the gas phase conversion of methane to carbon oxides, allowing the methane which would have reacted in the gas phase to react on the catalyst surface to produce C₂'s. These results demonstrate the concept of changing the gas phase chemistry during methane oxidation with volatile catalysts, promoters, or inhibitors.

Table 9. Vapor Phase CsCl Over 4 g of BaCO₃/Cl/α-Al₂O₃ Catalyst

Vaporizer T. °C	Reaction T. °C	CH ₄ Conv. %	C ₂ Sel. %	CO _x Sel. %
160 sccm feed gas flow rate, 0 ppm ECl				
185	750	21	46	51
750	750	21	53	44
80 sccm feed gas flow rate, 40 ppm ECl				
188	750	39	28	70
750	750	36	38	60

KDC Laboratory

Tables and Figures showing the important experimental results are presented in Appendices B and C. In the Tables (Appendix B), all results are for the cofeed mode (simultaneous feeding of methane and oxygen) unless indicated as sequential mode (sequential additions of methane, nitrogen, and oxygen). For the cofeed runs, reactant conversions are based on the molar amounts of reactants present at the inlet and outlet of the reactor. In the sequential runs, reactant conversions are based on the molar amount of reactant and the total molar amount of carbon present in the product stream. Carbon balances were not obtained for the sequential runs. For both cofeed and sequential, the product selectivities are based on the molar amount of carbon present in a particular product divided by the total molar amount of carbon present in all detected products. Appendix A contains the keys to the Tables.

Additional studies were carried out on the layered perovskite (K₂La₂Ti₃O₁₀) identified in the Third Quarterly Report²⁰ as a good coupling catalyst. Layered perovskites of the form A₂Ln₂Ti₃O₁₀ were first reported by J. Gopalakrishnan and V. Bhat²⁶. The material was prepared with the objective of forming a Ruddlesden-Popper type layered oxide (general formula : A₂[A_{n-1}B_nO_{3n+1}] where [A_{n-1}B_nO_{3n+1}] perovskite type slabs of n octahedra in thickness are interleaved by A cations) capable of exhibiting ion exchange and intercalation behavior. Gopalakrishnan and Bhat synthesized the new series of layered perovskites of the general formula A₂[Ln₂Ti₃O₁₀] (A = K,Rb; Ln =

La,Nd,Sm,Gd,Dy). In these materials three octahedrals of $[\text{Ln}_2\text{Ti}_3\text{O}_{10}]$ are separated by A cations (Figure 15 of the Third Quarterly Report²⁰). Thus, the perovskite layers are in intimate contact with an alkali ion dopant which is part of the crystalline materials. Such a structure assures all perovskite material is in contact with the alkali ion dopant and the loss of alkali ion dopant during reaction should be slower due to its positioning in the crystal lattice.

The materials exhibit ion exchange of the alkali metal in aqueous or molten salt media. Potassium ions of $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ are easily exchanged with Na^+ or Li^+ by treating with molten alkali-metal nitrates. Also, treatment with dilute acids results in the exchange of H^+ for K^+ ions.

Results obtained for the $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ catalyst using a $\text{CH}_4/\text{O}_2/\text{N}_2$ ratio of 9.1/1/0.27 at 803 °C are shown in Table B8 in Appendix B. The experiment was conducted to examine the long term stability of the catalyst, the effect of using methane as the diluent gas, and the effects of adding CO_2 or ethyl chloride (ECI) to the reactants. During the experiment the flow rate was raised in steps from 150 ccm to 415 ccm. The C_2 selectivities varied from 64-67% indicating a fairly stable system. During the last 24 hours of the 149 hour run, C_2 yields of 9% with C_2 selectivities of 65% were obtained using a 415 ccm flow rate.

At the end of the 149 hour run, 1.2% CO_2 (by volume) was introduced into the reactant stream. This resulted in a decrease in the CH_4 conversion from 14.6% to 12.7%, an increase in the C_2 selectivity from 65% to 66%, and a decrease in the CO_2/CO ratio from 4.2 to 3.2. The C_3 selectivity and ethylene/ethane ratio were not affected. When the CO_2 level was increased to 5.4% (by volume) of the reactant stream, no major changes were observed except the CO_2/CO ratio decreased from 2.8 to 2.1.

The CO_2 addition to the reactant stream was terminated at 222 hours and 10 ppm of ethyl chloride (ECI) was added to the stream. This change resulted in an increase of the CO_2/CO ratio from 2.1 to 3.1. Addition of the ECI appeared to cause a slow deactivation of the catalyst and did not result in any enhancement (increase) of the ethylene/ethane ratio. The ECI was only added over a 12 hour period which may not have been long enough to show any slow activation of the catalyst.

Materials containing highly mobile oxygen species are considered good candidates as methane coupling catalysts. In the literature²⁸ a $\text{Bi}_2\text{O}_3\text{-La}_2\text{O}_3$ oxide ion-conducting catalyst has been reported as being effective for the oxidative dehydrodimerization of propylene. Thus, $(\text{Bi}_2\text{O}_3)_{0.85}(\text{La}_2\text{O}_3)_{0.15}$ was tested for methane coupling ability in the

cofeed mode using a $\text{CH}_4/\text{O}_2/\text{N}_2$ ratio of 9.1/1/0.27 (Table B9 of Appendix B). At 803 °C and GHSV of 6920 h^{-1} , initial CH_4 conversions/ C_2 selectivities of 8.6%/64% were obtained. In Table B10 of Appendix B results are presented using a $\text{CH}_4/\text{O}_2/\text{N}_2$ ratio of 2.2/1/3.8. At 800 °C and GHSV between 2400 and 4800 h^{-1} , the catalyst gave CH_4 conversions between 32 and 34% (oxygen limited) with C_2 selectivities from 41 to 43% over a 27 hour period. The C_2 selectivity was not changed greatly as the GHSV was increased from 2400 to 4800 h^{-1} . Plans are to test this material after alkali doping and also to test it in the sequential mode where the multiple oxidation states of Bi could be important.

Vanadium-magnesium oxides have been reported²⁹ to be selective oxidative dehydrogenation catalysts for butane. Results obtained utilizing one of these materials (20 wt% $\text{V}_2\text{O}_5/\text{MgO}$) as a methane coupling catalyst are presented in Table B11 of Appendix B. The material was highly active (oxygen limited at 600 °C; GHSV of 1043 h^{-1}) but unselective (C_2 selectivity <1%). Alkali dopings of this material may result in C_2 selective catalysts with good activities.

Work was continued this quarter on a group of catalytic materials referred to as bifunctional catalysts. The concept of catalysts in which different species or components in a catalyst are responsible for different steps in the reaction pathway (polyfunctional catalysts) is commonly encountered in heterogeneous catalysis. Important examples are platinum on alumina as a reforming catalyst and bismuth molybdates for the ammoxidation of propylene to acrylonitrile. The platinum on alumina catalyst is an example of bifunctional behavior caused by separate phases present in the catalyst while the bismuth molybdate bifunctional behavior is due to the different metallic species present in the bismuth molybdate phase.

In the literature, three different oxidative methane coupling catalyst systems have been proposed to operate as bifunctional catalysts; however, many of the other literature examples could also operate by bifunctional mechanisms.

Workers at Exxon⁴⁶ proposed methane coupling catalysts in which Group VIII noble metals would dissociatively adsorb CH_4 , Group VIB metal oxides would be reduced by the adsorbed hydrogen to form water, and Group IIA metal oxides would convert the adsorbed hydrocarbon species to carbides. The carbides were thought to be intermediates in the formation of cyclic compounds. When pure methane was passed over these catalysts, the main products observed were ethane, ethylene, coke and benzene. In their work the catalysts were not tested in the cofeed mode.

Emesh and Amenomiya⁴⁷ proposed a bifunctional mechanism for the oxidative coupling of methane over $\text{Bi}_2\text{O}_3/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$. In their mechanism, methane was dissociated into $\text{CH}_3\cdot$ and $\text{H}\cdot$ on the alumina surface and the hydrogen was oxidized on the metal oxide by a redox mechanism. When the hydrogen was removed from the surface, surface methyl radicals dimerization was enhanced. The metal oxide was oxidized back to the original state by gas phase oxygen. These studies utilized a cofeed of methane and oxygen.

A similar mechanism was proposed by a Japanese group⁴⁸ for Li-doped BeO in which the active species is thought to be $\text{Li}_2\text{Be}_2\text{O}_3$. The surface of this material can be visualized as BeO infinite chains combined with LiO infinite chains. Methane adsorbed dissociatively on BeO sites and the adsorbed hydrogen was oxidized by the oxygen ions belonging to LiO chains. After removal of the adsorbed hydrogen, the adsorbed methyl radicals could couple to form ethane. Their study also used a cofeed of methane and oxygen.

While all the steps proposed in these mechanisms may not be correct (such as surface coupling of methyl radicals), the concept of different catalyst components carrying out specific tasks in the coupling process is of interest. Materials capable of dissociatively adsorbing methane at lower temperatures than 600 °C coupled with materials that oxidize adsorbed hydrogen to water and allow the surface coupling or the release of the methyl radicals into the gas phase could, if found, result in the development of lower temperature coupling catalysts.

In the Fourth Quarterly Report²¹, Pd/CaCO₃, Pd/BaCO₃, Pd/BaSO₄, Pd/alumina, Pt/CaCO₃, Pt/alumina, and alkali doped forms of these catalysts were tested as methane coupling catalysts. The undoped catalysts gave large CH₄ conversions and large amounts of H₂ indicative of the dissociative adsorption of CH₄. The alkali dopants used during the Fourth Quarter were not capable of controlling the high activities or of giving good C₂ selectivities.

In the Fifth Quarterly Report⁴, very interesting and important results were reported for Pd(NO₃)₂/SrCl₂/α-alumina and Pt(NO₃)₂/SrCl₂/α-alumina catalysts. Although the C₂ selectivities obtained were much lower than for SrCl₂/α-alumina, an unusually high C₃ selectivity was obtained. Also, the C₃ product was all propane instead of propylene which is usually observed for oxidative methane coupling catalysts. These differences indicated that a heterogeneous reaction was involved in the formation of the C₃ product with these catalysts representing a change in the normally observed heterogeneous-homogeneous mechanism.

Studies to examine the effects of changing the SrCl_2 to other chloride species were performed. Previous results indicated that chloride was a necessary component in the system. Its role is believed to involve preventing the formation of metallic Pd or Pt which results in total oxidation accompanied by high CO and H_2 formation.

Results for NaCl/α -alumina are given in Table B12 of Appendix B for comparison with results obtained with $\text{Pd}(\text{NO}_3)_2/\text{NaCl}/\alpha$ -alumina (Tables B13 and B14 of Appendix B). The NaCl/α -alumina catalyst is not very active (CH_4 conversion of 17% at 700 °C) but gives high C_2 selectivities (> 58% at 700 °C). Rapid deactivation is observed at 700 °C (CH_4 conversion falls from 17% to 10% in 14 hours). Only normal C_3 selectivities are observed. The addition of low levels of Pd to the NaCl/α -alumina catalyst (Table B13 of Appendix B) results in a very active material (> 45% CH_4 conversion at 590 °C) but negligible C_2 and C_3 selectivities. Large amounts of H_2 were observed in the products which is consistent with the formation of metallic Pd. Table B14 of Appendix B give results obtained when larger amounts of Pd were added to a NaCl/α -alumina catalyst. For this catalyst, higher activities were observed at lower temperatures with the corresponding high amounts of H_2 and CO. The ratio of CO_2/CO decreased as the temperature was increased from 575 to 625 °C.

Tables B15 and B16 of Appendix B present results for low levels of Pd doping on KCl/α -alumina catalysts. For Table B15 of Appendix B the catalyst contains 1.6 wt% KCl which is increased to 19.8 wt% in Table B16 of Appendix B. For the low level KCl catalyst, the CH_4 conversion is less than 15% at 649 °C while at 677 °C it is very high with high levels of CO and H_2 in the products. Both C_2 and C_3 selectivities are always less than 2%. With the higher KCl level the activity is less (CH_4 conversion of 5-6% at 623 °C) but the C_2 and C_3 selectivities are still very low. The experiment was terminated before going to higher temperatures (>650 °C) which were needed to obtain high C_2 selectivities with the NaCl/α -alumina catalyst (Table B12 of Appendix B).

Studies were carried out to see if the substitution of BaCl_2 for SrCl_2 in the $\text{Pd}(\text{NO}_3)_2/\text{SrCl}_2/\alpha$ -alumina would result in the high C_3 selectivities observed with SrCl_2 or enhance the catalytic results. Results obtained using BaCl_2/α -alumina are given in Table B17 of Appendix B. The BaCl_2/α -alumina catalyst gives very high C_2 selectivities in the 630-680 °C temperature range with a CH_4 conversion of 20% at 683 °C. Deactivation is occurring as the CH_4 conversion drops from 20% to 13% in 41 hours. This catalyst is just as selective as the SrCl_2/α -alumina catalyst (Fifth Quarterly Report⁴) but slightly less active thus similar results were expected upon Pd doping. Tables B18 and B19 of Appendix B show the results obtained using a $\text{Pd}/\text{BaCl}_2/\alpha$ -alumina catalyst.

The high C_2 selectivities obtained with the $BaCl_2/\alpha$ -alumina catalyst are not observed. C_2 selectivities of 20% were seen but these rapidly decreased. Unusually high C_3 selectivities like those observed for the $Pd/SrCl_2/\alpha$ -alumina catalyst were obtained (Table B19 of Appendix B). At 625 °C the C_3 selectivities (6-9%) were higher than the C_2 selectivities (3-4%). When the temperature was raised to 650 °C, the C_2 selectivities increased but higher than usual C_3 selectivities were still observed.

Lanthanum chloride ($LaCl_3$) was also attempted as a replacement for the $SrCl_2$. Results using the $Pd/LaCl_3/\alpha$ -alumina catalyst are given in Table B20 of Appendix B. High C_3 selectivities were not observed and the C_2 selectivities were very low (< 7%).

The above results indicate that the presence of chloride in the $Pd/X/\alpha$ -alumina catalysts systems (X is another species) does not assure the formation of higher than normal C_3 amounts. Only with the alkaline earth halides ($SrCl_2$ and $BaCl_2$) were the high C_3 levels observed. These halides on α -alumina without Pd dopant gave very high C_2 selectivities (>60%). Whether the high C_2 selectivity or the presence of an alkaline earth metal is a requirement for high C_3 formation is unknown.

Since very high loading of Na_2CO_3 on 5 wt% $Pd/CaCO_3$ (Fifth Quarterly Report⁴) had previously resulted in catalysts with low C_2 selectivities (16%), catalysts were prepared containing lower loadings of Pd and Na_2CO_3 . Results for a Na_2CO_3/α -alumina catalyst are given in Table B21 of Appendix B. The material was active at 675 °C (CH_4 conversion of 18%) but unselective (C_2 selectivity of 9-11%). The addition of Pd to this material resulted in increased activity but even lower C_2 selectivities shown in Table B22 of Appendix B. At 650 °C, high conversions (>50%) and high levels of CO and H_2 were observed indicating the formation of metallic Pd.

Since the pioneering work at Union Carbide⁴⁹ almost all of the literature studies dealing with the oxidative coupling of methane have utilized the concurrent feed of methane and oxygen. The main exceptions are the numerous works reported by Atlantic Richfield Company (ARCO) which uses a sequential or pulse flow of reactants like that proposed by Union Carbide. In the sequential technique, the catalyst is first oxidized by the passage of air or oxygen over the catalyst. The system is then flushed with an inert gas and methane is passed over the catalysts. The sequence can then be repeated. In the ARCO work, manganese-silica catalysts¹⁰ were reported to give the best C_2 yields. The effects of alkali or alkaline doping of the manganese-silica catalysts⁵⁰ were studied. Alkali- and alkaline-doping, especially Na, increased the yields of higher hydrocarbons. A 15% Mn - 5% $Na_4P_2O_7$ - silica catalyst repeatedly gave 17% yields of higher hydrocarbons for 2 minutes at 850 °C. The beneficial effect of sodium addition was

thought to be due to increased surface basicity, reduction of surface area, and a specific sodium-manganese interaction.

Most of the work reported by ARCO used transition metal oxides supported on silica. Only in a few cases were dopants added to the catalysts, such as the studies on Mn/silica, CeO₂, and Pr₆O₁₁. In a recent article, Otsuka⁵¹ proposed that the active species in a Li/NiO coupling catalyst was the complex oxide LiNiO₂. The oxidative coupling of methane was thought to proceed through the following redox cycle:

If such a cycle is occurring, this catalyst should give even better coupling results when studied using the sequential technique. Also, if this is the active species for Li/NiO it is possible that other alkali-doped coupling catalysts react by similar mechanisms; thus, they too should give good results using the sequential technique.

In order to carry out sequential studies, one of the reactor units was modified such that the product stream could be collected in gas sampling bags directly after exiting the reactor. Product samples were collected during timed intervals and analyzed using the same analytic GC procedure employed in the cofeed studies.

A double perovskite, LaCaMnCoO₆, was tested during the Fourth Quarter as a coupling catalyst due to its unique structure and redox properties. Synthesis of LaCaMnCoO₆ was first reported in 1988²⁷. The material was an ordered perovskite showing multiple occupation of both A (La and Ca) and B (Mn and Co) sublattices. X-ray diffraction patterns suggested the crystalline material possessed some ordered domains, while in other areas the cations were distributed at random. For the ordered domains, the most probable structural model was an ABO₃ perovskite-type structure in which Mn⁴⁺ and Co³⁺ ions occupied B positions in adjacent ABO₃ units while La³⁺ and Ca²⁺ ions alternate in the A positions. The material has a unique redox property in that two ions in the structure undergo reduction.

This makes the material of interest as a methane coupling catalyst for sequential studies as well as cofeed studies.

The LaCaMnCoO₆ catalyst was active (Fourth Quarterly Report²¹) in the cofeed mode (O₂ limited at 700 °C) but gave very low C₂ selectivities (<3%). In the sequential mode (Fifth Quarterly Report⁴), this material gave low C₂ selectivities (<6%) over a temperature range of 700 to 900 °C, but the CH₄ conversions were greater than those obtained using Mn/Na₄P₂O₇/silica (ARCO literature catalyst).

Sodium doping (Na_2CO_3) of LaCaMnCoO_6 drastically changed its catalytic properties. LaCaMnCoO_6 gave very low C_2 selectivities in cofeed and sequential studies; but, Na_2CO_3 doped LaCaMnCoO_6 (Fifth Quarterly Report⁴) gave good C_2 selectivities. K_2CO_3 doping resulted in lower activity and lower C_2 selectivity than Na_2CO_3 doping.

Comparison studies on Li_2CO_3 and Na_2CO_3 doped LaCaMnCoO_6 were performed in the sequential mode. Li_2CO_3 doping (Table B23 of Appendix B) resulted in lower activity but higher C_2 selectivity. For example, at 850 °C and 150 ccm of CH_4 (10 g catalyst), the Li_2CO_3 doped catalyst gave CH_4 conversions/ C_2 selectivities of 7.9%/91% and 3.8%/94% for collection times of 0 to 2 and 2 to 5 minutes. For the same conditions and time intervals, the Na_2CO_3 doped catalyst (Fifth Quarterly Report⁴) gave CH_4 conversions/ C_2 selectivities of 11.3%/77% and 10.0%/65%.

The effect of using a diluted CH_4 stream in the sequential mode was studied with the $\text{Li}_2\text{CO}_3/\text{LaCaMnCoO}_6$ catalyst. The results are presented on pages 2 and 3 of Table B23 of Appendix B. At 725 °C and 150 ccm of CH_4 , the Li_2CO_3 doped catalyst gave CH_4 conversions/ C_2 selectivities of 3.0%/66%, 2.6%/50%, and 1.2%/87% for collection times of 0 to 2, 2 to 5, and 5 to 10 minutes. For the same conditions and time intervals, a reactant stream of 20% CH_4 /80% N_2 gave CH_4 conversions/ C_2 selectivities of 18.2%/49%, 12.4%/51%, and 8.1%/66%. The use of the diluted reactant stream gave higher C_2 yields due to the higher conversion but the C_2 selectivities were less. Since the total amount of CH_4 reacted in both cases was approximately the same, the undiluted case gave the better overall results.

Oxygen carriers²⁵ consisting of oxide solid solutions of praseodymium and cerium were prepared for testing as methane coupling catalysts in the cofeed and sequential modes⁵. These materials were of interest due to their usefulness as oxygen carriers in a reversible cyclic oxidation-reduction process for separating oxygen from air.

Materials tested in the cofeed mode were Na_2CO_3 doped Pr-Ce oxides (Table B24 of Appendix B) and Na_2CO_3 doped Ag-Pr-Ce oxides (Tables B25 and B26 of Appendix B). Na-doping of the catalysts resulted in decreased activities but greatly enhanced C_2 selectivities. For example, CH_4 conversions of 32-33% with C_2 selectivities of 40-41% were obtained at 737 °C (GHSV = 1460 h^{-1} ; $\text{CH}_4/\text{O}_2/\text{N}_2 = 2/1/3.7$) with the $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ oxide. For the undoped materials (Sixth Quarterly Report⁵), high activities (O_2 limited at 600 °C; GHSV = 1200-1300 h^{-1} ; $\text{CH}_4/\text{O}_2/\text{N}_2 = 2/1/3.8$) but low C_2 selectivities (<20%) were observed in the temperature range of 550 to 750 °C.

The effects of changing the reactant composition ($\text{CH}_4/\text{O}_2/\text{N}_2$ ratio) was studied for the $\text{Na}_2\text{CO}_3/\text{Pr-Ce}$ oxide catalyst (Table B24 of Appendix B). In the experiment the O_2/N_2 ratio was held constant while the CH_4/O_2 ratio was changed. The results agree with previously observed trends. Increasing the CH_4/O_2 ratio resulted in decreased CH_4 conversion, increased O_2 conversion, increased C_2 selectivity, increased C_3 selectivity, decreased ethylene/ethane ratio, and decreased CO_2/CO ratio.

Na_2CO_3 doped Pr-Ce oxides (Table B27 of Appendix B) and Ag-Pr-Ce oxides (Table B28 of Appendix B) were tested using the sequential mode. Both catalysts showed high activities for sequential mode operation. The $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ catalyst was more active than the $\text{Na}_2\text{CO}_3/\text{Pr-Ce}$ catalyst. At 750°C and 50 ccm CH_4 (10g catalyst), the $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ catalyst gave initial CH_4 conversions/ C_2 selectivities of 45%/29% and 9.5%/58% for collection times of 0 to 2 and 2 to 5 minutes. Under the same conditions, the $\text{Na}_2\text{CO}_3/\text{Pr-Ce}$ catalyst gave CH_4 conversions/ C_2 selectivities of 27%/47% and 15%/38%. After heating to 850°C , the $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ catalyst gave CH_4 conversions/ C_2 selectivities at 750°C and 50 ccm CH_4 of 28%/44% and 8.2%/67% for collection times of 0 to 2 and 2 to 5 minutes. Both catalysts followed the normal trend that the C_2 selectivity increased as the catalyst was reduced (activity decreased).

The reproducibility of the sequential mode results and the effects of GHSV were examined for the $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ catalyst (Table B29 of Appendix B) at 725°C . After the initial collection of gas samples, the results show variations that are considered within the accuracy of the experimental system. For 0 to 2 minute sample collections at 725°C and 150 ccm flow rate, the CH_4 conversions were 16.6%, 15.1%, and 17.8% with corresponding C_2 selectivities of 64%, 66%, and 58%. When the methane flow rate was varied over the values 50, 100, 150, and 200 ccm, the CH_4 conversions for the 0 to 2 minute collections were 51%, 17%, 18%, and 15% with corresponding C_2 selectivities of 24%, 61%, 58%, and 64%. The highest C_2 yields were obtained for a flow rate of 50 ccm where the CH_4 conversion was the largest but the C_2 selectivity was lowest.

For comparison, experiments were carried out using the literature catalyst⁵² sodium carbonate (Na_2CO_3) doped praseodymium oxide (Pr_6O_{11}). At 750°C and 150 ccm CH_4 (10g catalyst), the $\text{Na}_2\text{CO}_3/\text{Pr}_6\text{O}_{11}$ catalyst gave CH_4 conversions/ C_2 selectivities of 19%/80%, 13%/82%, and 2.5%/82% for collection times of 0 to 2, 2 to 5, and 5 to 10 minutes. The results for the $\text{Na}_2\text{CO}_3/\text{Pr}_6\text{O}_{11}$ catalyst (Table B30 of Appendix B) were better than those obtained with the $\text{Na}_2\text{CO}_3/\text{Pr-Ce}$ oxide or $\text{Na}_2\text{CO}_3/\text{Ag-Pr-Ce}$ oxide.

NEK Laboratory

The temperature profiles of both furnaces were measured and are shown in Figure C18 of Appendix C. The profiles were measured with the quartz reactors packed with quartz chips in place via a thermocouple in the thermocouple well. The end of the thermocouple well in the middle of the reactor is designated as 0 inches and the profile is taken from that point to the end of the furnace on the outlet side of the reactor (i.e., through the area which will hold the catalyst and then downstream of the catalyst bed). The Thermpro furnace was equipped with shunt taps across which a resistance could be applied which enabled the temperature profile to be modified. The resistance and location of the resistor was varied and it was found that a 75 ohm resistor between shunts 3 and 8 resulted in the broadest and flattest profile in the center of the furnace.

Blank runs were made in both reactors to determine the extent of reaction in the absence of catalyst under various reaction conditions. At 750 °C, 2200 hr⁻¹ GHSV, 11 psig and 10:5:85 methane:oxygen:argon, the methane conversion was negligible (<1%). At 800 °C the conversion was about 2%. Both reactors performed virtually identically.

Samples from two separate preparations of a 4.77 weight percent barium carbonate on Norton SA5451 alumina, 30/60 mesh catalyst were evaluated side by side in the two reactors (see Tables B31 and B32 of Appendix B). The yields to C₂ hydrocarbons of 3-8% are much lower than expected based on BKW's results. The reason for this probably lies in the preparation of the catalyst. It was noted that the catalysts contained a significant amount of fines, and in addition, that the two catalyst preparations contained noticeably different amounts of fines. This explains why the two 15 ml catalyst charges weighed different amounts - 20.3 gm for 33-NEK-34-1 and 17.96 gm for 33-NEK-34-2. The difference in performance between the catalyst in reactor 1 versus in reactor 2 may be due in part to the different weights of the catalysts loaded, and in part to the different inlet pressures due to the differing amounts of fines contained in the two catalyst charges.

The reason for the large amount of fines is believed to be due to rapid stirring of the alumina/barium carbonate/water mixture during the evaporation of the water. The difference between the two preparations is probably due to the different lengths of time the two preparations were stirred during this same step in order to obtain a thick slurry.

The initial attempt to validate the reactors and to prepare catalyst were unsuccessful; however, the reasons are believed to be understood and a new batch of catalyst will be prepared and used for the validation runs.

SUMMARY:

BKW Laboratory

Three roles of chloride for alkaline earth/metal oxide/chloride catalysts were further defined and found to be consistent with results from catalysts containing Sr as well as those containing Ba. The chloride acts to increase the rate to C_2 's, which is consistent with the halide on the catalyst reacting with and breaking up stable carbonates or other salts (aluminates, titanates, etc.) to allow the formation of active oxygen species on barium or strontium. The rate to carbon dioxide decreases slowly with addition of chloride and increases if ethyl chloride is removed from the feed stream. Apparently, the chloride also reacts with and destroys surface catalyst species which oxidize C_2 's or methyl radicals to carbon dioxide. The increases in ethylene to ethane ratios from addition of ethyl chloride in the gas feed are consistent with conversion of ethane to ethylene in the gas phase by free radical chain reactions, involving halide radicals produced on the catalyst surface and released into the gas phase. Release of chlorine radicals from a catalyst surface into the gas phase is a concept parallel to the concept of surface methyl radical escape and subsequent reaction in the gas phase, proposed by J. H. Lunsford.

The behavior of alkaline earth/metal oxide/halide catalysts containing strontium was found to be different from the behavior of catalysts containing barium. This difference in behavior is consistent with differences in rates of transformations of alkaline earth compounds on the catalyst surface to form steady-states of metal dispersion and steady states of concentrations of the various anions. This explanation accounts for the observed differences between barium and strontium catalysts and for differences among catalysts containing one alkaline earth metal prepared with different anions. Electron microscopy results of fresh and used catalysts containing barium and strontium support this explanation.

Fresh catalysts made from barium carbonate and barium chloride have different dispersions of barium. Barium in a carbonate catalyst disperses and moves from the surface into the catalyst particles as methane oxidation occurs. The barium on catalysts made with chloride remains in clumps during the reaction. Microscopy shows strontium dispersions in catalysts made from chloride and carbonate to be different, and also different from the similar catalysts prepared from barium salts rather than strontium salts.

Two approaches were investigated to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations. One approach was to minimize or eliminate the typical gas phase combustion chemistry and make more of the reaction occur on the surface of the catalyst by using catalysts containing silver. Another was to change the gas phase chemistry to minimize the typical gas phase combustion reaction network by using vapor-phase catalysts. Both approaches succeeded in demonstrating that these concepts to avoid the heterogeneous/homogeneous mechanism are viable. The surface contribution of the reaction was enhanced using catalysts containing silver, and the vapor-phase conversion of methane to carbon oxides was inhibited by volatile metal salts.

KDC Laboratory

Studies were conducted on the $K_2La_2Ti_3O_{10}$ layered perovskite catalyst. The addition of CO_2 to the reactant stream resulted in a decrease in the CH_4 conversion, an increase in the C_2 selectivity, and a decrease in the CO_2/CO ratio. The addition of ethyl chloride appeared to cause a slow deactivation of the catalyst and did not result in any enhancement (increase) of the ethylene/ethane ratio.

Work on the $Pd/SrCl_2/\alpha$ -alumina bifunctional catalyst indicated that the presence of chloride in the $Pd/X/\alpha$ -alumina catalysts systems, where X is a species other than $BaCl_2$ or $SrCl_2$, does not assure the formation of higher than normal proportions of C_3 's. Only with the alkaline earth halides ($SrCl_2$ and $BaCl_2$) were the high C_3 levels observed. These halides on α -alumina without Pd dopant gave very high C_2 selectivities. Whether the high C_2 selectivity or the presence of an alkaline earth metal was a requirement for high C_3 formation could not be determined.

Comparison studies on Li_2CO_3 and Na_2CO_3 doped $LaCaMnCoO_6$ were performed in the sequential mode. Li_2CO_3 doping resulted in lower activity but higher C_2 selectivity. The effect of using a diluted CH_4 stream in the sequential mode was studied using the $Li_2CO_3/LaCaMnCoO_6$ catalyst. The use of the diluted reactant stream gave higher C_2 yields due to the higher conversion but the C_2 selectivities were less. Since the total amount of CH_4 reacted in the diluted and undiluted cases was approximately the same, the undiluted case gave the better results.

Oxygen carriers²⁵ consisting of oxide solid solutions of praseodymium and cerium were prepared for testing as methane coupling catalysts in the cofeed and sequential modes. Materials tested were Na_2CO_3 doped Pr-Ce oxides and Na_2CO_3 doped Ag-Pr-Ce

oxides. In the cofeed mode, Na-doping of the catalysts resulted in decreased activities but greatly enhanced C₂ selectivities. The effects observed upon changing the reactant composition agreed with previously observed trends. Increasing the CH₄/O₂ ratio resulted in decreased CH₄ conversion, increased O₂ conversion, increased C₂ selectivity, increased C₃ selectivity, decreased ethylene/ethane ratio, and decreased CO₂/CO ratio. Both catalysts showed high activities for sequential mode operation and followed the normal trend that the C₂ selectivity increased as the catalyst was reduced (activity decreased). Results obtained with a literature catalyst, Na₂CO₃/Pr₆O₁₁, were better than those obtained with the Na₂CO₃/Pr-Ce oxide or Na₂CO₃/Ag-Pr-Ce oxide.

NEK Laboratory

Two laboratory reactors were constructed and were used to investigate the effect of diluents, especially steam, and the effect of pressure. Initial tests without catalysts showed little or no conversion of methane or oxygen at 750 °C.

TASK 2: Process Conceptualization

INTRODUCTION:

This portion of the program covers all of the engineering studies. The intention is that engineering participation in economic evaluation, process conceptualization, and experimental design will speed up the development of a commercially attractive process.

The Comparison Case consists of the conversion of methane to synthesis gas followed by conversion of the synthesis gas to methanol. Methanol will be converted to liquid hydrocarbon fuels via olefins. All of the components of this technology have been demonstrated on a commercial or pilot scale. Case 1 will consist of the conversion of methane to ethylene. Case 2 will be the conversion of methane directly to C₂'s and then to liquid hydrocarbon fuels. These two cases address the primary interests of Union Carbide and DOE, respectively.

RESULTS AND DISCUSSION:

Within Task 2, sensitivity studies have continued based on mild extrapolations of actual Union Carbide laboratory results from promising catalysts. A fluidized-bed

catalytic reactor system has been assumed for all cases. The variables that have been evaluated are:

- reactor diluents (nitrogen, methane and steam),
- methane to oxygen feed ratio in the reactor feed, and
- sequential feed versus co-feed process configurations.

Nitrogen Diluent Cases

Three nitrogen diluent cases have been evaluated, each at a different methane to oxygen ratio in the reactor feed. All are based on an oxygen concentration in the feed to the reactor of 11.2%. These are summarized below:

Case	A1.1d	A1.1b	A1.1c
CH ₄ /O ₂ Ratio	<u>1</u>	<u>2</u>	<u>4</u>
CH ₄ Conversion, %	73.0	44.7	26.4
Selectivity to C ₂ 's, %	33.4	49.6	58.5
Yield to C ₂ 's, %	24.4	22.2	15.4
Total Fixed Investment, \$MM	709	613	590
Total Cash Cost, ¢/lb	24.6	19.7	18.1
ROIAT, %	0	6	8

Process Description

Figure C19 of Appendix C is the Simplified Block Diagram for the nitrogen diluent cases. As an example, the material balance for Case A1.1b is contained in Table B33 of Appendix B.

Fresh methane, air, and recycle methane/nitrogen (streams 1, 2, and 11, respectively) are combined to make the feed to the Catalytic Reactor System (stream 3). The primary advantage of the nitrogen diluent cases is that air can be fed to the process instead of high-purity oxygen. The large exothermic heat of reaction is recovered as steam, which is used to drive turbines in the downstream process systems. The reactor product gas (stream 4) is then quenched to both stop the reaction, and to condense the majority of the water-of-reaction (stream 5). The quenched reactor gas (stream 6) then is

fed to the Compression System, which brings the material from the reactor pressure (50 psig) up to the operating pressure of the recovery and refining systems (300-600 psig).

The first of these downstream systems is the Acid Gas Removal System, which removes not only carbon dioxide via a standard amine-scrubbing system, but also the remaining water with molecular sieve dryers (stream 9). The scrubbed and dried gas (stream 10) then enters the Cold Box System, which includes a methane column. Here, the unreacted methane (stream 11) is separated from the nitrogen/methane purge (stream 12), and the C_2 and heavier products (stream 13) are recovered for further refining. Note that the purge stream is unsuitable for fueling due to its low organics content.

The refining section of the process contains a De-ethanizer Column for removal of the C_3 and heavier fractions (stream 14) from the C_2 's (stream 15), and an Ethylene Column for the separation of ethylene product (stream 16) from ethane (stream 17). The ethylene thus produced is of pipeline quality (99.85%).

The ethane is sent to a conventional Steam Cracker System, where it is converted to additional ethylene. The quenched steam cracker product gas (stream 21) is combined with the quenched product from the Catalytic Reactor System (stream 6) in the Compressor System.

Economics

Table B34 of Appendix B summarizes the results of the investment estimates for the nitrogen diluent cases. Note that the Total ISBL (inside battery limits) investment for the cases decreases as the methane to oxygen ratio in the feed to the catalytic reactor system increases. This results from the fact that increasing the methane to oxygen ratio decreases the methane conversion, but increases the selectivity to C_2 's. The design of the Catalytic Reactor System is dominated by the need to remove the heat of reaction, which decreases with increasing selectivity. Increasing selectivity also reduces the air requirements for the process, and hence, the size of the Air Compression System. This trend overwhelms the tendency of decreasing methane conversion to increase the costs of the Steam Cracking, Cold Box, and Refrigeration Systems.

Table B35 of Appendix B summarizes the economics for the nitrogen diluent cases. Note that the total cash cost decreases with increasing methane to oxygen ratio, due to the previously noted effect of this variable on the selectivity to C_2 's, and hence the overall methane usage. This trend overwhelms the tendency of decreasing methane conversion to increase the utility costs. With both the investment and the cash cost decreasing with

increasing methane to oxygen ratio, the sensitivity of the resultant ROIAT (return on investment after tax) to this variable is significant.

However, it is not possible to increase the methane to oxygen ratio beyond 4 and still feed air to the process. Beyond this limit, purified oxygen would have to be fed instead, and much of the advantage of the nitrogen diluent case would be lost. At a methane to oxygen ratio of 7, the process arrangement and economics would be identical to the methane diluent case (Case A1.2a).

Methane Diluent Cases

Two methane diluent cases have been evaluated, differing in the oxygen concentration in the feed to the catalytic reactor. These were described previously in the Sixth Quarterly Report⁵, and are included herein for completeness:

<u>Case</u>	<u>A1.2a</u>	<u>A1.2b</u>
Oxygen concentration in Rx feed, %	11.2	5.2
Methane conversion, %	18.4	9.9
Selectivity to C ₂ 's, %	76.7	87.1
C ₂ yield, %	14.1	8.6
Total Fixed Investment, \$MM	475	599
Cash Cost, ¢/lb ethylene	12.7	15.4
ROIAT, %	19	11

Process Description

Figure C20 of Appendix C is the Simplified Block Diagram for the methane diluent cases. As an example, the material balance for Case A1.2a is contained in Table B36 of Appendix B.

Fresh methane, high-purity oxygen, and recycle methane (streams 1, 2, and 11, respectively) are combined to make the feed to the Catalytic Reactor System (stream 3). The primary advantage of the methane diluent cases is the high selectivity to C₂'s that results. The large exothermic heat of reaction is recovered as steam, which is used to drive turbines in the downstream process systems. The reactor product gas (stream 4) is then quenched to both stop the reaction, and to condense the majority of the water-of-reaction (stream 5). The quenched reactor gas (stream 6) then is fed to the Compression

System, which brings the material from the reactor pressure (50 psig) up to the operating pressure of the recovery and refining systems (300-600 psig).

The first of these downstream systems is the Acid Gas Removal System, which removes not only carbon dioxide via a standard amine-scrubbing system, but also the remaining water with molecular sieve dryers (stream 9). The scrubbed and dried gas (stream 10) then enters the Cold Box System, which includes a methane column. Here, the unreacted methane (stream 11) is separated from the methane/inerts purge (stream 12), and the C_2 and heavier products (stream 13) are recovered for further refining. Note that the purge stream has a high organics content, and would make an excellent fuel.

The refining section of the process contains a De-ethanizer Column for removal of the C_3 and heavier fractions (stream 14) from the C_2 's (stream 15), and an Ethylene Column for the separation of ethylene product (stream 16) from ethane (stream 17). The ethylene thus produced is of pipeline quality (99.85%).

The ethane is sent to a conventional Steam Cracker System, where it is converted to additional ethylene. The quenched steam cracker product gas (stream 21) is combined with the quenched product from the Catalytic Reactor System (stream 6) in the Compressor System.

Economics

Table B37 of Appendix B summarizes the results of the investment estimates for the methane diluent cases. Note that the Total ISBL (inside battery limits) investment for the cases increases as the oxygen concentration in the feed to the catalytic reactor system decreases. This results from the fact that increasing the methane to oxygen ratio increases the selectivity to C_2 's, but decreases the methane conversion. The design of the Catalytic Reactor System is normally dominated by the total heat of reaction, but in this instance is affected more strongly by the feed preheat and product quench heat loads. Decreasing methane conversion also increases the cost of the Compression, Acid Gas Removal, Cold Box and Refrigeration Systems.

Table B38 of Appendix B summarizes the economics for the methane diluent cases. Note that the total cash cost increases with decreasing oxygen concentration, due to the previously noted effect of this variable on the methane conversion, and hence the total utilities cost. This trend overwhelms the tendency of increasing selectivity to C_2 's to decrease the overall methane usage. With both the investment and the cash cost

increasing with decreasing oxygen concentration, the sensitivity of the resultant ROIAT to this variable is significant.

However, it has been assumed that the maximum oxygen concentration in the feed to the reactor significantly is about 11%, due to the explosive limits of the mixture. Obviously, determining precisely maximum limit for this variable is of prime importance from both an economic and a safety standpoint.

Steam Diluent Cases

Three steam diluent cases have been evaluated, each at a different methane to oxygen ratio in the reactor feed. All are based on a oxygen concentration in the feed to the reactor of 11.2%. The methane conversion and selectivity to C₂'s for these cases have been assumed to be equal to those for the nitrogen diluent cases. The steam diluent cases are summarized below:

Case	A1.3d	A1.3b	A1.3c
CH ₄ /O ₂ Ratio	<u>1</u>	<u>2</u>	<u>4</u>
CH ₄ Conversion, %	73.0	44.7	26.4
Selectivity to C ₂ 's, %	33.4	49.6	58.5
Yield to C ₂ 's, %	24.4	22.2	15.4
Total Fixed Investment, \$MM	588	496	492
Total Cash Cost, ¢/lb	28.7	19.4	15.6
ROIAT, %	-3	9	14

Process Description

Figure C21 of Appendix C is the Simplified Block Diagram for the steam diluent cases. As an example, the material balance for Case A1.3b is contained in Table B39 of Appendix B.

Fresh methane, oxygen, steam, and recycle methane (streams 1, 2, 3, and 12, respectively) are combined to make the feed to the Catalytic Reactor System (stream 4). The large exothermic heat of reaction is recovered as steam, which is used not only as the diluent in this case, but also to drive turbines in the downstream process systems. The

reactor product gas (stream 5) is then quenched to both stop the reaction, and to condense the majority of the contained water (stream 6). The primary advantage of the steam diluent cases is that most of the diluent condenses at this point, and does not have to be handled by the downstream process systems. The quenched reactor gas (stream 7) then is fed to the Compression System, which brings the material from the reactor pressure (50 psig) up to the operating pressure of the recovery and refining systems (300-600 psig).

The first of these downstream systems is the Acid Gas Removal System, which removes not only carbon dioxide via a standard amine-scrubbing system, but also the remaining water with molecular sieve dryers (stream 10). The scrubbed and dried gas (stream 11) then enters the Cold Box System, which includes a methane column. Here, the unreacted methane (stream 12) is separated from the methane/inerts purge (stream 13), and the C_2 and heavier products (stream 14) are recovered for further refining. Note that the purge stream has a high organics content, and would make an excellent fuel.

The refining section of the process contains a De-ethanizer Column for removal of the C_3 and heavier fractions (stream 15) from the C_2 's (stream 16), and an Ethylene Column for the separation of ethylene product (stream 17) from ethane (stream 18). The ethylene thus produced is of pipeline quality (99.85%).

The ethane is sent to a conventional Steam Cracker System, where it is converted to additional ethylene. The quenched steam cracker product gas (stream 22) is combined with the quenched product from the Catalytic Reactor System (stream 7) in the Compressor System.

Economics

Table B40 of Appendix B summarizes the results of the investment estimates for the steam diluent cases. Note that the Total ISBL (inside battery limits) investment for the cases reaches a minimum at a methane to oxygen ratio of 2, but generally decreases with increasing methane to oxygen ratio. This results from the fact that increasing the methane to oxygen ratio decreases the methane conversion, but increases the selectivity to C_2 's. The design of the Catalytic Reactor System is dominated by the need to remove the heat of reaction, which decreases with increasing selectivity. This trend is countered by the tendency of decreasing methane conversion to increase the costs of the Steam Cracking, Compression, Cold Box, and Refrigeration Systems.

Table B41 of Appendix B summarizes the economics for the steam diluent cases. Note that the Total Fixed Investment decreases with increasing methane to oxygen due to

the previously noted effect of this variable on the selectivity to C₂'s, and hence the cost of the Oxygen Plant (Air Separation Unit). Note also that the total cash cost decreases with increasing methane to oxygen ratio, due to the decrease in both the overall methane usage and the utility costs. The utility costs decrease with increasing methane to oxygen ratio due to the declining demand for steam diluent, allowing more of the reaction steam to be used in driving the Compression and Refrigeration System turbines. With both the investment and the cash cost decreasing with increasing methane to oxygen ratio, the sensitivity of the resultant ROIAT to this variable is significant.

However, as the methane to oxygen ratio is increased beyond 4, the process arrangement and economics approach that of the methane diluent case (Case A1.2a).

Sequential Feed Cases

Four sequential feed cases have been evaluated, each at a different methane to oxygen ratio. All are based on ARCO literature catalyst results. These are summarized below:

Case	A1.4c	A1.4b	A1.4d	A1.4e
CH ₄ /O ₂ Ratio	<u>2</u>	<u>5</u>	<u>7</u>	<u>10</u>
CH ₄ Conversion, %	44.7	24.0	20	16.0
Selectivity to C ₂ 's, %	41.9	62.8	67.3	71.8
Yield to C ₂ 's, %	18.7	15.1	13.5	11.5
Total Fixed Investment, \$MM	502	459	474	495
Total Cash Cost, ¢/lb	14.4	11.0	11.6	12.1
ROIAT, %	15	22	20	18

Process Description

Figure C22 of Appendix C is the Simplified Block Diagram for the sequential feed cases. As an example, the material balance for Case A1.4b is contained in Table B42 of Appendix B.

Fresh methane and recycle methane (streams 1 and 12, respectively) are combined to make the feed to the Catalytic Reactor System (stream 2). The primary advantage of the sequential feed cases is that air (stream 3) is fed to this system instead of high-purity oxygen, and that the nitrogen (stream 4) is exhausted without significantly crossing over

to the process stream. The large exothermic heat of reaction is recovered as steam, which is used to drive turbines in the downstream process systems. The reactor product gas (stream 5) is then quenched to both stop the reaction, and to condense the majority of the water-of-reaction (stream 6). The quenched reactor gas (stream 7) then is fed to the Compression System, which brings the material from the reactor pressure (50 psig) up to the operating pressure of the recovery and refining systems (300-600 psig).

The first of these downstream systems is the Acid Gas Removal System, which removes not only carbon dioxide via a standard amine-scrubbing system, but also the remaining water with molecular sieve dryers (stream 10). The scrubbed and dried gas (stream 11) then enters the Cold Box System, which includes a methane column. Here, the unreacted methane (stream 12) is separated from the methane/inerts purge (stream 13), and the C_2 and heavier products (stream 14) are recovered for further refining. Note that the purge stream has a high organics content, and would make an excellent fuel.

The refining section of the process contains a De-ethanizer Column for removal of the C_3 and heavier fractions (stream 15) from the C_2 's (stream 16), and an Ethylene Column for the separation of ethylene product (stream 17) from ethane (stream 18). The ethylene thus produced is of pipeline quality (99.85%).

The ethane is sent to a conventional Steam Cracker System, where it is converted to additional ethylene. The quenched steam cracker product gas (stream 22) is combined with the quenched product from the Catalytic Reactor System (stream 7) in the Compressor System.

Economics

Table B43 of Appendix B summarizes the results of the investment estimates for the sequential feed cases. Note that the Total ISBL (inside battery limits) investment for the cases goes through a minimum at a methane to oxygen ratio of 5. This results from the fact that increasing the methane to oxygen ratio decreases the methane conversion, but increases the selectivity to C_2 's. Increasing selectivity reduces the air requirements for the process, and hence, the size of the Air Compression System. This trend is countered by the tendency of decreasing methane conversion to increase the costs of the Compression, Cold Box, and Refrigeration Systems.

Table B44 of Appendix B summarizes the economic results for the sequential feed cases. Note that the total cash flow goes through a minimum at a methane to oxygen ratio of 5 due to the previously noted effect of this variable on the selectivity to C_2 's and methane.

conversion. Increasing the selectivity to C_2 's decreases the overall methane usage, but this trend is countered by the tendency of decreasing methane conversion to increase the utility costs. With both the investment and the cash cost reaching their minimums at a methane to oxygen ratio of 5, the resultant ROIAT reaches its maximum at this point as well.

Comparison of Different Cases

Figures C23 and C24 of Appendix C summarize the results of the sensitivity studies conducted on reactor diluent and methane to oxygen ratio described above. The top graph in Figure C23 of Appendix C shows how the Total Fixed Investment for the four diluent systems compare among themselves, and how each varies with methane to oxygen ratio. The nitrogen diluent cases require much more investment than any of the others. This is due to the high cost of compressing the nitrogen diluent from the catalytic reactor pressure up to the operating pressure of the recovery and refining systems, plus the high cost of separating this nitrogen from the unreacted methane. The investments for the methane and steam diluent cases and the sequential feed cases are all approximately equal to each other, differing by less than the $\pm 25\%$ investment accuracy.

The bottom graph in Figure C23 of Appendix C shows how the Total Cash Cost for the four diluent systems compare among themselves, and how each varies with methane to oxygen ratio. Both the nitrogen and steam diluent cases have a higher cash cost than either the methane diluent or the sequential feed case. These cases have a higher methane usage due to their lower selectivity to C_2 's. The Total Cash Cost for the methane diluent and the sequential feed cases are approximately equal to each other.

Figure C24 of Appendix C shows how the resulting ROIAT for the four diluent systems compare among themselves, and how each varies with methane to oxygen ratio. With their higher selectivity to C_2 's, both the methane diluent and the sequential feed cases have a higher ROIAT than the nitrogen or steam diluent cases. But the nitrogen and steam diluent cases had a higher overall yield to C_2 's. Therefore, yield-to- C_2 's is not a good general indicator of economics.

Rather, selectivity to C_2 's appears to be the more reliable economic indicator, so long as the oxygen concentration in the feed to the reactor is held at a fixed, maximum value (assumed to be 11.2% in these studies). Comparing case A1.2a to A1.2b (methane diluent), a lower oxygen concentration may itself increase the selectivity to C_2 's, but has a detrimental effect on the economics.

Support of Experimental Program

Support of the experimental program has continued through regular meetings of the chemists and engineers with discussions of the laboratory results, the proposed process configurations, results of heat and material balances, and preliminary economics.

SUMMARY:

Sensitivity studies were continued based on extrapolations of actual Union Carbide laboratory results from promising catalysts. Variables examined included reactor diluents (nitrogen, methane, and steam), methane to oxygen feed ratio in the reactor feed, and sequential feed versus co-feed process configurations.

The investments for methane and steam diluent cases and the sequential feed cases are all approximately equal to each other, differing by less than the $\pm 25\%$ investment accuracy. The nitrogen and steam diluent cases have higher cash cost and higher ROIAT's than either the methane diluent or the sequential feed case, due to the higher selectivity of these last two cases. The nitrogen and steam diluent cases have higher yields to C_2 's, so yield-to- C_2 's is not a good general indicator of overall process economics.

REFERENCES:

1. C. A. Jones, J. J. Leonard, and J. A. Sofranko, *Energy and Fuels*, **1**, 12 (1987).
2. F. M. Dautzenberg, R. L. Garten, and G. Klingman, "Fuels from Remote Natural Gas: Defining the Research and Development Challenge," paper presented at ACS 21st Symposium, Mares Island, Florida (1986).
3. S. A. Tabak, "Production of Synthetic Diesel Fuel From Light Olefins," 1984 AIChE National Meeting, Philadelphia, 1984.
4. B. K. Warren, K. D. Campbell, J. L. Matherne, and G. L. Culp, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Fifth Quarterly Progress Report, Contract DE-AC22-87PC79817, February 1, 1990.
5. B. K. Warren, K. D. Campbell, and J. L. Matherne, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Sixth Quarterly Progress Report, Contract DE-AC22-87PC79817, February 14, 1990.
6. D. J. Driscoll, W. Martin, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, **107**, 58 (1985).
7. K. D. Campbell, E. Morales, and J. H. Lunsford, *J. Am. Chem. Soc.*, **109**, 7900 (1987).
8. K. D. Campbell, H. Zhang, and J. H. Lunsford, *J. Phys. Chem.*, **92**, 750 (1988).
9. K. D. Campbell and J. H. Lunsford, *J. Phys. Chem.*, **92**, 5792 (1988).
10. J. A. Sofranko, J. J. Leonard, and C. A. Jones, *J. Catal.*, **103**, 302 (1987).
11. J. B. Kimble and J. H. Kolts, *Energy Progress*, **6**, 226 (1986).
12. K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, **100**, 353 (1986).
13. N. W. Cant, C. A. Lukey, P. F. Nelson, and R. J. Tyler, *J. Chem. Soc., Chem. Commun.*, 766 (1988).

14. A. Ekstrom and J. A. Lapszewicz, *J. Chem. Soc., Chem. Commun.*, 797 (1988).
15. J. B. Kimble and J. H. Kolts, Fall A.C.S. Meeting, 1988.
16. J. A. Labinger, *Catal. Letters* **1**, 371 (1988).
17. J. G. McCarty, A-B. McEwen, and M. A. Quinlan, Proceedings of International Symposium, "New Developments in Selective Oxidation," Rimini, Italy, 1989.
18. V. R. Choudhary, S. T. Chaudhari, A. M. Rajput, and V. H. Rane, *J. Chem. Soc., Chem. Commun.*, 555 (1989).
19. S. J. Korf, J. A. Roos, J. M. Diphoorn, R. H. J. Veehof, J. G. van Ommen, and J. R. H. Ross, *Catal. Today*, **4**, 279 (1989).
20. B. K. Warren and K. D. Campbell, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Third Quarterly Progress Report, Contract DE-AC22-87PC79817, November 22, 1989.
21. B. K. Warren and K. D. Campbell, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Fourth Quarterly Progress Report, Contract DE-AC22-87PC79817, January 24, 1990.
22. B. K. Warren and K. D. Campbell, "Direct Conversion of Methane to C₂'s and Liquid Fuels," First Quarterly Progress Report, Contract DE-AC22-87PC79817, April 4, 1989.
23. B. K. Warren and K. D. Campbell, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Second Quarterly Progress Report, Contract DE-AC22-87PC79817, June 15, 1988.
24. B. K. Warren, K. D. Campbell, J. L. Matherne, and G. L. Culp, "Direct Conversion of Methane to C₂'s and Liquid Fuels," Indirect Liquefaction Contractors' Review Meeting Proceedings, November 15, 1988, pp 177-204, U. S. Department of Energy, Pittsburgh Energy Technology Center (National Information Service U. S. Dept. of Commerce, Springfield, VA 22161).
25. U. S. Patent 3,980,763, to Union Carbide Corporation, September 14, 1976.

26. J. Gopalakrishnan and V. Bhat, *Inorg. Chem.*, **26**, 4301 (1987).
27. M. Vallet-Regi, E. Garcia, and J. M. Gonzalez-Calbet, *J. Chem. Soc. Dalton Trans.*, 775 (1988).
28. R. D. Cosirno, J. D. Burrington, and R. K. Grasselli, *J. Catal.*, **102**, 234 (1986).
29. M. A. Chaar, D. Patel, M. C. Kung, and H. H. Kung, *J. Catal.*, **105**, 483 (1987).
30. J. B. Kimble and J. H. Kolts, EP 210383 to Phillips, Dec. 12, 1986 (JP 61,282,322, U. S. Appl. 742,335, June 7, 1985).
31. K. Aika, T. Moriyama, T. Takasaki, and E. Iwamatsu, *J. Chem. Soc., Chem. Commun.*, 1210 (1986).
32. R. F. Hicks, WO 86/07351 to W. R. Grace & Co., Dec. 18, 1986 (priority June 14, 1985).
33. Ger. Patent No. 3,503,664 to AKZO, GmbH, Wuppertal, appl. Feb. 4, 1985 (EP 194425, Australia 86-212857-33).
34. A. I. Suleimanov, S. V. Akiev, and V. D. Sokolovskii, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No. 7220-V.
35. E. Iwamatsu, T. Moriyama, N. Takasaki, and K. Aika, *J. Chem. Soc. Chem. Commun.*, 19 (1987).
36. E. Yamagata, K. Tanaka, S. Sasaki, and S. Okazaki, *Chem. Lett.*, 81 (1987).
37. M. Ya. Sinev, V. N. Korchak, and O. V. Krylov, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reatsii" (Abstracts of the Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p.27.

38. R. D. Goodenough and V. A. Stenger, in *Comprehensive Inorganic Chemistry*, eds., J. C. Bailar, H. J. Emelius, R. Nyholm, and A.-F. Trotman-Dickenson, Chapter 10, Pergamon Press, New York, 1975.
39. S. Ahmed and J. B. Moffat, *Appl. Catal.*, **58**, 83 (1990); *ibid.*, *J. Catal.*, **121**, 408 (1990).
40. M. C. Kung, K. T. Nguyen, D. Patel, and H. H. Kung, in *Catalysis of Organic Reactions*, D. W. Blackburn--ed., Chapter 18, Marcel Dekker, New York (1990); K. T. Nguyen and H. H. Kung, *J. Catal.*, **122**, *in press* (1990)..
41. K. Otsuka, A. A. Said, K. Jinno, and T. Komatsu, *Chem. Letters*, 77 (1987).
42. C. F. Cullis and B. M. Willatt, *J. Catal.*, **86**, 187 (1984).
43. J. A. Labinger and K. C. Ott, *J. Phys. Chem.*, **91**, 2682 (1987).
44. J. W. M. H. Geerts, J. M. N. van Kasteren, and K. van der Wiele, *Catal. Today*, **4**, 453 (1989).
45. H. Matsushashi, K. Sakurai, and K. Arata, *Chem. Letters*, 585 (1989).
46. U. S. Patent 4,172,810, to Exxon Research & Engineering Co., October 30, 1979; U. S. Patent 4,205,194, to Exxon Research & Engineering Co., May 27, 1980; and U. S. Patent 4,239,658, to Exxon Research & Engineering Co., December 16, 1980.
47. I. T. Ali Emesh and Y. Amenomiya, *J. Phys. Chem.*, **90**, 4785 (1986).
48. I. Matsuura, T. Doi, and Y. Utsumi, *Chem. Letters*, 1473 (1987).
49. G. E. Keller and M. M. Bhasin, *J. Catal.*, **73**, 9 (1982).
50. C. A. Jones, J. J. Leonard, and J. A. Sofranko, *J. Catal.*, **103**, 311 (1987).
51. M. Hatano and K. Otsuka, *Inorg. Chim. Acta*, **146**, 243 (1988).
52. U. S. Patent 4,499,323, to Atlantic Richfield Company, February 12, 1985.

VIII. APPENDICES

Appendix A. KEY TO TABLES AND TERMS

The following symbols are used in the key:

$n(i)_r$: relative molar amount of component "i" in the reactant stream (see Experimental Section).

$n(i)_p$: relative molar amount of component "i" in the product stream after correction for volume changes with nitrogen as an internal standard (see Experimental)

$f(i)$: number of carbon atoms per molecule of component "i".

Ref., #-KDC-X-#, or #-BKW-#	Union Carbide notebook reference ID number.
Catalyst (Cat)	Union Carbide code number for catalyst or chemical composition.
Weight (Wt)	Weight of catalyst sample (g).
Volume	Volume of catalyst before dilution with quartz beads (cc).
CH ₄ /O ₂ /N ₂	Mole ratios of reactants in feed stream.
Flow (ccm)	Total reactant flow rate (cc/min at ambient conditions).
Temperature (Temp)	Temperature of the catalyst bed (°C).
Time	Time since reactant flow was started (minutes, unless hours indicated).
CH ₄ Conv. (CH ₄ C or CC)	Mole % of methane reacted. $= \{[n(\text{CH}_4)_r - n(\text{CH}_4)_p] / n(\text{CH}_4)_r\} \times 100$
O ₂ Conv. (O ₂ C)	Mole % of oxygen reacted. $= \{[n(\text{O}_2)_r - n(\text{O}_2)_p] / n(\text{O}_2)_r\} \times 100$
C Balance (C Bal)	Mole % carbon detected in the product stream compared to the reactant stream. $= \{[\sum f(i)n(i)_p] / n(\text{CH}_4)_r\} \times 100$; where the "Σ" is over all carbon containing components.
C ₂ Selectivity (Sel)	Selectivity to ethane + ethylene expressed as a percent, based on methane reacted. $= \{2[n(\text{C}_2\text{H}_6)_p + n(\text{C}_2\text{H}_4)_p] / [\sum f(i)n(i)_p]\} \times 100$; where the "Σ" excludes CH ₄

C ₃ Selectivity	<p>Selectivity to propane + propene expressed as a percent, based on methane reacted.</p> $= \{3[n(\text{C}_3\text{H}_8)_p + n(\text{C}_3\text{H}_6)_p]\} / [\sum f(i)n(i)_p] \times 100$ <p>; where the "Σ" excludes CH₄.</p>
C ₂ Yield (or Yield)	Mole % of methane converted to C ₂ 's, calculated as (CH ₄ conversion) X (C ₂ selectivity)/100.
Ethylene/Ethane (=/-)	Mole ratio of ethylene to ethane in the product stream.
CO ₂ /CO	Mole ratio of carbon dioxide to carbon monoxide in the product stream.
GHSV	Gas hourly space velocity (cc _{gas} cc _{cat} ⁻¹ h ⁻¹ at ambient temperature and room pressure).
ECI	Ethyl chloride in the feed gas in parts per million.
Reactor or R	The type of a reactor - A, B, C, D, E, F, G, or H.
R#	R#3 and R#4 refer to the two reactors in the BKW laboratory.
Activity	Methane conversion.

Appendix B. TABLES

Table B1. GC Program Conditions, NEK Laboratory

Injectors at 200°C

Detectors at 200°C

Detector: Thermal Conductivity

Column = 10' x 1/8" stainless steel Carbosieve SII

Carrier Gas flow rate = 23.5 cc/min

Carrier Gas = Helium or argon

Current = 72 ma

Sensitivity = 36 x 0.05 mV

Detector: Flame Ionization Detector

Column = 10' x 1/8" stainless steel Porapak R

Carrier Gas flow rate = 24.0 cc/min

Carrier Gas = Helium or argon

Air flow rate about 300 cc/min

Hydrogen flow rate about 30 cc/min

Sensitivity = 16 x 10⁻¹⁰ amps/mV

Oven Temperature Program

Initial Temperature = 50°C

Hold time = 10 minutes

Ramp rate = 10°C/min

Final Temperature = 200°C

Hold time = 16 minutes

Cool down and stabilization time = 14 minutes

Stream select and sampling valve box at room temperature.

Flow to stream select and sampling valves is about 10 cc/min.

Table B2. Calibration Table, NEK Laboratory

Thermal Conductivity Detector:

No.	Ret. Time	Name
1	7.82	Hydrogen
2	11.1	Oxygen
3	11.6	Nitrogen
4	13.4	Carbon monoxide
5	19.1	Methane
6	22.7	Carbon dioxide
7	26.8	Acetylene

Flame Ionization Detector:

No.	Ret. Time	Name
1	9.16	Ethylene
2	10.4	Ethane
3	11.1	Acetylene
4	18.76	Propylene + Propane
5	20-21.5	Butane and butylenes

Calibrations were done at two levels for each component by using the calibration gas mixture (described in Table 5 of the Second Quarterly report) for one level and the calibration gas mixture (described in Table 9 of the Second Quarterly report) for the other. The response factors were determined using a piecewise linear curve forced through the origin.

Table B3. Alkaline Earth/Metal Oxide Catalysts

Name	Wt Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	EQ	
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	160	12.5	68.3	8.5	15	1.0	0.6	2.0	10.2	5.2	100	65	2133	4
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	160	11.5	67.8	7.8	14	0.9	0.7	2.0	10.2	5.2	100	155	2133	4
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	160	8.1	70.0	5.7	8	0.6	0.8	2.0	10.1	5.0	101	5465	2133	4
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	80	18.4	59.8	10.9	24	1.5	0.7	2.0	10.1	5.0	99	5625	1067	4
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	80	19.1	59.1	11.2	25	1.6	0.7	2.0	10.1	5.0	99	5780	1067	4
33 BKW 81 R#4	5.0 BaC2Al2O3 5451.60/100	750	80	19.7	58.7	11.5	27	1.6	0.7	2.0	10.2	5.1	99	6905	1067	4
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	120	36.0	22.3	7.9	99	1.4	8.0	2.0	10.2	5.1	98	25	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	725	120	27.7	17.0	4.7	75	1.0	6.4	2.0	10.2	5.1	100	130	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	725	120	26.1	19.7	5.1	68	1.0	5.3	2.0	10.2	5.1	99	220	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	725	120	21.3	25.9	5.5	51	0.9	2.7	2.0	10.2	5.1	100	400	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	725	120	13.0	36.9	4.8	23	0.9	0.8	2.0	10.3	5.1	100	1210	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	120	19.6	37.2	7.3	38	1.3	1.0	2.0	10.3	5.1	101	1300	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	120	19.8	36.7	7.3	38	1.3	1.0	2.0	10.3	5.1	100	1390	1895	8
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	80	28.3	38.0	10.8	54	2.3	0.9	2.0	10.2	5.1	100	1570	1263	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	80	28.8	38.1	11.0	55	2.4	0.9	2.0	10.2	5.1	100	1660	1263	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	80	29.3	36.6	10.8	57	2.5	0.9	2.0	10.2	5.1	101	2065	1263	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	80	28.7	36.3	10.5	57	2.4	0.9	2.0	10.3	5.1	101	2160	1263	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	80	28.2	36.2	10.3	56	2.4	0.9	2.0	10.3	5.1	101	2260	1263	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	75	20.4	35.4	7.2	79	1.9	1.0	3.9	38.8	9.8	100	2575	1184	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	75	20.4	35.3	7.2	79	1.9	1.0	3.9	38.8	9.8	100	2665	1184	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	75	19.6	34.2	6.8	79	1.9	1.0	3.9	38.7	9.9	101	3430	1184	30
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	70	10.3	43.3	4.6	97	1.7	1.0	8.0	79.2	9.9	103	3790	1105	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	70	13.0	43.0	5.6	98	1.8	1.0	8.0	79.2	9.9	100	4060	1105	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	70	16.1	42.1	6.5	98	1.7	0.9	8.1	79.6	9.9	96	5545	1105	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	70	13.5	41.5	5.6	98	1.7	0.9	8.0	80.1	10.0	99	6445	1105	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	70	13.2	38.0	5.0	98	1.4	1.2	8.0	80.0	10.0	99	7975	1105	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	12.5	43.4	5.4	84	1.4	0.8	8.0	80.0	10.0	99	8055	1579	47
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	14.3	46.6	6.5	88	1.7	0.7	8.0	80.0	10.0	98	8155	1579	100
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	14.7	46.2	6.6	89	1.7	0.7	8.0	80.0	10.0	98	8245	1579	100
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	14.7	46.0	6.6	89	1.7	0.7	8.0	80.0	10.0	98	8425	1579	100
33 BKW 35 R#4	5.0 BaCO3 TiO2 30/100	750	100	7.6	48.1	3.9	94	2.1	0.6	8.0	79.7	10.0	107	9280	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	9.8	48.3	4.9	94	2.1	0.6	8.0	79.7	10.0	105	9370	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	12.4	48.2	6.1	95	2.1	0.6	8.0	79.7	10.0	102	9550	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	35.6	39.2	14.4	69	5.4	0.5	2.0	10.1	5.1	103	9685	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	36.6	39.3	14.6	69	5.5	0.5	2.0	10.1	5.1	102	9775	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	36.9	39.4	14.8	69	5.6	0.5	2.0	10.1	5.1	101	9865	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	36.6	38.8	14.6	70	5.8	0.5	2.0	10.1	5.1	103	10630	1579	200
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	23.3	21.4	5.0	49	1.5	0.9	2.0	10.1	5.1	101	10765	1579	4
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	23.0	20.7	4.8	49	1.4	0.9	2.0	10.1	5.1	100	10855	1579	4
33 BKW 85 R#4	5.0 BaCO3 TiO2 30/100	750	100	20.7	19.8	4.1	45	1.3	0.8	1.9	9.7	5.2	101	11485	1579	4
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	100	38.6	26.1	9.9	99	1.3	6.9	2.0	10.1	5.2	99	30	1579	4
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	38.0	25.1	9.4	99	1.3	8.4	2.0	10.1	5.2	99	175	2526	4
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	38.4	25.6	9.8	99	1.4	7.3	1.9	10.1	5.2	99	310	2526	4
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	39.0	29.8	11.6	95	1.5	4.5	2.0	10.2	5.2	100	940	2526	4
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	43.6	34.5	15.0	94	2.2	3.6	2.0	10.3	5.1	100	1075	2526	200
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	41.0	51.1	21.0	63	4.3	0.6	2.0	10.3	5.1	100	1165	2526	200
33 BKW 91 R#3	5.0 BaCO3 TiO2 30/100	750	160	33.0	52.7	17.5	30	4.5	0.4	2.0	10.3	5.2	101	2620	2526	200

Table B3. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt. Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	±	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	33.5	51.1	16.9	48	4.0	0.4	2.0	10.3	5.2	99	2710	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	33.5	50.8	16.8	48	4.0	0.4	2.0	10.3	5.2	99	2800	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	29.9	53.4	15.9	42	3.4	0.4	1.9	10.0	5.2	99	3655	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	32.7	49.5	16.4	50	4.2	0.4	2.0	10.0	5.2	101	4015	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	32.1	50.1	16.3	49	4.1	0.4	2.0	10.0	5.2	101	4045	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	39.8	42.1	17.2	68	5.9	0.4	2.0	10.0	5.2	102	4150	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	39.7	42.2	17.1	67	5.9	0.4	2.0	10.0	5.2	102	4195	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	39.6	42.2	17.1	67	5.9	0.4	2.0	10.0	5.2	102	4240	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	43.2	43.8	19.4	72	9.0	0.3	2.1	10.3	5.0	103	4330	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	44.3	43.8	19.7	72	10.8	0.4	2.1	10.3	5.0	101	4410	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	51.5	32.3	16.5	96	25.3	0.2	2.1	10.5	5.0	99	12055	1579	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	47.7	34.7	16.4	85	16.8	0.2	2.1	10.5	5.0	99	12120	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	47.5	34.4	16.3	85	16.9	0.2	2.1	10.5	5.0	100	12175	2526	150
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	40.2	35.4	14.8	76	10.2	0.2	2.0	10.0	5.1	104	12245	2526	50
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	39.9	35.5	14.6	76	9.9	0.2	2.0	10.0	5.1	103	12355	2526	50
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	39.5	35.4	14.5	75	9.7	0.2	1.9	10.1	5.2	103	12555	2526	50
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	45.0	33.8	16.1	87	17.6	0.2	1.9	9.8	5.2	106	13345	2526	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	44.6	33.8	16.1	87	17.8	0.2	1.9	9.8	5.2	106	13375	2526	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	36.6	52.7	19.3	54	5.9	0.3	1.9	9.9	5.2	100	14695	2526	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	160	36.3	52.9	19.3	53	5.9	0.3	1.9	9.9	5.2	100	14785	2526	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	43.9	44.6	19.9	73	8.5	0.3	1.9	9.9	5.2	101	14830	1579	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	43.9	44.6	19.9	73	8.5	0.3	1.9	9.9	5.2	101	14875	1579	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	44.3	44.6	19.9	73	8.6	0.3	1.9	9.9	5.2	101	14950	1579	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	30.0	60.4	18.1	40	4.2	0.3	1.9	9.9	5.2	100	14995	3553	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	30.5	59.7	18.1	40	4.3	0.3	1.9	9.9	5.2	100	15055	3553	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	29.9	60.2	18.0	41	4.2	0.3	1.9	9.9	5.2	100	15095	3553	300
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	18.0	26.1	4.7	36	1.0	0.7	2.0	10.4	5.2	101	15190	3553	0
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	18.4	19.3	3.6	38	0.8	0.8	2.0	10.4	5.2	101	15280	3553	0
33 BKW 91 R#3	5.0 BaCO ₃ , TiO ₂ 30/100	750	225	16.8	12.9	2.2	37	0.7	0.9	2.0	10.5	5.2	101	16000	3553	0
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	19.6	19.0	3.8	41	1.2	0.8	2.0	10.1	5.2	101	110	1579	4
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	19.4	19.6	3.9	41	1.2	0.7	2.0	10.1	5.2	102	200	1579	4
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	19.3	19.7	3.9	42	1.2	0.8	1.9	10.1	5.2	102	355	1579	4
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	18.5	20.2	3.8	40	1.2	0.8	2.0	10.2	5.2	102	985	1579	4
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	36.3	37.3	13.7	65	5.3	0.5	2.0	10.3	5.1	101	1120	1579	200
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	36.2	37.9	14.1	66	5.5	0.5	2.0	10.3	5.1	102	1210	1579	200
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	37.3	37.9	14.4	67	5.7	0.5	2.0	10.3	5.1	102	1525	1579	200
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	37.1	37.8	14.4	69	5.8	0.5	2.0	10.3	5.2	103	2575	1579	200
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	37.5	37.8	14.5	68	5.8	0.5	2.0	10.3	5.2	102	2665	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	37.4	36.7	13.7	65	5.1	0.5	2.0	10.3	5.2	103	2755	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	37.2	35.8	13.4	66	5.2	0.5	2.0	10.2	5.2	101	4275	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	40.5	37.6	15.8	74	8.2	0.4	2.1	10.3	5.0	103	4375	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	46.4	29.1	14.7	95	29.5	0.2	2.1	10.3	5.0	109	4615	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	750	100	50.4	30.4	15.4	96	24.3	0.2	2.1	10.5	5.0	100	12085	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	725	100	45.0	29.6	13.3	84	16.5	0.1	2.1	10.5	5.0	100	12145	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	725	100	44.6	29.7	13.3	84	16.4	0.1	2.1	10.5	5.0	100	12220	1579	150
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	725	100	36.3	30.7	11.5	72	9.1	0.2	2.0	10.0	5.1	104	12310	1579	50
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ 30/100	725	100	35.9	30.6	11.4	72	9.1	0.2	2.0	10.0	5.1	104	12400	1579	50

Table B3. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	%	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	725	100	34.8	30.4	11.1	72	9.0	0.2	1.9	10.0	5.2	105	13165	1579	50 EBr
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	27.3	27.3	7.7	55	6.3	0.2	1.9	10.1	5.2	103	13285	1579	50 EBr
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	26.9	27.4	7.6	55	6.3	0.2	1.9	10.1	5.2	103	13315	1579	50 EBr
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	32.9	27.4	9.5	67	11.5	0.1	1.9	9.8	5.2	106	13545	1579	300
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	30.4	32.7	10.3	58	9.9	0.1	1.9	9.8	5.2	104	13605	1579	300
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	23.9	51.0	12.2	36	3.9	0.2	1.9	9.9	5.2	100	14920	1579	300
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	13.3	30.7	4.1	24	1.1	0.5	2.0	10.4	5.2	100	15145	1579	0
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	12.6	14.6	1.8	26	0.8	0.6	2.0	10.4	5.2	100	15235	1579	0
33 BKW 101 R#4	5.0 BaCO ₃ , TiO ₂ , 30/100	700	100	12.1	5.0	0.6	28	0.5	0.7	2.0	10.5	5.2	101	16045	1579	0
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	100	41.4	25.1	11.0	99	4.7	2.2	2.0	10.0	5.0	106	25	1935	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	43.2	29.2	13.1	99	7.4	1.3	2.0	10.0	5.0	104	80	3097	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	190	42.5	31.1	13.8	95	9.2	0.8	2.0	10.0	5.0	104	135	3677	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	190	41.4	33.9	14.7	87	14.1	0.4	2.0	10.0	4.9	105	230	3677	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	190	40.6	36.8	15.4	81	11.9	0.2	2.1	10.1	4.9	103	635	3677	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	190	38.6	37.4	15.0	76	9.7	0.2	2.1	10.1	4.9	104	1220	3677	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	40.8	35.9	15.3	82	11.7	0.2	2.1	10.1	4.9	104	1310	3097	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	40.8	36.1	15.2	81	11.5	0.2	2.1	10.1	4.9	104	1400	3097	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	35.1	36.0	13.2	70	9.8	0.2	2.0	10.0	5.0	105	3875	3097	250 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	31.7	36.2	11.7	60	5.7	0.3	2.0	9.9	4.9	102	4020	3097	50 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	31.8	36.3	11.7	61	5.6	0.3	2.0	9.9	4.9	101	4055	3097	50 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	31.6	36.3	11.7	61	5.6	0.3	2.0	9.9	4.9	102	4220	3097	50 EBr
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	33.4	37.3	13.0	66	7.9	0.2	2.0	9.7	4.9	104	4290	3097	250
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	23.9	59.1	14.2	34	2.8	0.3	2.0	9.7	4.9	101	4385	3097	250
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	20.4	64.9	13.3	28	2.5	0.4	2.0	9.7	4.9	100	5640	3097	250
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	18.5	56.1	10.3	26	1.5	0.6	1.9	9.6	4.9	99	5730	3097	50
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	18.1	52.9	9.5	26	1.5	0.6	1.9	9.6	4.9	99	5805	3097	50
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	17.1	49.0	8.4	26	1.4	0.6	1.9	9.6	5.0	100	6765	3097	50
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	17.0	35.3	5.9	27	0.9	0.8	2.0	9.9	5.0	99	6900	3097	0
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	17.2	25.9	4.4	32	0.7	0.8	2.0	9.9	5.0	99	6975	3097	0
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	20.6	16.7	3.4	42	0.6	1.0	2.0	9.9	5.0	98	7125	3097	0
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	23.5	57.4	13.8	32	3.5	0.3	2.0	9.8	5.0	103	7225	3097	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	23.4	64.6	15.1	32	3.4	0.3	2.0	9.8	5.0	100	7305	3097	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	23.9	67.2	15.9	31	3.4	0.3	2.0	9.9	5.0	99	8205	3097	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	22.5	68.8	15.5	30	3.3	0.3	2.0	9.9	4.9	100	8340	3097	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	225	17.9	73.9	13.2	22	2.4	0.3	2.0	9.9	4.9	100	8430	4355	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	225	17.7	72.1	12.8	20	2.3	0.3	2.0	9.9	4.9	100	8520	4355	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	100	30.3	60.5	18.5	44	5.4	0.3	2.0	9.9	4.9	99	8595	1935	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	100	31.9	58.4	18.4	45	5.4	0.3	2.0	9.9	4.9	99	8695	1935	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	80	35.3	55.9	19.4	53	6.6	0.3	2.0	9.9	4.9	98	8780	1548	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	80	34.7	56.4	19.3	52	6.4	0.3	2.0	9.9	4.9	99	8880	1548	500
33 BKW 114 R#3	5.0 BaCO ₃ , TiO ₂ , 30/60	750	80	33.6	55.6	18.7	51	6.4	0.3	2.0	9.9	4.9	100	9960	1548	500
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	100	43.1	23.4	10.9	99	26.9	0.2	2.0	10.0	5.0	108	50	1935	250 EBr
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	38.4	28.0	11.4	83	14.8	0.2	2.0	10.0	5.0	105	160	3097	250 EBr
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	39.2	32.7	13.3	79	13.9	0.1	2.1	10.1	4.9	104	3155	3097	250 EBr
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	38.2	32.8	13.2	79	13.7	0.1	2.0	10.0	5.0	105	3920	3097	250 EBr
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	30.3	37.1	11.5	57	5.6	0.2	2.0	9.9	4.9	102	4100	3097	50 EBr
33 BKW 115 R#4	5.0 BaCO ₃ , TiO ₂ , 30/60	750	160	30.4	37.1	11.5	56	5.9	0.2	2.0	9.9	4.9	102	4190	3097	50 EBr

Table B3. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	=/	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	30.5	37.3	11.5	56	5.7	0.2	2.0	9.9	4.9	101	4245	3097	50
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	23.1	52.1	12.1	37	3.1	0.3	2.0	9.7	4.9	101	4340	3097	250
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	24.0	51.5	12.5	39	3.4	0.2	2.0	9.7	4.9	101	4415	3097	250
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	22.9	59.0	13.5	33	2.9	0.3	2.0	9.6	4.9	100	5360	3097	250
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	21.8	59.3	13.0	31	2.8	0.3	2.0	9.7	4.9	101	5685	3097	250
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	17.2	50.4	8.6	25	1.4	0.6	1.9	9.6	4.9	99	5770	3097	50
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	16.8	49.4	8.2	25	1.4	0.6	1.9	9.6	4.9	99	5835	3097	50
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	15.9	46.4	7.4	25	1.4	0.6	1.9	9.6	5.0	100	6810	3097	50
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	14.8	19.4	2.8	28	0.5	0.8	2.0	9.9	5.0	99	6945	3097	0
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	15.9	13.4	2.1	31	0.5	0.9	2.0	9.9	5.0	98	7080	3097	0
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	16.7	12.1	2.0	32	0.5	0.9	2.0	9.9	5.0	98	7155	3097	0
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	25.4	55.4	14.3	38	4.0	0.2	2.0	9.8	5.0	102	7250	3097	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	25.2	58.9	14.9	38	4.0	0.2	2.0	9.8	5.0	101	7345	3097	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	25.9	63.3	16.2	36	3.9	0.2	2.0	9.9	5.0	99	8250	3097	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	24.4	63.1	15.4	35	3.9	0.2	2.0	9.9	4.9	101	8385	3097	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	100	33.3	53.8	17.9	52	6.3	0.3	2.0	9.9	4.9	100	8475	1935	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	100	33.3	53.7	17.9	52	6.3	0.3	2.0	9.9	4.9	100	8565	1935	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	100	33.8	53.1	17.9	53	6.4	0.3	2.0	9.9	4.9	100	8635	1935	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	80	37.1	50.5	18.6	60	7.4	0.3	2.0	9.9	4.9	100	8745	1548	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	80	37.6	49.7	18.5	60	7.4	0.3	2.0	9.9	4.9	99	8835	1548	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	80	36.0	50.8	18.3	58	7.3	0.3	2.0	9.9	4.9	100	8915	1548	500
33 BkW 115 R#4	5.0	BaCO ₃ , TiO ₂ , 30/60	750	160	38.8	38.6	14.9	76	1.9	2.1	2.0	9.5	4.9	100	295	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	38.6	39.1	15.0	77	1.9	2.2	2.0	9.5	4.9	100	385	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	36.0	44.1	15.6	60	1.8	1.5	2.0	9.7	4.9	98	6100	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	34.4	45.2	15.4	61	1.8	1.4	2.0	9.6	4.9	99	7180	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	34.3	45.6	15.7	60	1.9	1.4	1.9	9.4	4.9	100	7450	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	34.9	45.8	16.0	57	2.0	1.3	1.9	9.4	4.9	100	7540	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	34.9	50.0	17.3	51	2.1	1.2	2.0	9.4	4.8	99	8980	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	33.0	51.0	16.9	52	2.2	1.2	2.0	9.5	4.9	101	9745	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	31.8	53.1	16.8	47	1.9	1.2	2.0	9.5	4.9	100	10005	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	30.9	54.2	16.8	47	1.9	1.3	2.0	9.5	4.9	100	10080	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	32.1	55.8	17.6	47	1.9	1.3	2.0	9.5	4.9	98	10285	2400	50
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	30.3	56.0	17.1	47	1.9	1.4	2.0	9.8	4.8	101	10375	2400	500
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	27.8	59.0	16.4	42	1.8	1.5	2.0	9.8	4.8	100	10465	2400	500
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	17.2	74.7	12.6	18	2.0	0.4	2.1	9.9	4.8	98	12625	2400	500
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	16.9	76.7	12.8	18	1.8	0.6	2.0	9.8	4.8	99	12795	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	20.3	74.2	14.9	22	2.1	0.8	2.0	9.8	4.8	99	12890	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	20.8	72.3	14.9	24	2.0	0.9	2.0	9.8	4.8	99	12950	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	18.5	65.8	12.1	22	1.2	1.0	2.0	9.7	4.8	99	14060	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	18.5	60.3	10.9	22	1.0	0.8	2.0	9.8	4.8	98	14600	2400	0
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	18.2	59.1	10.6	21	1.0	0.8	2.0	9.8	4.8	98	14735	2400	0
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	17.0	54.1	9.2	23	0.9	0.7	2.0	9.5	4.8	100	15500	2400	0
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	16.8	54.6	9.2	22	0.9	0.7	2.0	9.6	4.8	101	15745	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	17.1	54.1	9.3	24	0.9	0.7	2.0	9.6	4.8	101	16045	2400	5
34 BkW 18 R#3	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	160	16.8	53.4	8.9	20	0.8	0.6	2.0	9.8	4.8	99	22700	2400	5
34 BkW 19 R#4	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	28.5	60.5	17.2	36	3.9	0.5	2.0	9.5	4.9	100	210	1200	5
34 BkW 19 R#4	5.0	SrCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	29.6	62.3	18.2	38	4.0	0.6	2.0	9.5	4.9	99	340	1200	5

Table B3. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI	
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	43.3	54.1	22.8	72	5.4	2.2	2.0	9.5	4.9	98	3265	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	23.9	60.2	14.0	33	1.5	2.1	2.0	9.6	4.9	98	7225	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	22.4	60.3	13.4	31	1.5	1.9	1.9	9.4	4.9	99	7495	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	22.5	60.6	13.4	31	1.5	1.9	1.9	9.4	4.9	99	7585	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	19.5	64.9	12.6	25	1.7	1.2	1.9	9.5	4.9	100	9790	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	21.1	65.1	13.4	25	1.7	1.2	2.0	9.5	4.9	98	10040	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	19.1	65.5	12.4	24	1.6	1.2	2.0	9.5	4.9	99	10120	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	20.4	65.4	13.1	24	1.6	1.1	2.0	9.5	4.9	98	10230	1200	50
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	21.5	63.9	13.4	24	1.7	1.0	2.0	9.8	4.8	97	10310	1200	500
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	21.2	66.5	14.0	27	2.1	0.8	2.0	9.8	4.8	99	10420	1200	500
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	19.4	65.1	12.6	25	3.1	0.2	2.0	9.7	4.8	100	12750	1200	500
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	22.0	65.6	14.3	27	2.8	0.6	2.0	9.8	4.8	99	12850	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	24.0	64.7	15.3	31	3.0	0.7	2.0	9.8	4.8	98	12925	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	24.9	63.2	15.6	33	3.0	0.9	2.0	9.8	4.8	99	13040	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	19.0	63.7	11.9	25	1.4	1.3	2.0	9.7	4.8	98	14105	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	18.4	58.2	10.5	23	1.3	1.0	2.0	9.8	4.8	98	14545	1200	0
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	17.7	58.9	10.2	22	1.2	1.0	2.0	9.8	4.8	98	14660	1200	0
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	15.9	56.5	8.9	22	1.1	1.0	2.0	9.5	4.8	100	15425	1200	0
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	14.6	56.2	8.2	21	1.1	1.0	2.0	9.6	4.8	101	15785	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	15.7	55.9	8.7	21	1.1	1.0	2.0	9.6	4.8	99	16085	1200	5
34 BKW 19 R#4	5.0	SrCl ₂ ·6H ₂ O, Al ₂ O ₃ , 5451, 60/100	750	80	15.3	51.6	7.8	20	0.9	0.9	2.0	9.8	4.8	98	22745	1200	5
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	8.4	49.8	4.2	53	0.8	1.1	7.9	78.9	10.0	101	95	3300	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	9.6	53.5	5.1	57	0.8	1.0	7.9	78.9	10.0	100	185	3300	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	11.2	55.0	6.1	65	0.9	1.1	7.9	78.9	10.0	100	275	3300	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	8.1	57.6	4.7	43	0.8	0.7	7.9	78.9	10.0	101	440	3300	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	10.2	53.7	5.5	59	1.2	0.7	7.9	78.9	10.0	101	449	2010	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	10.6	54.6	5.8	59	1.2	0.7	7.8	78.4	10.0	101	4585	2010	50
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.4	56.3	6.5	62	1.3	0.8	7.8	78.4	10.0	100	4675	2010	50
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	12.9	57.7	7.3	61	1.3	0.9	7.9	79.2	10.0	98	5710	2010	50
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	10.3	57.2	6.0	59	1.3	0.9	7.9	78.7	10.0	101	5800	2010	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.2	55.9	6.2	57	1.2	0.8	7.9	78.7	10.0	99	5890	2010	10
34 BKW 59 R#3	2.5	SrCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.5	55.5	6.3	57	1.2	0.8	7.9	78.7	10.0	99	5970	2010	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	9.5	41.7	4.0	71	0.7	1.9	7.9	78.9	10.0	100	50	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	9.2	45.5	4.2	67	0.8	1.7	7.9	78.9	10.0	101	140	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	13.1	63.2	8.2	68	1.2	2.1	7.9	78.9	10.0	99	3110	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	11.6	63.1	7.4	70	1.2	2.3	7.9	78.9	10.0	101	4055	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	10.7	67.2	7.2	59	0.9	2.6	7.9	78.9	10.0	100	4280	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	10.6	66.6	7.1	59	0.9	2.4	7.9	78.9	10.0	100	4370	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	110	10.7	66.1	7.1	59	0.9	2.4	7.9	78.9	10.0	100	4430	3300	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	13.7	61.0	8.3	79	1.3	2.0	7.9	78.9	10.0	100	4540	2010	50
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.8	62.7	7.5	72	1.2	1.9	7.8	78.4	10.0	101	4630	2010	50
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.9	61.9	7.4	70	1.2	1.8	7.8	78.4	10.0	100	4720	2010	50
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.4	61.8	7.0	63	1.1	1.7	7.9	79.2	10.0	99	5755	2010	50
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	11.9	61.2	7.3	69	1.2	1.7	7.9	78.7	10.0	100	5845	2010	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	12.7	61.5	7.8	73	1.3	1.8	7.9	78.7	10.0	100	5935	2010	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	67	12.1	61.7	7.5	75	1.3	1.9	7.8	78.3	10.0	101	6035	2010	10
34 BKW 61 R#4	2.5	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	94	9.7	65.8	6.4	51	0.9	2.1	7.8	78.3	10.0	100	6115	2820	10

EBr
EBr
EBr

Table B3. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI	
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	94	11.8	65.4	7.6	58	1.0	2.1	7.8	78.3	10.0	99	6205	2820	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	94	12.7	66.0	8.3	68	1.1	2.6	7.8	78.5	10.1	99	7105	2820	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	94	11.2	65.4	7.4	67	1.1	2.8	7.8	78.5	10.1	101	7385	2820	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	94	15.4	65.1	10.1	93	1.6	4.6	7.8	78.5	10.1	100	7420	2820	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	60	14.7	62.0	9.2	99	1.9	5.2	7.9	78.7	10.0	101	7485	1800	10
34 BK... 1 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	60	15.7	62.2	9.7	98	1.9	4.7	7.9	78.7	10.0	100	7600	1800	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	60	15.3	60.9	9.3	97	1.9	3.6	7.9	78.9	10.0	100	8410	1800	10
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	60	16.2	60.6	9.7	97	1.9	3.6	7.9	78.9	10.0	99	8545	1800	5
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	60	16.6	60.8	10.0	98	1.9	3.8	7.9	78.9	10.0	99	8625	1800	5
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	188	15.3	69.4	10.6	83	1.3	3.7	7.9	78.9	10.0	100	8710	5640	5
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	138	16.5	68.5	11.1	83	1.3	3.4	7.9	78.9	10.0	98	8800	5640	5
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	188	16.3	68.1	10.9	81	1.3	3.1	7.9	78.9	10.0	98	8905	5640	5
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	188	13.9	70.0	9.6	71	1.2	3.2	7.9	78.8	10.0	99	8995	5640	20
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	188	12.7	70.6	8.9	62	1.1	2.7	7.9	78.8	10.0	99	9085	5640	20
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	188	8.4	72.0	6.0	39	0.8	1.8	7.9	78.9	10.0	99	9985	5640	20
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	160	8.4	69.0	5.8	41	0.9	1.3	7.9	78.9	10.0	100	10480	4800	20
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	160	5.7	69.3	4.0	37	0.8	1.3	7.9	78.8	10.0	102	10660	4800	20
34 BKW 61 R#4	2.5	BaCO ₃ /Al ₂ O ₃ /5451/30/60	775	160	4.8	68.5	3.3	22	0.6	0.8	7.9	78.9	10.0	100	15840	4800	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	12.7	52.0	6.6	85	1.1	2.3	7.8	78.3	10.0	100	50	2820	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	13.8	55.0	7.6	81	1.2	1.8	7.8	78.3	10.0	99	140	2820	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	13.2	61.8	8.1	72	1.3	1.5	7.9	79.0	10.0	100	905	2820	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	12.5	62.6	7.9	70	1.2	1.7	7.8	78.5	10.1	100	1220	2820	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	120	13.4	60.0	8.1	81	1.5	1.8	7.8	78.5	10.1	101	1305	1800	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	120	13.0	60.1	7.9	81	1.5	1.8	7.8	78.5	10.1	101	1335	1800	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	13.9	57.9	8.1	92	1.9	2.2	7.9	78.7	10.0	101	1405	750	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	14.5	57.6	8.4	92	1.9	2.2	7.9	78.7	10.0	100	1505	750	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.3	57.8	8.8	92	1.9	2.2	7.9	78.7	10.0	100	1595	750	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	14.0	57.5	8.1	91	1.9	2.2	7.9	78.9	10.0	101	2315	750	10
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.2	57.8	8.7	90	1.9	2.2	7.9	78.9	10.0	99	2450	750	5
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.4	57.7	8.8	91	1.9	2.3	7.9	78.9	10.0	99	2540	750	5
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.8	57.4	8.9	90	1.8	2.3	7.9	78.9	10.0	99	2810	750	5
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.4	57.4	8.8	90	1.9	2.2	7.9	78.8	10.0	99	2900	750	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.2	58.0	8.8	90	1.9	2.2	7.9	78.8	10.0	99	2990	750	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	50	15.7	59.0	9.1	91	1.9	2.7	7.9	78.9	10.0	99	3890	750	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	13.0	63.6	8.3	71	1.2	2.2	7.9	78.9	10.0	100	4035	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	12.5	65.1	8.1	68	1.2	2.4	7.9	78.9	10.0	100	4350	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	13.5	65.5	8.7	67	1.1	2.5	7.9	78.9	10.0	99	4475	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	9.7	69.6	6.7	46	0.9	3.3	7.9	78.9	10.0	99	8570	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	10.2	68.7	7.0	50	0.9	2.8	7.9	78.9	10.0	99	8660	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	9.8	69.6	6.7	46	0.9	3.0	7.9	78.9	10.0	98	8725	2820	20
34 BKW 63 R#3	5.0	BaCO ₃ /Al ₂ O ₃ /5451/30/60	750	188	7.1	69.5	4.9	36	0.8	2.7	7.9	78.9	10.0	100	9080	2820	20

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Numbers are too small for significant results.

Reactor D was used for all experiments.

Catalyst compositions are described in Appendix D, and preparation methods are described in Appendix E.

Table B4. Enhancement of Vapor Phase Reactions by Surface Generated Radicals

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
33 BKW 130 R#3	0.0	• (void space)	750	80	1.4 49.3	1.4	0.7	2	0.1	0.2	2.0	9.9	4.9	99	35 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	1.2 63.0	1.2	0.7	1	0.1	0.2	2.0	9.9	4.9	99	90 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	1.3 88.2	1.3	1.1	1	0.1	0.8	2.0	9.9	4.9	99	170 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	1.5 84.5	1.5	1.2	1	0.1	0.4	2.0	9.9	4.9	99	225 ###	5
33 BKW 130 R#3	0.0	• (void space)	750	80	1.3 59.4	1.3	0.8	1	0.2	0.1	2.0	9.9	4.9	99	285 ###	5
33 BKW 130 R#3	0.0	• (void space)	750	80	1.1 64.8	1.1	0.7	1	0.2	0.1	2.0	9.9	4.9	99	335 ###	5
33 BKW 130 R#3	0.0	• (void space)	750	80	3.0 48.0	3.0	1.4	3	0.4	0.0	2.0	9.8	4.9	99	440 ###	50
33 BKW 130 R#3	0.0	• (void space)	750	80	2.8 53.1	2.8	1.3	3	0.4	0.0	2.0	9.8	4.9	99	530 ###	50
33 BKW 130 R#3	0.0	• (void space)	750	80	2.6 49.9	2.6	1.3	3	0.4	0.0	2.0	9.8	4.9	99	1250 ###	50
33 BKW 130 R#3	0.0	• (void space)	750	80	3.1 52.7	3.1	1.6	4	0.6	0.0	2.0	9.9	4.9	99	1385 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	80	3.4 53.4	3.4	1.8	4	0.6	0.0	2.0	9.9	4.9	99	1450 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	80	2.7 54.6	2.7	1.4	3	0.6	0.0	2.0	9.9	4.9	99	1515 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	160	0.9 99.7	0.9	0.9	0	1.1 ###	2.0	2.0	9.9	4.9	100	1575 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	160	0.8 98.9	0.8	0.8	0	1.2 ###	2.0	2.0	9.9	4.9	100	1660 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	160	-0.4 99.0	-0.4	0.4	1	1.3 ###	2.0	2.1	10.2	4.9	101	1725 ###	150
33 BKW 130 R#3	0.0	• (void space)	750	80	1.4 57.4	1.4	0.8	3	0.2	0.0	2.1	10.2	4.9	100	1790 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	2.0 52.2	2.0	1.1	3	0.2	0.0	2.1	10.3	4.9	99	1880 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	2.2 61.7	2.2	1.3	2	0.2	0.0	2.1	10.3	4.9	99	2330 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	1.6 57.0	1.6	0.9	1	0.2	0.0	2.1	10.3	4.9	100	2690 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	2.4 61.2	2.4	1.4	2	0.2	0.0	2.1	10.3	4.9	99	2825 ###	5 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	1.7 62.4	1.7	1.0	2	0.2	0.0	2.1	10.3	4.9	99	2910 ###	5 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	1.8 61.3	1.8	1.1	2	0.2	0.0	2.1	10.3	4.9	99	3050 ###	5 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	1.8 56.3	1.8	1.0	4	0.3	0.0	2.0	9.8	5.0	100	3110 ###	50 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	2.0 49.0	2.0	1.4	4	0.3	0.0	2.0	9.8	5.0	99	3165 ###	50 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	3.8 46.9	3.8	1.8	6	0.4	0.0	2.0	9.8	5.0	99	3210 ###	50 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	6.1 43.5	6.1	2.6	8	0.6	0.0	2.0	9.7	5.0	99	3275 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	5.6 42.6	5.6	2.4	7	0.6	0.0	2.0	9.7	5.0	99	3365 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	4.6 44.5	4.6	2.0	4	0.5	0.0	2.0	9.7	4.9	98	7325 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	160	2.4 80.1	2.4	1.9	1	0.4	0.0	2.0	9.7	4.9	98	7435 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	160	2.3 65.5	2.3	1.5	2	0.4	0.0	2.0	9.7	4.9	99	7500 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	160	2.2 67.9	2.2	1.5	3	0.4	0.0	2.0	9.7	4.9	99	7550 ###	150 EBr
33 BKW 130 R#3	0.0	• (void space)	750	80	2.6 57.9	2.6	1.5	3	0.2	0.0	2.0	9.8	4.9	99	7640 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	2.2 65.7	2.2	1.5	3	0.2	0.0	2.0	9.8	4.9	99	7730 ###	0
33 BKW 130 R#3	0.0	• (void space)	750	80	1.6 59.8	1.6	0.9	2	0.2	0.0	2.0	9.8	4.9	100	8090 ###	0
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	1.2 94.3	1.2	1.1	1	0.1 ###	2.0	2.0	9.9	4.9	99	60 ###	0
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	0.7 ###	0.7	0.7	0	0.0 ###	2.0	2.0	9.9	4.9	99	120 ###	0
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	0.8 ###	0.8	0.8	0	0.0 ###	2.0	2.0	9.9	4.9	99	195 ###	0
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	0.9 81.4	0.9	0.7	1	0.1	0.2	2.0	9.9	4.9	99	260 ###	5
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	0.9 71.2	0.9	0.6	1	0.2	0.1	2.0	9.9	4.9	100	310 ###	5
33 BKW 131 R#4	0.0	• (quartz chips)	750	80	0.9 64.2	0.9	0.6	1	0.2	0.1	2.0	9.9	4.9	100	360 ###	5

Table B4. Enhancement of Vapor Phase Reactions by Surface Generated Radicals (continued)

Name	Wt Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.8 79.3	1.4	2	0.4	0.0	2.0	9.8	4.9	99	485	###	50
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.9 76.9	1.5	2	0.5	0.0	2.0	9.8	4.9	99	665	###	50
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.5 74.0	1.1	2	0.5	0.0	2.0	9.8	4.9	99	1295	###	50
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.6 80.9	1.3	2	1.0	0.0	2.0	9.9	4.9	99	1410	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.6 88.9	1.4	2	1.1	0.0	2.0	9.9	4.9	99	1480	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.1 99.6	1.1	1	1.2	###	2.0	9.9	4.9	99	1540	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	160	0.3###	0.3	0	2.4###	0.0	2.0	9.9	4.9	100	1620	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	160	-0.6###	-0.6	0	2.4###	0.0	2.0	9.9	4.9	101	1690	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	160	-1.2###	-1.2	0	2.5###	0.0	2.0	9.9	4.9	102	1760	###	150
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.8 91.9	0.8	1	0.1	0.0	2.1	10.2	4.9	99	1835	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.2###	1.1	1	0.1	###	2.1	10.2	4.9	99	1925	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.3 97.2	1.3	0	0.0	0.0	2.1	10.3	4.9	99	2375	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.3###	0.3	0	0.1	###	2.1	10.3	4.9	100	2735	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.8 92.0	0.8	0	0.1	0.0	2.1	10.3	4.9	99	2865	###	5 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.8 90.5	0.7	0	0.2	0.0	2.1	10.3	4.9	100	2940	###	5 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.9 92.4	0.8	0	0.0	0.0	2.1	10.3	4.9	99	3005	###	5 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.2 83.9	1.0	1	0.3	0.0	2.0	9.8	5.0	99	3080	###	50 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.4 76.7	1.0	2	0.3	0.0	2.0	9.8	5.0	99	3135	###	50 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	2.2 58.6	1.3	3	0.3	0.0	2.0	9.8	5.0	99	3190	###	50 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	4.5 48.5	2.2	6	0.5	0.0	2.0	9.7	5.0	99	3320	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	4.2 48.7	2.0	5	0.5	0.0	2.0	9.7	5.0	99	3415	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	3.2 48.6	1.5	3	0.5	0.0	2.0	9.7	4.9	98	7280	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	160	2.2 84.5	1.8	1	0.4	0.0	2.0	9.7	4.9	98	7370	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	160	1.9 90.5	1.7	2	0.4	0.0	2.0	9.7	4.9	99	7480	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	160	1.7 93.3	1.6	2	0.4	0.0	2.0	9.7	4.9	99	7525	###	150 EBr
33 BKW 131 R#4	0.0* (quartz chips)	750	80	2.0 91.8	1.8	2	0.1	0.0	2.0	9.8	4.9	98	7595	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	1.8###	1.8	1	0.1	###	2.0	9.8	4.9	99	7685	###	0
33 BKW 131 R#4	0.0* (quartz chips)	750	80	0.5###	0.6	0	0.0	###	2.0	9.8	4.9	100	8135	###	0
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	27.4 42.0	11.6	51	1.7	1.0	2.0	9.5	4.9	101	30	3200	0
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	28.3 41.2	11.7	54	1.5	1.5	2.0	9.5	4.9	101	100	3200	0
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	31.7 38.9	12.4	64	1.5	1.9	2.0	9.5	4.9	100	235	3200	0
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	35.9 36.4	12.5	67	1.5	2.1	2.0	9.6	4.9	96	300	3200	50
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	39.9 33.2	13.2	87	3.0	1.8	2.0	9.6	4.9	100	435	3200	50
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	28.3 47.5	13.3	47	1.8	1.1	2.0	9.6	4.9	99	1470	3200	50
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	26.0 47.0	12.1	43	1.6	1.1	2.0	9.6	4.9	99	1545	3200	50
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	24.6 46.8	11.4	41	1.5	1.0	2.0	9.6	4.9	99	1730	3200	50
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	26.5 48.3	12.8	43	1.9	0.9	1.9	9.5	4.9	100	1795	3200	50 EBr
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	38.2 33.0	12.7	81	3.3	1.3	1.9	9.5	4.9	101	1920	3200	50 EBr
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	35.2 28.9	10.4	75	3.0	1.0	1.9	9.5	4.9	102	2640	3200	50 EBr
34 BKW 1 R#3	2.0 BaCO ₃ /Al ₂ O ₃ /5451, 60/100	750	80	33.4 23.1	7.7	84	1.3	3.1	2.1	10.0	4.9	100	2820	3200	0

Table B4. Enhancement of Vapor Phase Reactions by Surface Generated Radicals (continued)

Name	Wt Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	±	CO ₂ CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
34 BkW 1 R#3	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	33.0	21.4	7.0	85	1.1	3.7	2.1	10.0	4.9	100	2895	3200	0
34 BkW 1 R#3	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	31.8	19.6	6.1	82	0.9	4.1	2.1	10.0	4.9	99	3050	3200	0
34 BkW 1 R#3	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	30.2	18.6	5.6	81	0.9	4.2	2.0	9.8	4.9	100	3135	3200	6.5
34 BkW 1 R#3	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	29.8	18.1	5.4	80	0.8	4.3	2.0	9.8	4.9	100	3225	3200	6.5
34 BkW 1 R#3	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	21.9	25.3	5.5	46	0.8	1.1	2.0	9.9	4.9	100	4080	3200	6.5
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	28.9	38.5	11.3	57	2.4	0.9	2.0	9.5	4.9	101	70	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	31.4	37.9	12.0	63	2.5	1.1	2.0	9.5	4.9	101	130	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	34.7	37.5	13.0	70	2.5	1.4	2.0	9.5	4.9	100	270	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	41.8	35.6	14.7	87	4.1	1.5	2.0	9.6	4.9	99	390	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	41.7	34.4	14.3	89	4.4	1.5	2.0	9.6	4.9	100	480	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	29.5	39.8	11.8	52	2.7	0.6	2.0	9.6	4.9	100	1245	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	28.2	39.6	11.2	51	2.5	0.7	2.0	9.6	4.9	100	1515	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	27.9	36.9	10.5	49	2.4	0.7	2.0	9.6	4.9	102	1585	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	27.6	38.7	10.7	48	2.4	0.6	2.0	9.6	4.9	100	1695	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	29.8	40.2	12.1	53	2.9	0.6	1.9	9.5	4.9	101	1770	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	38.5	32.2	12.6	77	4.6	0.7	1.9	9.5	4.9	102	1875	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	37.3	26.8	10.4	82	5.0	0.8	1.9	9.5	4.9	104	2685	3200	50
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	35.5	23.4	8.3	88	1.9	2.9	2.1	10.0	4.9	99	2855	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	34.9	22.3	7.7	89	1.7	3.5	2.1	10.0	4.9	99	2930	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	34.5	20.6	7.1	88	1.6	3.7	2.1	10.0	4.9	100	3010	3200	0
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	33.1	20.4	6.7	86	1.5	3.9	2.0	9.8	4.9	100	3090	3200	6.5
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	32.4	19.7	6.4	85	1.4	3.9	2.0	9.8	4.9	100	3180	3200	6.5
34 BkW 2 R#4	2.0 BaCO ₃ , Al ₂ O ₃ , 5451, 60/100	750	80	23.3	24.6	5.8	49	1.5	0.8	2.0	9.9	4.9	100	4125	3200	6.5

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Numbers are too small for significant results.

Reactor D was used for all experiments.

Catalyst compositions are described in Appendix D, and preparation methods are described in Appendix E.

Table B5. Catalysts Containing Silver

Name	Wt Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	750	80	26.7	1.8	0.5	98	2.1	10.1	4.9	99	20	1171	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	725	80	26.8	1.1	0.3	98	2.1	10.1	4.9	98	80	1171	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	675	160	26.4	0.9	0.2	98	2.1	10.1	4.9	99	130	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	675	160	25.9	0.9	0.2	99	2.1	10.1	4.9	99	245	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	675	160	25.7	1.2	0.3	98	2.0	10.0	4.9	100	2720	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	675	160	25.5	1.1	0.3	98	2.0	10.0	4.9	100	3845	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	600	160	25.1	0.3	0.1	98	2.0	10.0	4.9	100	3960	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	600	160	25.9	0.3	0.1	98	2.0	10.0	4.9	100	3985	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	500	160	25.0	0.0	0.0	98	2.0	10.0	4.9	100	4020	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	500	160	25.8	0.0	0.0	99	2.0	10.0	4.9	100	4045	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	400	160	25.3	0.0	0.0	98	2.0	10.0	4.9	100	4080	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	400	160	24.9	0.0	0.0	98	2.0	10.0	4.9	100	4115	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	300	160	24.0	0.0	0.0	7	2.0	10.0	4.9	101	4160	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	300	160	1.3	0.0	0.0	8	2.0	10.0	4.9	101	4185	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	350	160	14.2	0.0	0.0	57	2.0	10.0	4.9	101	4210	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	350	160	17.8	0.0	0.0	72	2.0	10.0	4.9	100	4250	2341	0
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	350	160	26.6	0.0	0.0	98	2.0	9.7	4.9	100	4340	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	350	160	2.7	0.0	0.0	14	2.0	9.7	4.9	101	4430	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	350	160	1.2	0.0	0.0	8	2.0	9.7	4.9	101	5285	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	600	160	26.8	0.3	0.1	98	2.0	9.8	4.9	99	5410	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	700	160	27.2	1.8	0.5	99	2.0	9.8	4.9	99	5455	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	700	160	26.8	1.7	0.5	99	2.0	9.8	4.9	99	5485	2341	10
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	700	160	26.7	2.1	0.6	99	2.0	9.8	4.9	100	5555	2341	200
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	700	160	26.8	2.3	0.6	99	2.0	9.8	4.9	100	5635	2341	200
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	550	160	26.0	0.0	0.0	99	2.0	9.8	4.9	100	5730	2341	200
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	550	160	25.7	-0.1	0.0	99	2.1	10.1	4.9	101	5870	2341	500
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	550	160	25.4	-0.1	0.0	99	2.1	10.1	4.9	101	5960	2341	500
33 BKW 120 R#2	5.0 Ag, BaCO3, 30/60	550	160	26.1	0.2	0.1	99	2.1	10.1	4.9	100	6725	2341	500
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.1	0.2	0.1	98	2.0	9.8	4.9	100	30	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	26.2	0.0	0.0	98	2.0	9.8	4.9	100	180	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	450	160	26.2	0.0	0.0	98	2.0	9.8	4.9	100	240	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	14.7	0.0	0.0	56	2.0	9.8	4.9	100	300	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	425	160	26.7	0.0	0.0	97	2.0	9.8	4.9	99	350	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	425	160	26.2	0.0	0.0	98	2.0	9.8	4.9	100	455	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	14.7	0.0	0.0	56	2.0	9.7	4.9	100	3515	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	14.8	0.0	0.0	58	2.0	9.8	4.9	101	3725	2341	0
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	15.9	0.0	0.0	57	2.0	9.9	4.8	99	3830	2341	10
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	12.0	0.0	0.0	40	2.1	9.9	4.8	99	3915	2341	10
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	400	160	4.1	0.0	0.0	14	2.1	9.9	4.8	100	4080	2341	10
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.6	0.2	0.1	98	2.1	9.9	4.8	99	4190	2341	10
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.8	0.2	0.1	98	2.0	9.8	4.9	98	4325	2341	10
34 BKW 6 R#3	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.0	0.2	0.1	98	2.0	9.8	4.9	100	4955	2341	10
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	26.3	0.1	0.0	96	2.0	9.8	4.9	100	95	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	14.7	0.0	0.0	56	2.0	9.8	4.9	100	210	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	600	160	26.1	0.0	0.0	98	2.0	9.8	4.9	100	270	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	575	160	22.4	0.0	0.0	83	2.0	9.8	4.9	100	325	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	575	160	23.3	0.0	0.0	86	2.0	9.8	4.9	100	410	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	575	160	25.8	0.0	0.0	98	2.0	9.7	4.9	101	3560	2341	0
34 BKW 7 R#4	5.0 Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	23.9	0.0	0.0	90	2.0	9.8	4.9	100	3685	2341	0

Table B5. Catalysts Containing Silver (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI	
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	23.8	0.0	0.0	90	###	2.0	9.8	4.9	100	3775	2341	0
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	24.5	0.0	0.0	89	###	2.1	9.9	4.8	99	3865	2341	10
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	11.2	0.0	0.0	40	###	2.1	9.9	4.8	99	3965	2341	10
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	11.3	0.0	0.0	42	###	2.1	9.9	4.8	100	4045	2341	10
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.9	0.2	0.0	98	###	2.1	9.9	4.8	99	4145	2341	10
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	26.2	0.0	0.0	98	###	2.1	9.9	4.8	100	4235	2341	10
34 BKW 7 R#4	5.0	Pr(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	24.9	0.2	0.1	98	0.0	2.0	9.8	4.9	101	5000	2341	10
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	550	160	0.8	0.0	0.0	5	###	2.0	9.9	4.9	100	30	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	600	160	2.4	0.0	0.0	10	###	2.0	9.9	4.9	100	90	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	650	160	7.3	0.0	0.0	31	###	2.0	9.9	4.9	101	145	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	22.6	1.3	0.3	83	0.1	2.0	9.9	4.9	100	200	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	22.2	1.3	0.3	84	0.1	2.0	9.9	4.9	100	310	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.2	1.4	0.3	87	0.1	2.0	9.9	4.9	100	715	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.3	1.3	0.3	85	0.1	2.0	9.9	4.9	100	1075	2341	0
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.4	1.3	0.3	86	0.1	2.0	9.9	4.9	100	1255	2341	10
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.0	1.4	0.3	91	0.1	2.0	9.9	4.9	101	1340	2341	10
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.0	1.3	0.3	88	0.1	2.0	9.9	4.9	101	1570	2341	10
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	24.5	1.0	0.3	84	0.1	2.0	9.5	4.9	99	1660	2341	50
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.8	1.1	0.3	86	0.1	2.0	9.5	4.9	99	1750	2341	50
34 BKW 10 R#3	5.0	Bi(NO3)3, Ag2O, Al2O3, 5451, 30/60	700	160	23.1	1.0	0.2	79	0.0	2.0	9.6	4.9	99	2515	2341	50
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	550	160	27.0	0.0	0.0	98	###	2.0	9.9	4.9	99	65	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	550	160	26.0	0.0	0.0	98	###	2.0	9.9	4.9	100	115	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	450	160	26.1	0.0	0.0	98	###	2.0	9.9	4.9	100	170	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	16.0	0.0	0.0	61	###	2.0	9.9	4.9	100	265	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	16.0	0.0	0.0	61	###	2.0	9.9	4.9	100	355	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	15.8	0.0	0.0	60	###	2.0	9.9	4.9	100	1120	2341	0
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	5.3	0.0	0.0	22	###	2.0	9.9	4.9	101	1310	2341	10
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	3.0	0.0	0.0	16	###	2.0	9.9	4.9	101	1375	2341	10
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	3.5	0.0	0.0	17	###	2.0	9.9	4.9	101	1540	2341	10
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	26.0	0.6	0.2	98	0.0	2.0	9.9	4.9	100	1605	2341	10
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	26.5	0.7	0.2	99	0.1	2.0	9.9	4.9	100	1630	2341	10
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	27.8	0.7	0.2	98	0.1	2.0	9.5	4.9	99	1705	2341	50
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	27.7	0.6	0.2	99	0.1	2.0	9.5	4.9	99	1795	2341	50
34 BKW 11 R#4	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	27.8	0.5	0.1	99	0.0	2.0	9.6	4.9	99	2560	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	550	160	27.8	0.0	0.0	99	###	2.0	9.7	4.9	98	25	2341	0
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	500	160	27.9	0.0	0.0	99	###	2.0	9.7	4.9	99	90	2341	0
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	450	160	27.2	0.0	0.0	99	###	2.0	9.7	4.9	99	145	2341	0
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	22.0	0.0	0.0	78	###	2.0	9.7	4.9	99	215	2341	0
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	19.8	0.0	0.0	83	###	1.9	9.4	4.9	103	270	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	1.1	0.0	0.0	3	###	1.9	9.4	4.9	100	375	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	400	160	-1.1	0.0	0.0	1	###	1.9	9.4	4.9	101	1280	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	27.4	0.6	0.2	99	0.0	1.9	9.5	4.9	99	1385	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	26.3	0.6	0.2	99	0.1	1.9	9.5	4.9	101	1490	2341	50
34 BKW 14 R#3	5.0	Ba(NO3)2, Ag2O, Al2O3, 5451, 30/60	700	160	26.0	1.7	0.4	99	0.2	2.1	10.0	4.8	100	1540	2341	500
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	550	160	6.1	0.0	0.0	21	###	2.0	9.7	4.9	99	60	2341	0
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	600	160	19.4	0.0	0.0	69	0.0	2.0	9.7	4.9	99	115	2341	0
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	600	160	23.1	0.4	0.1	82	0.0	2.0	9.7	4.9	99	180	2341	0
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	625	160	19.7	0.3	0.1	70	0.0	2.0	9.7	4.9	99	245	2341	0
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	625	160	14.8	0.3	0.0	49	0.0	1.9	9.4	4.9	99	310	2341	50
34 BKW 15 R#4	5.0	KNO3, Ag2O, Al2O3, 5451, 30/60	625	160	4.8	0.9	0.0	18	1.6	1.9	9.4	4.9	100	425	2341	50

Table B5. Catalysts Containing Silver (continued)

Name	Wt. Catalyst	Temp	Cm	CH ₄ C	Sel	Yield	O ₂ C	±	CH ₄ O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
34 BKW 15 R#4	5.0 KNO ₃ Ag ₂ O,Al ₂ O ₃ 5451,30/60	625	160	3.4	1.7	0.1	14	1.6	1.9	9.4	4.9	100	515	2341	50
34 BKW 15 R#4	5.0 KNO ₃ Ag ₂ O,Al ₂ O ₃ 5451,30/60	625	160	0.2	11.1	0.0	3	1.7	1.9	9.4	4.9	102	1325	2341	50
34 BKW 15 R#4	5.0 KNO ₃ Ag ₂ O,Al ₂ O ₃ 5451,30/60	700	160	26.3	0.6	0.2	99	0.1	1.9	9.5	4.9	101	1460	2341	50
34 BKW 15 R#4	5.0 KNO ₃ Ag ₂ O,Al ₂ O ₃ 5451,30/60	700	160	15.8	19.5	3.1	52	0.6	2.1	10.0	4.8	101	1520	2341	500
34 BKW 15 R#4	5.0 KNO ₃ Ag ₂ O,Al ₂ O ₃ 5451,30/60	700	160	17.2	23.3	4.0	54	0.7	2.1	10.0	4.8	100	1565	2341	500
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	350	160	2.9	0.0	0.0	10	###	2.0	9.8	4.9	100	70	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	400	160	12.6	0.0	0.0	42	###	2.0	9.8	4.9	98	145	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	400	160	12.3	0.0	0.0	41	###	2.0	9.8	4.9	98	235	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	450	160	28.2	0.0	0.0	99	###	2.0	9.8	4.9	97	280	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	20.4	0.0	0.0	70	###	2.0	9.8	4.9	97	363	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	1.3	0.0	0.0	5	###	2.0	9.9	4.9	100	540	2341	5
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	0.8	0.0	0.0	6	###	2.0	9.9	4.9	101	675	2341	5
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	-0.5	0.0	0.0	3	###	2.0	9.8	4.8	102	4185	2341	5
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	2.9	0.0	0.0	11	###	2.0	9.9	4.9	100	4320	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	4.3	0.0	0.0	12	###	2.0	9.9	4.9	99	4365	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	425	160	6.9	0.0	0.0	17	###	2.0	9.9	4.9	97	5625	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	475	160	10.1	0.0	0.0	38	7.4	2.0	9.7	4.8	100	7705	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	475	160	9.5	0.0	0.0	37	7.4	2.0	9.7	4.8	100	7885	2341	0
34 BKW 32 R#3	5.0 Ag ₂ O,5451,30/60	525	160	17.3	0.0	0.0	65	0.0	2.0	9.6	4.8	99	8710	2341	0
34 BKW 32 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	0.0	5.1	0.0	1	###	2.0	9.8	4.8	100	30	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	0.0	7.9	0.0	0	0.9	2.0	9.8	4.8	100	100	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	600	160	0.6	18.2	0.1	4	0.2	2.0	9.8	4.8	101	150	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	650	160	5.2	32.6	1.7	13	0.3	2.0	9.8	4.8	102	205	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	17.2	25.4	4.5	44	0.6	2.0	9.8	4.8	102	255	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	16.7	24.9	4.2	43	0.5	2.0	9.8	4.8	101	305	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	27.6	2.3	0.6	99	0.6	2.0	9.7	4.9	99	410	1263	50
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	27.1	0.9	0.2	99	0.1	2.0	9.7	4.9	99	500	1263	50
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	26.6	0.5	0.1	99	0.0	2.0	9.6	4.8	100	1220	1263	50
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	26.9	0.4	0.1	99	0.0	2.0	9.7	4.8	99	1400	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	27.1	0.4	0.1	99	0.0	2.0	9.7	4.8	98	1490	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	625	80	27.3	0.0	0.0	99	###	2.0	9.7	4.8	98	1580	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	26.2	0.0	0.0	95	###	2.0	9.7	4.8	98	1670	1263	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	26.5	0.0	0.0	98	###	2.0	9.7	4.8	99	1745	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	25.9	0.0	0.0	98	###	2.0	9.7	4.8	99	1835	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	0.2	4.8	0.0	0	28.8	2.0	9.8	4.8	100	55	2526	5
34 BKW 36 R#3	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	-0.7	0.0	0.0	0	###	2.0	9.8	4.8	101	120	2526	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	600	160	0.8	18.4	0.2	2	0.2	2.0	9.8	4.8	100	175	2526	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	650	160	4.3	36.3	1.6	10	0.2	2.0	9.8	4.8	99	225	2526	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	15.8	28.0	4.5	38	0.6	2.0	9.8	4.8	101	290	1263	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	14.5	28.8	4.2	35	0.6	2.0	9.7	4.9	101	365	1263	50
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	20.4	18.8	3.9	59	0.5	2.0	9.7	4.9	101	455	1263	50
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	26.2	0.4	0.1	99	0.0	2.0	9.6	4.8	100	1265	1263	50
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	27.1	0.3	0.1	99	0.0	2.0	9.7	4.8	98	1445	1263	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	670	80	27.0	0.3	0.1	99	0.0	2.0	9.7	4.8	98	1535	1263	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	625	80	27.4	0.0	0.0	99	###	2.0	9.7	4.8	98	1625	1263	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	550	80	27.1	0.0	0.0	99	###	2.0	9.7	4.8	98	1695	1263	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	26.4	0.0	0.0	99	###	2.0	9.7	4.8	99	1790	2526	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	26.5	0.0	0.0	99	###	2.0	9.7	4.8	99	1895	2526	5
34 BKW 37 R#4	5.0 BaCl ₂ La ₂ O ₃ Ag ₂ O,Al ₂ O ₃ 30/60	550	160	25.3	0.0	0.0	99	###	2.0	9.7	4.8	100	2705	2526	5

Table B5. Catalysts Containing Silver (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	550	160	0.9	2.6	0.0	2	###	2.0	9.8	4.9	100	25	2526	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	550	160	0.9	1.5	0.0	2	###	2.0	9.8	4.9	100	85	2526	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	600	160	1.8	7.0	0.1	6	0.2	2.0	9.8	4.9	102	155	2526	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	650	160	6.3	20.2	1.3	16	0.3	2.0	9.8	4.9	102	220	2526	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	670	80	26.7	15.3	4.1	80	0.6	2.0	9.8	4.9	100	325	1263	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	670	80	27.9	0.9	0.3	99	0.1	2.0	9.8	4.9	98	415	1263	5
34 BKW 44 R#3	5.0	BaCl2/La2O3, Ag2O, Al2O3, 30/60	670	80	26.0	0.5	0.1	99	0.0	2.0	9.6	4.8	100	3790	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	600	80	6.1	14.4	0.9	17	0.2	2.0	9.8	4.9	100	55	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	650	80	15.8	25.4	4.0	40	0.4	2.0	9.8	4.9	100	115	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	650	80	15.2	24.8	3.8	39	0.4	2.0	9.8	4.9	100	185	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	700	80	29.0	3.4	1.0	99	2.1	2.0	9.8	4.9	98	280	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	700	80	28.2	1.7	0.5	99	0.5	2.0	9.8	4.9	98	370	1263	5
34 BKW 45 R#4	5.0	CaCl2, XH2O, Ag2O, Al2O3, 30/60	700	80	26.2	0.6	0.2	99	0.0	2.0	9.6	4.8	100	3835	1263	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	600	80	4.8	15.4	0.8	17	0.2	2.0	9.6	4.8	102	30	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	650	80	14.6	27.7	4.1	43	0.3	2.0	9.6	4.8	101	100	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	650	80	14.1	28.3	4.0	41	0.3	2.0	9.6	4.8	101	165	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	22.8	28.7	5.6	66	0.6	2.0	9.6	4.8	101	235	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	27.2	23.7	6.5	81	0.6	2.0	9.6	4.8	100	325	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	27.2	0.8	0.2	99	0.1	2.0	9.8	4.8	98	1180	1171	5
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	28.4	1.5	0.4	99	0.1	1.9	9.4	4.9	98	1360	1171	50
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	26.2	5.5	1.4	99	0.2	2.0	9.7	4.8	100	1495	1171	500
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	17.1	26.0	4.5	54	0.4	2.0	9.7	4.8	101	1585	1171	500
34 BKW 50 R#3	5.0	BaCl2, Ag, Al2O3, 30/60	675	80	21.3	30.4	6.5	59	0.7	2.0	9.7	4.8	100	4060	1171	500
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	600	80	4.8	13.9	0.7	17	0.2	2.0	9.6	4.8	101	70	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	650	80	16.9	27.4	4.6	48	0.4	2.0	9.6	4.8	100	135	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	650	80	16.0	27.6	4.5	46	0.4	2.0	9.6	4.8	101	190	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	26.6	27.2	7.2	76	0.6	2.0	9.6	4.8	100	280	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	30.7	23.1	7.1	91	0.7	2.0	9.6	4.8	99	370	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	26.9	1.3	0.3	99	0.1	2.0	9.8	4.8	99	1225	1171	5
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	30.8	11.9	3.6	99	0.4	1.9	9.4	4.9	98	1330	1171	50
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	26.8	20.0	5.4	86	0.5	2.0	9.7	4.8	100	1540	1171	500
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	22.9	30.9	7.0	65	0.6	2.0	9.7	4.8	100	1630	1171	500
34 BKW 51 R#4	5.0	BaCl2/La2O3, Ag, Al2O3, 30/60	675	80	27.1	30.4	8.2	75	0.8	2.0	9.7	4.8	100	4105	1171	500

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Numbers are too small for significant results.

Reactor D was used for all experiments.

Catalyst compositions are described in Appendix D, and preparation methods are described in Appendix E.

Table B6. Vapor Phase Reactions

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	±	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
35 BKW 23 R#2	0.0	None (Control Run)	750	160	36.9	13.4	5.6	76	2.7	0.1	2.0	20.4	10.1	113	35	---	0
35 BKW 23 R#2	0.0	None (Control Run)	750	160	39.8	12.4	5.6	81	2.9	0.1	2.0	20.4	10.1	113	65	---	0
35 BKW 23 R#2	0.0	None (Control Run)	750	160	27.3	18.5	5.4	67	2.2	0.1	2.0	20.4	10.1	107	115	---	0
35 BKW 23 R#2	0.0	None (Control Run)	700	160	15.2	22.1	3.4	31	1.1	0.0	2.0	20.4	10.1	102	155	---	0
35 BKW 23 R#2	0.0	None (Control Run)	700	160	21.0	18.0	4.0	36	1.5	0.1	2.0	20.4	10.1	107	195	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	8.4	21.9	1.8	8	0.5	0.0	2.0	20.4	10.1	99	295	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	7.2	24.7	1.7	14	0.4	0.0	2.0	20.4	10.1	98	1230	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	9.0	22.9	2.0	11	0.5	0.0	2.0	20.4	10.1	97	1390	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	7.2	25.7	1.8	14	0.4	0.0	2.0	20.4	10.1	98	1420	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	7.7	22.5	1.7	10	0.5	0.0	2.0	20.4	10.1	99	1530	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	8.6	21.6	1.9	10	0.5	0.0	2.0	20.4	10.1	99	1560	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	5.7	25.0	1.4	17	0.4	0.0	2.0	20.4	10.1	99	1595	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	7.6	23.1	1.7	13	0.5	0.0	2.0	20.4	10.1	99	1620	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	11.2	20.0	2.2	8	0.6	0.0	2.0	20.4	10.1	99	1650	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	8.5	21.7	1.8	7	0.5	0.0	2.0	20.4	10.1	99	1675	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	6.0	24.3	1.5	13	0.4	0.0	2.1	20.4	9.9	99	1710	---	0
35 BKW 23 R#2	0.0	None (Control Run)	650	160	4.9	25.1	1.2	12	0.4	0.0	2.1	20.4	9.9	100	1795	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	5.8	25.0	1.4	2	0.4	0.0	2.2	20.4	9.5	100	35	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	6.4	22.9	1.5	0	0.5	0.0	2.2	20.4	9.5	102	80	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	5.2	25.3	1.3	6	0.4	0.0	2.2	20.4	9.5	100	105	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	3.1	37.6	1.1	-3	0.2	0.0	2.2	20.4	9.5	99	135	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	3.5	31.6	1.1	-8	0.3	0.0	2.2	20.4	9.5	99	160	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	1.2	43.0	0.5	1	0.2	0.0	2.2	20.4	9.5	100	190	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	700	160	5.4	30.6	1.6	-9	0.5	0.0	2.2	20.4	9.5	100	215	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	700	160	3.0	39.8	1.2	8	0.3	0.1	2.2	20.4	9.5	99	250	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	700	160	3.3	33.0	1.1	-8	0.4	0.1	2.2	20.4	9.5	100	275	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	700	160	2.8	33.2	0.9	3	0.3	0.1	2.2	20.4	9.5	100	310	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	1.7	42.8	0.7	-9	0.2	0.1	2.1	20.1	9.7	100	1270	---	0
35 BKW 26 R#2	5.0	CsOH, XH2O, 100+	650	160	2.5	38.0	0.9	##	0.2	0.0	2.1	20.1	9.7	99	1320	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	5.4	27.2	1.5	10	0.3	0.1	2.1	20.4	9.8	99	55	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	6.9	22.6	1.6	7	0.5	0.0	2.1	20.4	9.8	100	80	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	6.2	28.3	1.7	14	0.3	0.1	2.1	20.4	9.8	97	125	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	6.8	22.0	1.5	7	0.5	0.0	2.1	20.4	9.8	101	155	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	10.4	21.5	2.2	7	0.5	0.0	2.1	20.4	9.8	98	215	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	7.0	22.0	1.6	6	0.5	0.0	2.1	20.4	9.8	101	245	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	9.4	21.9	2.0	7	0.5	0.0	2.1	20.4	9.8	99	295	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	7.1	26.1	1.8	12	0.4	0.0	2.1	20.4	9.8	98	345	---	0
35 BKW 29 R#2	1.4	LiOH, 100+	650	160	4.2	29.9	1.2	##	0.2	0.1	2.1	20.4	9.8	98	375	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	5.4	23.9	1.3	4	0.4	0.0	2.1	20.1	9.8	100	45	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	7.0	22.6	1.6	2	0.5	0.0	2.1	20.1	9.8	100	70	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	5.3	25.4	1.4	7	0.4	0.0	2.1	20.1	9.8	100	95	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	3.7	27.5	1.0	13	0.3	0.0	2.1	20.1	9.8	100	125	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	5.6	23.1	1.3	7	0.5	0.0	2.1	20.1	9.8	102	160	---	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	6.4	24.1	1.5	7	0.5	0.0	2.1	20.1	9.8	100	205	---	0

Table B6. Vapor Phase Reactions (continued)

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	CO ₂ /CO	CH ₄ /O ₂	CH ₄ in	O ₂ in	C Bal	Time	GHSV	ECI
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	0.8	60.5	0.5	0	0.2	0.1	2.1	20.1	9.8	100	245	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	###	83.2	###	1	0.1	###	2.1	20.1	9.8	101	305	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	###	80.6	###	###	0.0	###	2.1	20.1	9.8	101	335	0
35 BKW 32 R#2	5.0	CsCl, 100+	700	160	###	47.2	0.0	2	0.2	0.2	2.1	20.1	9.8	101	365	0
35 BKW 32 R#2	5.0	CsCl, 100+	750	160	4.1	31.0	1.3	6	0.6	0.1	2.1	20.1	9.8	101	390	0
35 BKW 32 R#2	5.0	CsCl, 100+	750	160	3.5	32.0	1.1	10	0.6	0.1	2.1	20.1	9.8	101	420	0
35 BKW 32 R#2	5.0	CsCl, 100+	750	160	15.5	25.6	4.0	31	1.4	0.1	2.0	20.2	10.3	101	1400	0
35 BKW 32 R#2	5.0	CsCl, 100+	650	160	3.2	42.6	1.3	7	0.2	0.0	2.0	20.1	9.9	98	55	0
35 BKW 35 R#1	2.0	LiCl, 100+	650	160	3.1	28.6	0.9	2	0.2	0.0	2.0	20.1	9.9	99	85	0
35 BKW 35 R#2	2.0	LiCl, 100+	650	160	1.4	64.3	0.9	###	0.1	0.1	2.0	20.1	9.9	99	125	0
35 BKW 35 R#2	2.0	LiCl, 100+	650	160	0.6	50.1	0.3	###	0.2	0.1	2.0	20.1	9.9	100	155	0
35 BKW 35 R#2	2.0	LiCl, 100+	650	160	###	64.6	###	6	0.1	0.0	2.0	20.1	9.9	101	185	0
35 BKW 35 R#2	2.0	LiCl, 100+	750	160	12.5	22.2	2.9	18	1.5	0.0	2.0	20.1	9.9	106	220	0
35 BKW 35 R#2	2.0	LiCl, 100+	750	160	12.9	22.4	3.0	22	1.7	0.0	2.0	20.1	9.9	104	265	0
35 BKW 35 R#2	2.0	LiCl, 100+	850	160	30.4	3.8	1.2	96	6.2	1.7	2.0	20.1	9.9	103	300	0
35 BKW 35 R#2	2.0	LiCl, 100+	800	160	29.1	3.7	1.1	95	3.5	1.9	2.0	20.1	9.9	103	345	0
35 BKW 35 R#2	2.0	LiCl, 100+	750	160	27.6	3.5	1.0	93	1.7	2.6	2.0	20.1	9.9	101	430	0
35 BKW 35 R#2	2.0	LiCl, 100+	750	160	30.8	2.9	0.9	94	1.6	2.5	2.0	20.1	9.9	102	520	0
35 BKW 37 R#2	5.0	CsCl, 100+	650	160	###	6.8	0.0	8	0.0	3.2	2.0	20.1	10.3	101	35	0
35 BKW 37 R#2	5.0	CsCl, 100+	650	160	0.3	7.3	0.0	9	0.0	2.6	2.0	20.1	10.3	100	65	0
35 BKW 37 R#2	5.0	CsCl, 100+	650	160	0.5	9.2	0.0	3	0.0	12.3	2.0	20.1	10.3	100	100	0
35 BKW 37 R#2	5.0	CsCl, 100+	700	160	1.7	14.5	0.2	10	0.2	0.8	2.0	20.1	10.3	100	130	0
35 BKW 37 R#2	5.0	CsCl, 100+	700	160	1.9	14.3	0.3	7	0.2	0.6	2.0	20.1	10.3	100	160	0
35 BKW 37 R#2	5.0	CsCl, 100+	700	160	2.3	17.0	0.4	7	0.2	0.6	2.0	20.1	10.3	99	190	0
35 BKW 37 R#2	5.0	CsCl, 100+	750	160	4.0	21.9	0.9	17	0.5	0.2	2.0	20.1	10.3	100	220	0
35 BKW 37 R#2	5.0	CsCl, 100+	750	160	3.8	23.0	0.9	10	0.4	0.2	2.0	20.1	10.3	100	340	0
35 BKW 37 R#2	5.0	CsCl, 100+	750	160	3.1	21.4	0.7	12	0.4	0.2	2.0	20.1	10.3	101	3985	0
35 BKW 37 R#2	5.0	CsCl, 100+	750	160	2.7	18.1	0.5	8	0.3	0.2	2.0	20.1	10.3	101	4150	0
35 BKW 37 R#2	5.0	CsCl, 100+	750	160	3.5	17.8	0.6	3	0.3	0.2	2.0	20.1	10.3	100	4190	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	5.0	24.7	1.3	5	0.4	0.2	2.1	20.1	9.8	101	30	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	5.9	27.8	1.6	9	0.4	0.2	2.1	20.1	9.8	98	60	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	5.8	24.5	1.4	6	0.4	0.2	2.1	20.1	9.8	100	90	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	4.0	27.7	1.1	6	0.4	0.2	2.1	20.1	9.8	101	120	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	6.5	23.6	1.5	7	0.5	0.1	2.1	20.1	9.8	100	160	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	5.9	24.7	1.5	9	0.4	0.1	2.1	20.1	9.8	100	195	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	3.0	28.4	0.9	7	0.3	0.1	2.1	20.1	9.8	101	230	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	650	160	2.5	30.5	0.8	###	0.3	0.2	2.1	20.1	9.8	100	275	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	32.8	12.0	4.4	77	2.2	0.2	2.1	20.1	9.8	113	320	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	29.0	13.8	4.4	71	2.0	0.2	2.1	20.1	9.8	110	360	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	33.3	12.2	4.6	76	2.3	0.2	2.1	20.1	9.8	113	460	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	26.8	14.3	4.2	69	1.9	0.2	2.1	20.1	9.8	110	595	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	34.6	12.5	4.9	76	2.1	0.2	2.1	20.4	9.8	112	1310	0
35 BKW 41 R#2	4.0	RuO ₂ , powder	750	160	27.3	17.1	5.0	62	2.1	0.2	2.1	20.4	9.8	107	1385	0

Table B6. Vapor Phase Reactions (continued)

Name	Wt	Catalyst	Temp	Ccm	CH ₄ C	Sel	Yield	O ₂ C	±/	CO ₂ /CO	CH ₄ /O ₂	CH ₄ In	O ₂ In	C Bal	Time	GHSV	ECI
35 BKW 41 R#2	4.0	RuO ₂ powder	750	160	28.9	15.8	5.0	65	2.2	0.2	2.1	20.4	9.8	109	1435	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	34.7	13.9	5.5	78	2.8	0.1	2.0	20.2	10.2	114	45	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	34.2	13.8	5.4	79	2.8	0.1	2.0	20.2	10.2	115	70	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	5.7	29.9	1.7	16	0.8	0.1	2.0	20.2	10.2	101	100	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	9.6	27.5	2.7	18	1.4	0.1	2.0	20.2	10.2	101	150	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	9.9	28.3	2.8	23	1.5	0.1	2.0	20.2	10.2	101	190	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	17.2	20.5	3.7	40	2.7	0.1	2.0	20.2	10.2	106	270	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	21.8	18.1	4.2	45	3.1	0.1	2.0	20.2	10.2	106	310	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	9.7	28.4	2.8	18	1.0	0.1	2.0	20.2	10.2	101	5605	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	10.4	28.8	3.0	19	1.0	0.1	2.0	20.2	10.2	100	5900	...	0
35 BKW 44 R#2	5.0	CsCl, 100+	750	160	20.8	49.1	10.1	33	1.7	1.1	2.0	20.2	10.3	99	55	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	21.1	46.5	9.8	36	1.9	0.9	2.0	20.2	10.3	100	85	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	21.0	48.9	10.3	35	1.8	1.0	2.0	20.2	10.3	100	120	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	21.7	50.9	10.9	37	1.8	1.1	2.0	20.2	10.3	99	155	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	20.0	52.2	10.5	35	1.7	1.2	2.0	20.2	10.3	100	185	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	21.3	53.1	11.2	36	1.7	1.2	2.0	20.2	10.3	99	220	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	20.7	54.4	11.2	41	1.7	1.3	2.0	20.2	10.3	99	255	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	23.7	50.8	12.0	42	1.8	1.4	2.0	20.2	10.3	100	1155	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	160	23.2	50.2	11.8	43	1.8	1.4	2.0	20.2	10.3	101	1290	3000	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	34.8	41.2	14.3	76	3.3	1.3	2.0	20.2	10.3	99	1355	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	39.6	33.8	13.7	65	4.1	1.2	2.0	20.2	10.3	102	1395	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	34.3	37.9	12.8	70	3.3	1.2	2.0	20.2	10.3	98	1440	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	41.0	29.8	12.0	70	4.6	1.0	2.0	20.2	10.3	98	1480	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	39.3	27.7	11.0	67	4.6	0.9	2.0	20.2	10.3	101	1520	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	41.4	28.7	12.0	67	4.8	1.0	2.0	20.2	10.3	101	1555	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	36.0	37.6	13.6	75	3.7	1.2	2.0	20.2	10.3	100	1605	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	40.5	36.1	14.7	64	3.8	1.4	2.0	20.2	10.3	103	1645	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	41.9	35.3	14.8	60	3.8	1.4	2.0	20.2	10.3	100	1690	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	40.5	36.1	14.6	57	3.6	1.4	2.0	20.2	10.3	100	1745	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	36.2	34.7	12.7	69	3.8	1.1	2.0	20.2	10.3	101	1800	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	39.8	27.7	11.3	66	4.7	1.0	2.0	20.2	10.3	102	1890	1500	0
35 BKW 47 R#2	4.0	BaCO ₃ , Al ₂ O ₃ , 5451, 30/60	750	80	41.5	25.2	10.8	76	5.2	0.9	2.0	20.2	10.3	103	2655	1500	0

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Numbers are too small for significant results.

*** Gas flow rate was 160 ccm (ambient conditions).

Reactor V was used for all experiments.

Reaction 35-BKW-47 contained CsCl in the Vaporizer and BaCO₃/Al₂O₃ in the reactor (see Experimental Section, Discussion Section, and Appendix F).

Table B7. Vapor-Phase Catalysts

35-BKW-23, No Catalyst

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
750	232	115	106.7	27.27	66.93	0.377	5.557	0.213	0.467	18.47	80.58
700	218	195	106.5	20.99	36.06	0.247	4.457	0.207	0.313	18.03	81.70
650	203	1420	97.6	7.20	13.98	0.014	0.731	0.093	0.035	25.66	74.33
650	300	1560	99.1	8.63	9.57	0.028	1.214	0.113	0.058	21.62	78.38
650	500	1675	99.5	8.50	7.48	0.028	1.244	0.117	0.060	21.65	77.66
650	650	1980	99.5	6.63	10.55	0.020	0.949	0.102	0.044	23.05	76.27

35-BKW-26, CsOH

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
650	225	105	100.3	5.23	6.21	0.021	0.823	0.101	0.042	25.28	74.39
650	300	160	99.2	3.52	-8.38	0.009	0.365	0.069	0.017	31.61	68.39
650	400	190	100.0	1.23	0.94	0.004	0.143	0.047	0.008	43.01	56.99
700	400	215	100.3	5.36	-8.75	0.031	0.758	0.117	0.058	30.55	68.73
700	500	250	99.2	2.97	7.91	0.013	0.253	0.068	0.020	39.82	60.18
700	600	275	99.8	3.27	-7.69	0.023	0.388	0.075	0.026	32.98	66.79
700	650	310	99.6	2.84	3.47	0.020	0.308	0.063	0.019	33.23	66.77
650	225	1350	100.0	0.57	-0.05	0.003	0.036	0.032	0.004	65.14	34.86

35-BKW-29, LiOH

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
650	149	125	97.5	6.23	13.66	0.027	0.525	0.083	0.026	28.33	71.48
650	250	155	101.5	6.79	6.55	0.050	1.271	0.123	0.063	21.99	78.01
650	300	215	98.2	10.43	6.82	0.053	1.349	0.125	0.067	21.52	78.48
650	350	245	101.4	7.04	6.32	0.050	1.293	0.125	0.065	21.98	77.77
650	400	295	98.5	9.36	7.45	0.049	1.222	0.117	0.061	21.87	78.13
650	450	345	97.7	7.07	12.15	0.032	0.707	0.095	0.036	26.10	73.90
650	500	375	97.8	4.17	-3.32	0.029	0.257	0.050	0.011	29.85	70.14

Table B7. Vapor-Phase Catalysts (continued)

35-BKW-32, CsCl

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
650	196	95	99.9	5.34	7.44	0.023	0.771	0.096	0.039	25.35	74.35
650	300	125	100.2	3.72	12.96	0.014	0.513	0.083	0.026	27.50	66.08
650	400	160	101.6	5.57	6.69	0.031	1.069	0.112	0.054	23.08	76.24
650	500	205	100.3	6.36	7.18	0.026	0.998	0.112	0.051	24.10	75.90
650	600	245	99.8	0.77	-0.34	0.005	0.043	0.032	0.005	60.45	39.55
650	650	305	100.6	-0.48	1.27	0.004	0.000	0.009	0.000	83.21	16.79
700	650	365	101.0	-0.07	2.27	0.016	0.085	0.037	0.008	47.17	52.83
750	650	390	101.0	4.06	5.50	0.042	0.659	0.097	0.061	31.04	68.96
750	700	420	100.8	3.48	10.19	0.035	0.550	0.089	0.051	32.02	67.10
750	226	1400	101.5	15.49	31.34	0.134	2.463	0.188	0.266	25.58	73.15

35-BKW-35, LiCl

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
650	165	85	99.4	3.14	1.76	0.008	0.359	0.059	0.014	28.58	71.42
650	550	125	99.0	1.43	-1.42	0.002	0.030	0.025	0.003	64.25	35.75
650	600	155	100.1	0.64	-7.44	0.003	0.069	0.031	0.005	50.06	49.94
650	650	185	101.1	-0.70	6.21	0.001	0.027	0.022	0.003	64.60	35.40
750	750	220	105.7	12.46	17.82	0.104	2.704	0.162	0.247	22.17	76.09
850	850	300	103.3	30.36	96.25	4.481	2.634	0.020	0.120	3.75	95.57
800	800	345	102.6	29.09	94.58	4.351	2.349	0.029	0.101	3.72	95.57
750	183	1400	101.9	25.88	92.28	4.296	1.604	0.041	0.067	3.52	96.25

35-BKW-37, CsCl

Reactor Temp	Vaporizer Temp	Run Time (min)	% C Bal	CH ₄ Conv	O ₂ Conv	% CO ₂	% CO	% C ₂ H ₆	% C ₂ H ₄	Total C ₂ Sel	Total C ₁ Sel
650	183	65	100.2	0.25	8.51	0.063	0.024	0.003	0.000	7.28	92.73
650	650	100	100.0	0.48	3.11	0.084	0.007	0.005	0.000	9.24	90.76
700	650	130	100.1	1.65	10.18	0.129	0.170	0.021	0.004	14.46	85.53
700	700	160	99.9	1.85	7.47	0.110	0.187	0.021	0.004	14.28	85.72
700	750	190	99.3	2.30	6.75	0.097	0.172	0.023	0.005	16.98	83.02
750	750	3985	100.8	3.07	12.18	0.094	0.520	0.061	0.024	21.38	77.78
750	195	4190	100.0	3.50	2.65	0.091	0.489	0.048	0.016	17.84	82.16

Table B7. Vapor-Phase Catalysts (continued)

35-BKW-41, RuO₂

Reactor	Vaporizer	Run Time	% C	CH ₄	O ₂	%	%	%	%	Total	Total
<u>Temp</u>	<u>Temp</u>	<u>(min)</u>	<u>Bal</u>	<u>Conv</u>	<u>Conv</u>	<u>CO₂</u>	<u>CO</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂ Sel</u>	<u>C₁ Sel</u>
650	152	60	98.4	5.85	9.11	0.094	0.524	0.088	0.031	27.75	72.25
650	200	90	100.2	5.79	6.04	0.117	0.798	0.105	0.045	24.49	74.91
650	300	120	100.5	4.01	6.46	0.085	0.578	0.094	0.033	27.74	72.26
650	400	160	100.5	6.50	7.07	0.114	0.964	0.113	0.053	23.58	76.42
650	500	195	100.2	5.93	8.93	0.080	0.851	0.108	0.046	24.67	74.61
650	600	230	100.6	3.03	6.58	0.046	0.483	0.080	0.025	28.36	71.64
650	650	275	100.2	2.54	-5.16	0.053	0.326	0.066	0.017	30.45	69.55
750	650	360	110.2	28.95	70.71	1.289	5.821	0.194	0.380	13.79	85.42
750	750	1310	112.1	34.63	75.86	1.390	7.388	0.188	0.443	12.49	86.88
750	183	1475	113.2	28.59	68.50	1.139	6.477	0.203	0.447	14.50	84.97

35-BKW-44, CsCl

Reactor	Vaporizer	Run Time	% C	CH ₄	O ₂	%	%	%	%	Total	Total
<u>Temp</u>	<u>Temp</u>	<u>(min)</u>	<u>Bal</u>	<u>Conv</u>	<u>Conv</u>	<u>CO₂</u>	<u>CO</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂ Sel</u>	<u>C₁ Sel</u>
750	188	70	114.8	34.15	79.12	0.718	8.338	0.196	0.533	13.77	86.23
750	750	100	100.8	5.68	16.35	0.048	0.875	0.115	0.091	29.92	68.96
750	800	190	101.0	9.85	22.62	0.083	1.523	0.134	0.188	28.27	71.74
750	850	270	106.0	17.19	39.55	0.245	3.528	0.139	0.362	20.48	77.97
750	864	310	106.4	21.82	44.76	0.350	4.499	0.134	0.406	18.06	81.94
750	188	5975	101.0	10.46	16.63	0.082	1.596	0.161	0.170	27.55	71.03

Table B7. Vapor-Phase Catalysts (continued)

35-BKW-47, CsCl in Vaporizer and BaCO₃/Al₂O₃ in Reactor

Reactor	Vaporizer	Run Time	% C	CH ₄	O ₂	%	%	%	%	Total	Total	ppm
<u>Temp</u>	<u>Temp</u>	<u>(min)</u>	<u>Bal</u>	<u>Conv</u>	<u>Conv</u>	<u>CO₂</u>	<u>CO</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂ Sel</u>	<u>C₁ Sel</u>	<u>ECI</u>
750	185	85	99.7	21.08	35.88	1.063	1.188	0.365	0.665	46.49	51.10	20
750	650	120	100.0	21.03	34.54	1.088	1.050	0.390	0.706	48.87	47.92	20
750	700	185	100.0	20.02	34.60	1.027	0.878	0.417	0.698	52.22	47.85	20
750	750	220	99.2	21.32	35.92	1.045	0.857	0.436	0.728	53.06	43.57	20
750	750	1290	101.2	23.16	42.94	1.441	1.007	0.466	0.846	50.17	47.01	20
750	750	1395	102.1	39.57	64.53	3.154	2.598	0.311	1.238	33.83	63.06	40
750	188	1440	98.2	34.26	69.97	2.238	1.927	0.322	1.051	37.90	57.75	40
750	188	1520	101.0	39.31	66.77	2.895	3.329	0.224	1.005	27.68	70.44	40
750	750	1605	100.2	36.04	74.71	2.674	2.163	0.330	1.191	37.60	60.02	40
750	850	1745	99.7	40.49	56.57	3.130	2.303	0.349	1.241	36.13	61.96	40
750	185	1800	101.1	36.16	69.25	2.776	2.428	0.303	1.126	34.66	63.39	40
750	185	2655	103.0	41.54	76.35	3.458	3.757	0.205	1.040	25.20	73.38	40
750	185	2720	101.7	41.25	74.15	3.246	3.635	0.202	0.993	25.09	72.60	10
750	185	2900	101.1	43.04	74.26	3.403	3.909	0.187	0.960	23.39	74.95	10
750	185	3055	104.2	41.54	72.43	3.444	4.064	0.185	0.946	22.48	75.01	20
750	750	3115	101.1	39.36	62.83	3.217	2.783	0.264	1.079	30.23	67.84	20
750	750	4590	100.5	28.31	49.98	2.127	1.784	0.344	0.752	35.18	63.12	20

Initial results at 160 sccm flow rate. After 1395 m, 80 sccm flow rate.

Table B8. Methane Coupling Activity of K2La2Ti3O10

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105														
Weight (g): 4		Volume (cc): 4.2														
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5														
Temperature (°C)		803	803	803	803	803	803	803	803	803	803	803	803	803	803	803
Flow (cc/min)		150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
GHSV (h-1)		2143	2143	2143	2143	2143	2143	2143	2143	2143	2143	2143	2143	2143	2143	2143
Time (h)		3	5	7	9	11	13	15	17	21	25	27	29	33	35	35
CH4 Conv., %		10.56	11.58	11.71	11.96	11.88	11.20	13.72	13.69	13.84	13.84	14.53	13.90	13.02	12.63	12.63
O2 Conv., %		99.88	99.88	99.88	99.88	99.88	99.88	99.89	99.89	99.89	99.88	99.89	99.89	99.89	99.88	99.88
C Balance, %		103.90	102.54	102.49	102.22	102.11	102.97	100.45	100.45	100.32	100.30	99.42	100.24	101.30	101.96	101.96
C2 Selectivity, %		63.56	63.68	63.54	63.49	63.41	63.31	64.34	64.53	64.20	64.15	64.22	64.13	63.94	65.19	65.19
C3 Selectivity, %		3.58	3.55	3.47	3.45	3.49	3.47	3.42	3.44	3.50	3.39	3.37	3.37	3.30	3.17	3.17
C2 Yield, %		6.98	7.56	7.63	7.76	7.69	7.30	8.87	8.87	8.92	8.90	9.28	8.93	8.43	8.40	8.40
Ethylene/Ethane		1.44	1.44	1.44	1.44	1.44	1.44	1.34	1.35	1.35	1.36	1.36	1.36	1.36	1.23	1.23
CO2/CO		4.85	4.56	4.52	4.47	4.41	4.41	4.53	4.53	4.43	4.40	4.31	4.38	4.39	4.66	4.66

Table B8. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105														
Weight (g): 4		Volume (cc): 4.2														
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5														
Temperature (°C)		803	803	803	803	803	803	803	803	803	803	803	803	803	803	803
Flow (cc/min)		250	250	250	250	250	250	250	250	250	250	250	250	250	250	250
GHSV (h-1)		3571	2857	2857	2857	3571	3571	3571	3571	3571	3571	3571	3571	3571	3571	3571
Time (h)		37	43	45	47	49	53	55	59	61	63	65	67	71	73	73
CH4 Conv., %		12.31	12.17	12.21	12.19	12.11	12.03	12.07	13.64	13.22	13.59	13.90	13.92	14.58	14.15	14.15
O2 Conv., %		99.88	99.88	99.89	99.88	99.88	99.88	99.88	99.89	99.88	99.88	99.88	99.88	99.88	99.88	99.88
C Balance, %		102.38	102.49	102.37	102.38	102.44	102.49	102.45	100.94	101.50	100.86	100.46	100.39	99.83	100.15	100.15
C2 Selectivity, %		64.82	64.98	64.98	64.88	64.93	64.81	64.69	65.63	65.75	65.71	65.71	65.68	65.86	65.64	65.64
C3 Selectivity, %		3.22	3.21	3.23	3.21	3.18	3.16	3.14	3.06	3.05	3.10	3.09	3.09	3.07	3.09	3.09
C2 Yield, %		8.17	8.11	8.12	8.09	8.06	7.99	8.00	9.04	8.82	9.01	9.18	9.18	9.59	9.31	9.31
Ethylene/Ethane		1.24	1.25	1.25	1.25	1.25	1.25	1.25	1.19	1.19	1.19	1.19	1.19	1.18	1.18	1.18
CO2/CO		4.74	4.63	4.62	4.58	4.56	4.51	4.50	4.64	4.60	4.48	4.46	4.44	4.46	4.39	4.39

Table B8. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105									
Weight (g): 4		Volume (cc): 4.2									
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5									
Temperature (°C)		803	803	803	803	803	803	803	803	803	803
Flow (cc/min)		300	300	400	400	400	400	400	400	400	400
GHSV (h-1)		4286	4286	5714	5714	5714	5714	5714	5714	5714	5714
Time (h)		75	77	81	83	85	95	97	99	107	113
CH4 Conv., %		14.04	13.62	14.21	14.50	14.88	14.21	14.50	14.88	14.47	13.69
O2 Conv., %		99.88	99.88	99.89	99.86	99.88	99.89	99.86	99.88	99.85	99.85
C Balance, %		100.28	100.76	100.47	99.91	99.39	100.47	99.91	99.39	99.39	100.26
C2 Selectivity, %		65.52	65.40	67.50	67.07	66.65	67.50	67.07	66.65	65.21	64.79
C3 Selectivity, %		3.06	3.02	2.99	3.02	3.01	2.99	3.02	3.01	3.04	3.08
C2 Yield, %		9.22	8.98	9.64	9.72	9.86	9.64	9.72	9.86	9.38	8.89
Ethylene/Ethane		1.19	1.19	1.05	1.07	1.10	1.05	1.07	1.10	1.16	1.18
CO2/CO		4.41	4.47	4.66	4.43	4.49	4.66	4.43	4.49	4.23	4.27

Table B8. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105									
Weight (g): 4		Volume (cc): 4.2									
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5									
Temperature (°C)		803	803	803	803	803	803	803	803	803	803
Flow (cc/min)		415	415	415	415	415	415	415	415	415	415
GHSV (h-1)		5929	5929	5929	5929	5929	5929	5929	5929	5929	5929
Time (h)		125	127	129	131	133	135	137	139	141	147
CH4 Conv., %		13.69	13.61	13.06	13.59	13.88	13.97	14.02	14.19	14.07	14.25
O2 Conv., %		99.50	99.45	99.42	99.41	99.43	99.41	99.35	99.37	99.35	99.29
C Balance, %		100.19	100.34	100.93	100.56	100.19	100.06	100.01	99.71	99.93	99.57
C2 Selectivity, %		65.35	65.16	65.17	65.16	65.18	65.05	65.11	65.15	65.02	64.97
C3 Selectivity, %		3.10	3.06	3.08	2.99	3.00	3.21	3.01	3.04	3.01	3.04
C2 Yield, %		8.96	8.90	8.59	8.91	9.06	9.09	9.13	9.21	9.14	9.22
Ethylene/Ethane		1.10	1.10	1.10	1.10	1.10	1.09	1.10	1.10	1.10	1.10
CO2/CO		4.43	4.41	4.41	4.45	4.42	4.37	4.37	4.33	4.33	4.25

Table B8. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105	
Weight (g): 4		Volume (cc): 4.2	
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5	
Temperature (°C)	803	803	803
Flow (cc/min)	415	415	415
GHSV (h-1)	5929	5929	5929
Time (h)	149	151	157
CH4 Conv., %	14.56	12.69	12.30
O2 Conv., %	99.26	98.96	98.88
C Balance, %	99.20	100.94	101.41
C2 Selectivity, %	64.98	66.25	66.01
C3 Selectivity, %	3.07	3.20	3.13
C2 Yield, %	9.38	8.43	8.23
Ethylene/Ethane	1.09	1.08	1.08
CO2/CO	4.24	3.19	3.20
		3.14	3.05
		2.97	2.94
		2.98	2.96
		2.98	2.98
		2.96	2.96
		2.98	2.98
		2.94	2.94
		2.99	2.99
		1.08	1.08
		8.79	8.81
		8.61	8.65
		8.49	8.59
		3.23	3.19
		65.82	66.01
		100.76	100.56
		98.53	98.46
		12.81	12.94
		184	187
		5929	5929
		415	415
		803	803

1.2% CO2 in reactant stream.

Table B8. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10		NOTEBOOK: 9-KDC-X-105									
Weight (g): 4		Volume (cc): 4.2									
CH4/O2/N2: 9.07/1/0.27		Pressure (psig): 5									
Temperature (°C)		803	803	803	803	803	803	803	803	803	803
Flow (cc/min)		415	415	415	415	415	415	415	415	415	415
GHSV (h-1)		5929	5929	5929	5929	5929	5929	5929	5929	5929	0
Time (h)		136	199	202	205	211	218	219	220	224	234
CH4 Conv., %		12.70	12.77	12.96	12.65	12.79	12.57	12.32	12.62	13.27	12.89
O2 Conv., %		98.32	98.56	98.53	98.68	98.45	98.11	98.16	98.07	96.88	95.92
C Balance, %		100.73	100.47	100.19	100.33	100.40	100.57	100.86	100.55	100.15	100.69
C2 Selectivity, %		66.00	65.14	64.85	64.08	64.35	64.53	64.33	64.55	63.25	63.79
C3 Selectivity, %		3.21	3.19	3.22	3.22	3.18	3.11	3.14	3.12	3.46	3.63
C2 Yield, %		8.45	8.36	8.42	8.13	8.26	8.16	7.99	8.19	8.41	8.28
Ethylene/Ethane		1.08	1.13	1.14	1.20	1.16	1.16	1.16	1.16	1.08	0.99
CO2/CO		2.78	2.83	2.78	2.72	2.77	2.14	2.17	2.14	3.08	2.75
		1.2% CO2 in reactant stream.					5.4% CO2 in reactant stream.				
							No CO2 in reactant stream.				
							ECI added to reactant stream at 10ppm level.				

Table B9. Methane Coupling Activity of [Bi2O3](0.85)[La2O3](0.15): [Run 1]

CATALYST: [Bi2O3](0.85)[La2O3](0.15)															NOTEBOOK: 8-KDC-X-63																	
Weight (g): 3.23			Volume (cc): 1.3																													
CH4/O2/N2: 9.07/1/0.27			Pressure (psig): 5																													
Temperature (°C)	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803	803							
Flow (cc/min)	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150							
GHSV (h-1)	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922	6922							
Time (h)	1	3	5	9	11	13	15	17	21	25	27	29	33	33	33	33	33	33	33	33	33	33	33	33	33							
CH4 Conv., %	8.59	9.94	8.69	9.86	10.10	10.22	9.25	8.93	8.47	10.51	9.60	8.61	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30							
O2 Conv., %	66.80	66.94	67.68	67.11	66.93	66.85	66.75	84.55	84.94	83.56	83.77	84.06	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34	84.34							
C Balance, %	100.45	98.91	100.40	99.66	98.64	98.37	99.62	102.05	102.64	100.16	101.13	102.40	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84	102.84							
C2 Selectivity, %	63.58	63.14	63.38	63.54	63.66	63.56	63.68	62.18	61.69	62.25	61.98	61.67	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45	61.45							
C3 Selectivity, %	4.79	4.71	4.77	5.00	4.74	4.81	4.79	5.42	5.62	5.98	5.43	5.82	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93							
C2 Yield, %	5.48	6.21	5.53	6.20	6.34	6.39	5.87	5.67	5.36	6.55	6.02	5.44	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25							
Ethylene/Ethane	1.22	1.23	1.25	1.24	1.24	1.24	1.25	1.51	1.54	1.50	1.52	1.52	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53							
CO2/CO	5.14	5.20	4.99	4.77	4.75	4.66	4.79	6.45	6.38	5.82	6.14	6.26	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44	6.44							

Table B9. Methane Coupling Activity of [Bi2O3](0.85)[La2O3](0.15): [Run 1] (Continued)

CATALYST: [Bi2O3](0.85)[La2O3](0.15)			NOTEBOOK: 8-KDC-X-63									
Weight (g): 3.23			Volume (cc): 1.3									
CH4/O2/N2: 9.07/1/0.27			Pressure (psig): 5									
Temperature (°C)	803	803	803	803	803	803	801	801	801	801	801	801
Flow (cc/min)	50	50	50	50	50	50	75	75	75	75	75	75
GHSV (h-1)	2307	2307	2307	2307	2307	2307	3462	3462	3462	3462	3462	3462
Time (h)	37	41	43	49	53	55	59	63	65	67	71	71
CH4 Conv., %	7.93	7.37	7.20	7.07	7.14	7.38	8.98	9.53	9.62	10.98	9.74	9.74
O2 Conv., %	99.87	99.87	99.87	99.87	99.87	99.87	99.87	99.88	99.88	99.88	99.88	99.88
C Balance, %	103.46	103.82	103.89	103.99	103.92	103.98	102.22	101.58	101.43	100.10	101.29	101.29
C2 Selectivity, %	54.17	54.24	54.30	54.14	54.36	56.28	56.57	56.84	57.20	58.07	57.78	57.78
C3 Selectivity, %	5.64	5.60	5.58	5.63	5.68	4.66	4.83	4.99	4.67	5.11	4.78	4.78
C2 Yield, %	4.45	4.15	4.06	3.98	4.03	4.32	5.19	5.50	5.58	6.38	5.70	5.70
Ethylene/Ethane	1.94	1.93	1.92	1.95	1.96	1.59	1.63	1.68	1.69	1.68	1.72	1.72
CO2/CO	19.66	18.24	18.04	18.26	17.54	11.37	11.29	11.80	12.00	11.92	16.51	16.51

Table B10. Methane Coupling Activity of [Bi2O3](0.85)[La2O3](0.15): [Run 2]

CATALYST: [Bi2O3](0.85)[La2O3](0.15)			NOTEBOOK: 9-KDC-X-99									
Weight (g): 8.046			Volume (cc): 2.5									
CH4/O2/N2: 2.24/1/3.8			Pressure (psig): 5									
Temperature (°C)	800	800	800	800	800	800	800	800	800	800	800	800
Flow (cc/min)	100	100	100	100	150	150	150	150	150	150	200	200
GHSV (h-1)	2400	2400	2400	2400	3600	3600	3600	3600	3600	3600	4800	4800
Time (h)	1	3	5	11	17	23	25	26	27	27	27	27
CH4 Conv., %	32.47	32.56	32.43	32.02	32.58	32.74	32.74	32.84	31.99	32.84	31.99	31.99
O2 Conv., %	94.87	94.82	94.82	94.82	94.85	94.80	94.80	94.80	94.79	94.80	94.79	94.79
C Balance, %	96.30	97.45	97.92	98.25	97.61	97.65	98.07	98.07	98.05	98.07	98.05	98.05
C2 Selectivity, %	41.41	41.36	41.54	42.74	41.88	41.88	43.46	42.37	41.70	42.37	41.70	41.70
C3 Selectivity, %	2.18	2.09	2.10	2.22	2.23	2.25	2.31	2.29	1.82	2.29	1.82	1.82
C2 Yield, %	12.95	13.12	13.19	13.44	13.32	13.39	13.95	13.97	13.08	13.97	13.08	13.08
Ethylene/Ethane	1.44	1.44	1.45	1.45	1.49	1.50	1.36	1.37	1.17	1.37	1.17	1.17
CO2/CO	50.05	51.28	51.65	49.63	54.42	54.74	58.82	61.14	60.32	61.14	60.32	60.32

Table B11. Methane Coupling Activity of 20 wt% V2O5/MgO

CATALYST: 20 wt% V2O5/MgO		NOTEBOOK: 9-KDC-X-42									
Weight (g): 4.004		Volume (cc): 11.5									
CH4/O2/N2: 2.04/1/3.69		Pressure (psig): 5									
Temperature (°C)		600	600	650	650	700	700	700	750	750	800
Flow (cc/min)		200	200	200	200	200	200	200	200	200	200
GHSV (h-1)		1043	1043	1043	1043	1043	1043	1043	1043	1043	1043
Time (h)		1	4	6	8	10	14	16	24	28	30
CH4 Conv., %		25.03	24.45	24.57	24.47	25.07	24.73	24.19	26.29	26.30	25.95
O2 Conv., %		94.79	94.82	94.82	94.81	94.82	94.82	94.82	94.81	94.80	94.82
C Balance, %		98.79	98.78	98.64	98.76	98.40	98.55	98.97	98.93	98.89	98.82
C2 Selectivity, %		0.32	0.26	0.26	0.28	0.46	0.32	0.31	2.57	3.30	8.26
C3 Selectivity, %		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59
C2 Yield, %		0.08	0.06	0.06	0.07	0.11	0.08	0.07	0.67	0.86	2.44
Ethylene/Ethane		1.16	1.32	1.29	1.14	1.60	2.43	2.29	1.64	1.70	2.79
CO2/CO		6.36	4.89	4.33	3.91	5.39	5.65	5.41	3.40	3.53	2.41
											2.48

Table B12. Methane Coupling Activity of 5 wt% NaCl/ alpha alumina

CATALYST: 5 wt% NaCl/ alpha alumina			NOTEBOOK: 9-KDC-X-128									
Weight (g): 4.009			Volume (cc): 4.2									
CH4/O2/N2: 2.15/1/20.12			Pressure (psig): 5									
Temperature (°C)	575	575	575	575	575	575	575	575	575	575	600	625
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	714	714	714	714	714	714	714	714	714	714	714	714
Time (h)	1	9	29	49	67	71	75	77	79	1.00	7.28	101.65
CH4 Conv., %	**	**	**	**	**	**	**	**	**	**	**	**
O2 Conv., %	**	**	**	**	**	**	**	**	**	**	**	**
C Balance, %	**	**	**	**	**	**	**	**	**	**	**	**
C2 Selectivity, %	**	**	**	**	**	**	**	**	**	**	**	**
C3 Selectivity, %	**	**	**	**	**	**	**	**	**	**	**	**
C2 Yield, %	**	**	**	**	**	**	**	**	**	**	**	**
Ethylene/Ethane	**	**	**	**	**	**	**	**	**	**	**	**
CO2/CO	**	**	**	**	**	**	**	**	**	**	**	**

** : Conversion too low for meaningful results.

Table B12. Methane Coupling Activity of 5 wt% NaCl/ alpha alumina (Continued)

CATALYST: 5 wt% NaCl/ alpha alumina			NOTE: OOK: 9-KDC-X-128											
Weight (g): 4.009			Volume (cc): 4.2											
CH4/O2/N2: 2.15/1/20.12			Pressure (psig): 5											
Temperature (°C)	625	625	650	650	650	650	700	700	700	700	700	700	700	700
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	714	714	714	714	714	714	714	714	714	714	714	714	714	714
Time (h)	89	99	115	117	117	121	115	117	117	121	121	125	129	129
CH4 Conv., %	1.21	0.68	2.72	3.04	3.04	1.09	16.85	14.61	14.61	12.28	10.99	25.87	9.92	9.92
O2 Conv., %	6.76	4.52	9.65	9.82	9.82	10.91	42.55	35.73	35.73	29.12	25.87	24.71	24.71	24.71
C Balance, %	101.24	101.63	101.34	100.61	100.61	104.33	103.53	102.99	102.99	102.50	102.78	102.72	102.72	102.72
C2 Selectivity, %	17.46	17.86	30.27	33.18	33.18	38.82	58.16	60.38	60.38	61.68	62.28	61.13	61.13	61.13
C3 Selectivity, %	0.74	0.68	0.17	0.71	0.71	0.31	1.86	1.99	1.99	2.05	2.11	1.99	1.99	1.99
C2 Yield, %	0.21	0.12	0.84	1.01	1.01	0.44	10.14	9.08	9.08	7.76	7.03	6.23	6.23	6.23
Ethylene/Ethane	0.25	0.24	0.35	0.34	0.34	0.48	2.70	2.31	2.31	1.88	1.67	1.50	1.50	1.50
CO2/CO	1.69	1.46	1.24	1.68	1.68	1.55	2.07	2.04	2.04	1.98	2.54	2.02	2.02	2.02

Table B13. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/ 2.4 wt% NaCl/ alpha alumina

CATALYST: 0.66 wt% Pd(NO₃)₂/ 2.4 wt% NaCl/ alpha alumina

NOTEBOOK: 9-KDC-X-68

Weight (g): 4.006

Volume (cc): 4.8

CH₄/O₂/N₂: 2.04/1/3.69

Pressure (psig): 5

Temperature (°C)	590	590	590	590	590
Flow (cc/min)	50	50	50	50	50
GHSV (h-l)	625	625	625	625	625
Time (h)	1	3	9	11	13
CH ₄ Conv., %	49.04*	48.20*	47.82*	47.67*	47.57*
O ₂ Conv., %	94.97	94.96	94.95	94.95	94.94
C Balance, %	95.88	97.94	98.11	98.27	98.24
C ₂ Selectivity, %	**	**	**	**	**
C ₃ Selectivity, %	**	**	**	**	**
C ₂ Yield, %	**	**	**	**	**
Ethylene/Ethane	**	**	**	**	**
CO ₂ /CO	0.71	0.69	0.70	0.70	0.70

*: H₂ observed in the products.

**: C₂'s and C₃'s too low for meaningful results.

Table B14. Methane Coupling Activity of 7.4 wt% Pd(NO₃)₂/5 wt% NaCl/ alpha alumina

CATALYST: 7.4 wt% Pd(NO3)2/ 5 wt% NaCl/ alpha alumina										NOTEBOOK: 8-KDC-X-84															
Weight (g): 4.013		Volume (cc): 4		Pressure (psig): 5																					
CH4/O2/N2: 2.15/1/20.12																									
Temperature (°C)	575	575	575	575	575	600	600	600	625	625	625	625	650	650	650										
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50										
GHSV (h-1)	750	750	750	3000	750	750	750	750	750	750	750	750	750	750	750										
Time (h)	1	9	49	65	67	69	73	79	89	99	113	115	117	121	121										
CH4 Conv., %	56.38*	55.72*	53.22*	52.50*	62.49*	62.32*	62.48*	74.40*	73.16*	72.25*	71.05*	75.41*	75.63*	75.17*	75.17*										
O2 Conv., %	93.82	93.85	93.86	93.85	93.87	93.82	93.85	93.81	93.83	93.80	93.82	93.84	93.86	93.76	93.76										
C Balance, %	101.88	100.92	100.31	101.60	100.36	101.10	101.19	100.47	99.89	101.55	100.61	100.17	100.73	100.72	100.72										
C2 Selectivity, %	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**										
C3 Selectivity, %	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**										
C2 Yield, %	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**										
Ethylene/Ethane	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**										
CO2/CO	0.39	0.42	0.46	0.49	0.22	0.22	0.23	0.07	0.08	0.09	0.09	0.05	0.06	0.07	0.07										

*: Large amounts of H₂ observed in products.
 **: C₂'s and C₃'s are too low for meaningful results.

Table B15. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/1.6 wt% KCl/alpha alumina

NOTEBOOK: 9-KDC-X-64													
CATALYST: 0.66 wt% Pd(NO3)2/ 1.6 wt% KCl/ alpha alumina													
Weight (g): 4.02		Volume (cc): 3.9											
CH4/O2/N2: 2.04/1/3.69		Pressure (psig): 5											
Temperature (°C)	505	505	505	562	562	562	615	615	615	649	649	649	677
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	769	769	769	769	769	769	769	769	769	769	769	769	769
Time (h)	1	9	15	17	25	29	31	37	43	45	49	53	79
CH4 Conv., %	**	**	**	**	**	**	6.59	6.51	7.13	11.84	12.08	13.67	55.83*
O2 Conv., %	**	**	**	**	**	**	28.98	29.49	29.61	51.35	55.37	63.44	94.96
C Balance, %	**	**	**	**	**	**	100.17	100.47	99.90	100.19	100.75	100.75	95.42
C2 Selectivity, %	**	**	**	**	**	**	0.38	0.40	0.36	1.25	1.33	1.29	0.26
C3 Selectivity, %	**	**	**	**	**	**	0.93	1.03	0.89	0.92	0.78	0.16	0.00
C2 Yield, %	**	**	**	**	**	**	0.02	0.03	0.03	0.15	0.16	0.18	0.16
Ethylene/Ethane	**	**	**	**	**	**	***	***	***	***	***	***	***
CO2/CO	**	**	**	**	**	**	262.47	39.48	48.54	72.43	75.53	90.80	0.35
													0.18

** : Conversion too low for meaningful results.

*** : C₂'s too low for meaningful results.

Table B16. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/ 19.8 wt% KCl/ alpha alumina

CATALYST: 0.66 wt% Pd(NO ₃) ₂ / 19.8 wt% KCl/ alpha alumina				NOTEBOOK: 9-KDC-X-80			
Weight (g): 4.006	Volume (cc): 4.1						
CH ₄ /O ₂ /N ₂ : 2.24/1/4.21	Pressure (psig): 5						
Temperature (°C)	424	424	424	474	474	526	526
Flow (cc/min)	50	50	50	50	50	50	50
GHSV (h-1)	732	732	732	732	732	732	732
Time (h)	1	3	7	11	15	17	29
CH ₄ Conv., %	**	**	**	**	**	1.37	1.21
O ₂ Conv., %	**	**	**	**	**	3.04	2.76
C Balance, %	**	**	**	**	**	99.90	99.99
C ₂ Selectivity, %	**	**	**	**	**	***	***
C ₃ Selectivity, %	**	**	**	**	**	***	***
C ₂ Yield, %	**	**	**	**	**	***	***
Ethylene/Ethane	**	**	**	**	**	***	***
CO ₂ /CO	**	**	**	**	**	****	****

**: Conversion too low for meaningful results.
 ***: C₂'s and C₃'s too low for meaningful results.
 ****: CO too low for meaningful results.

Table B16. Methane Coupling Activity of 0.66 wt% Pd(NO3)2/ 19.8 wt% KCl/ alpha alumina (Continued)

NOTEBOOK: 9-KDC-X-80														
CATALYST: 0.66 wt% Pd(NO3)2/ 19.8 wt% KCl/ alpha alumina														
Weight (g): 4.006		Volume (cc): 4.1		Pressure (psig): 5										
CH4/O2/N2: 2.24/1/4.21														
Temperature (°C)	553	553	553	580	580	580	606	606	606	623	623	623	623	623
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	732	732	732	732	732	732	732	732	732	732	732	732	732	732
Time (h)	31	33	35	37	41	47	49	53	57	69	73	77	83	83
CH4 Conv., %	2.51	1.99	2.17	3.81	3.40	3.85	6.24	5.75	5.06	6.39	5.85	5.12	5.77	5.77
O2 Conv., %	6.62	6.68	7.20	13.14	12.87	13.22	23.63	22.10	20.32	22.30	21.92	21.18	20.73	20.73
C Balance, %	99.69	100.09	100.23	100.14	100.28	99.76	100.25	100.01	100.23	99.51	100.32	100.53	99.56	99.56
C2 Selectivity, %	**	**	**	4.89	0.32	0.30	2.78	0.73	0.85	1.11	4.00	1.27	1.25	1.25
C3 Selectivity, %	**	**	**	0.22	0.22	0.22	0.17	0.20	0.26	0.17	0.15	0.20	0.13	0.13
C2 Yield, %	**	**	**	0.19	0.01	0.01	0.17	0.04	0.04	0.07	0.24	0.07	0.07	0.07
Ethylene/Ethane	**	**	**	0.35	0.21	0.23	0.29	0.02	0.02	0.01	0.44	0.01	0.01	0.01
CO2/CO	**	**	**	33.50	21.63	27.09	31.46	27.53	24.39	38.52	32.16	27.91	26.31	26.31

** : Conversion too low for meaningful results.

Table B17. Methane Coupling Activity of 14.4 wt% BaCl₂/ alpha alumina

CATALYST: 14.4 wt% BaCl2/ alpha alumina				NOTEBOOK: 9-KDC-X-88								
Weight (g): 4.043		Volume (cc): 3.9										
CH4/O2/N2: 2.24/1/4.21				Pressure (psig): 5								
Temperature (°C)	478	478	478	478	529	529	529	580	580	580	632	
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	
GHSV (h-1)	769	769	769	769	769	769	769	769	769	769	769	
Time (h)	1	7	17	21	23	32	33	37	41	**	42	
CH4 Conv., %	**	**	**	**	**	**	**	**	**	**	8.65	
O2 Conv., %	**	**	**	**	**	**	**	**	**	**	45.55	
C Balance, %	**	**	**	**	**	**	**	**	**	**	100.15	
C2 Selectivity, %	**	**	**	**	**	**	**	**	**	**	65.34	
C3 Selectivity, %	**	**	**	**	**	**	**	**	**	**	1.80	
C2 Yield, %	**	**	**	**	**	**	**	**	**	**	5.66	
Ethylene/Ethane	**	**	**	**	**	**	**	**	**	**	0.81	
CO2/CO	**	**	**	**	**	**	**	**	**	**	1.64	

**: Conversion too low for meaningful results.

Table B17. Methane Coupling Activity of 14.4 wt% BaCl₂/alpha alumina (Continued)

NOTEBOOK: 9-KDC-X-88

Volume (cc): 3.9

Pressure (psig): 5

Temperature (°C)	632	632	632	632	657	657	657	683	683	683	683
Flow (cc/mln)	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	769	769	769	769	769	769	769	769	769	769	769
Time (h)	45	48	51	52	57	62	63	67	104		
CH4 Conv., %	8.42	7.89	8.30	14.14	13.69	11.74	20.10	19.82	12.95		
O2 Conv., %	44.26	42.53	43.83	52.40	52.53	50.85	66.54	63.75	55.80		
C Balance, %	99.73	99.50	99.85	99.52	98.68	100.17	100.25	99.15	100.46		
C2 Selectivity, %	65.07	65.17	66.12	70.47	70.70	68.99	69.09	68.89	61.84		
C3 Selectivity, %	2.19	1.50	3.76	3.06	2.93	3.00	3.95	3.87	2.26		
C2 Yield, %	5.46	5.12	5.48	9.92	9.55	8.11	13.92	13.54	8.05		
Ethylene/Ethane	0.74	0.66	0.64	1.30	1.13	1.02	1.96	1.67	0.87		
CO2/CO	1.59	1.63	1.80	1.98	2.03	2.32	2.14	2.41	2.08		

Table B18. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/ 14.4 wt% BaCl₂/ alpha alumina: [Run 1]

CATALYST: 0.66 wt% Pd(NO ₃) ₂ / 14.4 wt% BaCl ₂ / alpha alumina				NOTEBOOK: 9-KDC-X-73			
Weight (g): 4.024		Volume (cc): 3.8					
CH ₄ /O ₂ /N ₂ : 2.24/1/4.21		Pressure (psig): 5					
Temperature (°C)	495	495	495	546	546	546	596
Flow (cc/min)	50	50	50	50	50	50	50
GHSV (h ⁻¹)	789	789	789	789	789	789	789
Time (h)	1	5	9	17	23	25	33
CH ₄ Conv., %	**	**	**	**	**	3.67	3.67
O ₂ Conv., %	**	**	**	**	**	14.32	13.80
C Balance, %	**	**	**	**	**	99.90	99.71
C ₂ Selectivity, %	**	**	**	**	**	0.18	0.41
C ₃ Selectivity, %	**	**	**	**	**	2.11	2.20
C ₂ Yield, %	**	**	**	**	**	0.01	0.02
Ethylene/Ethane	**	**	**	**	**	***	***
CO ₂ /CO	**	**	**	**	**	****	****

***: Conversion too low for meaningful results.

****: C₂'s too low for meaningful results.

*****: CO too low for meaningful results.

Table B18. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/ 14.4 wt% BaCl₂/ alpha alumina: [Run 1] (Continued)

CATALYST: 0.66 wt% Pd(NO ₃) ₂ / 14.4 wt% BaCl ₂ / alpha alumina				NOTEBOOK: 9-KDC-X-73			
Weight (g): 4.024		Volume (cc): 3.8					
CH ₄ /O ₂ /N ₂ : 2.24/1/4.21		Pressure (psig): 5					
Temperature (°C)	651	651	651	685	685	717	717
Flow (cc/min)	50	50	50	50	50	50	50
GHSV (h ⁻¹)	789	789	789	789	789	789	789
Time (h)	35	39	43	47	51	57	59
CH ₄ Conv., %	12.30	11.83	11.89	20.58	21.08	23.65	28.56
O ₂ Conv., %	49.41	46.93	47.99	76.89	80.58	94.67	94.70
C Balance, %	100.14	100.39	100.48	100.45	100.38	100.70	100.13
C ₂ Selectivity, %	9.19	11.51	10.54	21.96	21.86	11.06	0.84
C ₃ Selectivity, %	1.74	1.78	1.94	0.66	0.54	0.29	0.00
C ₂ Yield, %	1.13	1.37	1.26	4.54	4.63	2.63	0.24
Ethylene/Ethane	0.63	0.56	0.62	1.14	1.05	0.22	0.18
CO ₂ /CO	52.23	43.42	44.64	66.23	61.09	11.03	2.44

NOTEBOOK: 9-KDC-X-85

132

Table B20. Methane Coupling Activity of 0.66 wt% Pd(NO₃)₂/11.8 wt% LaCl₃/alpha alumina

CATALYST: 0.66 wt% Pd(NO ₃) ₂ /11.8 wt% LaCl ₃ /alpha alumina				NOTEBOOK: 9-KDC-X-92									
Weight (g): 4.005		Volume (cc): 4											
CH ₄ /O ₂ /N ₂ : 2.24/1/4.21		Pressure (psig): 5											
Temperature (°C)		496	496	547	547	547	597	597	597	597	597	649	649
Flow (cc/min)		50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h ⁻¹)		750	750	750	750	750	750	750	750	750	750	750	750
Time (h)		1	2	4	5	7	13	15	19	23	26	27	28
CH ₄ Conv., %		**	**	**	**	**	**	3.02	4.67	3.41	24.90	24.74	24.55
O ₂ Conv., %		**	**	**	**	**	**	48.45	51.31	51.20	93.89	94.01	93.88
C Balance, %		**	**	**	**	**	**	100.42	99.49	100.87	102.17	103.11	103.82
C ₂ Selectivity, %		**	**	**	**	**	**	7.02	5.84	5.43	0.44	0.53	0.52
C ₃ Selectivity, %		**	**	**	**	**	**	0.65	0.32	0.00	0.00	0.00	0.00
C ₂ Yield, %		**	**	**	**	**	**	0.21	0.27	0.19	0.11	0.13	0.13
Ethylene/Ethane		**	**	**	**	**	**	0.30	0.29	0.31	0.14	0.45	0.45
CO ₂ /CO		**	**	**	**	**	**	***	***	***	2.46	2.45	2.41

**: Conversion too low for meaningful results.

***: CO too low for meaningful results.

Table B21. Methane Coupling Activity of 10 wt% Na₂CO₃/alpha alumina

CATALYST: 10 wt% Na ₂ CO ₃ /alpha alumina			NOTEBOOK: 9-KDC-X-123											
Weight (g): 4.004	Volume (cc): 4		Pressure (psig): 5											
CH ₄ /O ₂ /N ₂ : 2.15/1/20.12														
Temperature (°C)	575	575	575	575	600	600	600	625	625	625	650	650	675	675
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h ⁻¹)	750	750	750	750	750	750	750	750	750	750	750	750	750	750
Time (h)	1	5	13	15	17	21	29	31	37	39	43	45	49	59
CH ₄ Conv., %	**	**	**	**	**	**	7.77	7.88	8.21	11.35	11.78	17.75	17.27	17.53
O ₂ Conv., %	**	**	**	**	**	**	34.97	35.63	36.64	49.42	54.19	71.29	70.55	72.25
C Balance, %	**	**	**	**	**	**	100.23	100.30	100.17	100.74	101.80	100.55	101.62	100.72
C ₂ Selectivity, %	**	**	**	**	**	**	1.86	1.82	1.78	4.00	4.83	9.59	9.88	10.76
C ₃ Selectivity, %	**	**	**	**	**	**	0.00	0.00	0.00	0.00	0.00	0.10	0.08	0.11
C ₂ Yield, %	**	**	**	**	**	**	0.14	0.14	0.15	0.46	0.58	1.71	1.73	1.90
Ethylene/Ethane	**	**	**	**	**	**	0.21	0.20	0.22	0.35	0.37	0.48	0.48	0.47
CO ₂ /CO	**	**	**	**	**	**	5.89	5.86	5.66	7.72	8.13	11.18	10.64	9.67

** : Conversion too low for meaningful results.

Table B22. Methane Coupling Activity of 1.0 wt% Pd(NO₃)₂/ 10 wt% Na₂CO₃/ alpha alumina

CATALYST: 1.0 wt% Pd(NO₃)₂/ 10 wt% Na₂CO₃/ alpha alumina NOTEBOOK: 8-KDC-X-79

CH4/O2/N2: 2.15/1/20.12	Weight (g): 4.069			Volume (cc): 4			Pressure (psig): 5										
	Temperature (°C)	Flow (cc/min)	GHSV (h-1)	Time (h)	575	575	575	575	600	600	625	625	650	650	675	675	675
Temperature (°C)	575	50	750	1	5	9	13	19	27	29	35	37	41	43	47	53	53
Flow (cc/min)	50	50	750	2.83	3.25	4.16	4.98	12.61	12.54	12.86	13.48	56.01*	52.83*	51.89*	57.91*	54.98*	54.98*
GHSV (h-1)	750	750	750	35.93	37.04	40.09	43.81	71.44	71.91	73.18	76.28	93.67	93.70	93.67	93.66	93.69	93.69
Time (h)	106.04	105.90	105.63	105.70	105.06	104.94	104.67	104.56	103.86	104.88	104.44	104.02	104.02	105.32	105.32	105.32	105.32
CH4 Conv., %	**	**	**	**	**	**	**	1.57	2.08	2.02	1.84	**	**	**	**	**	**
O2 Conv., %	**	**	**	**	**	**	**	0.06	0.05	0.05	0.04	**	**	**	**	**	**
C Balance, %	**	**	**	**	**	**	**	0.21	0.27	0.27	0.26	**	**	**	**	**	**
C2 Selectivity, %	**	**	**	**	**	**	**	0.20	0.29	0.29	0.30	**	**	**	**	**	**
C3 Selectivity, %	**	**	**	**	**	**	**	0.20	0.29	0.29	0.30	**	**	**	**	**	**
C2 Yield, %	**	**	**	**	**	**	**	0.20	0.29	0.29	0.30	**	**	**	**	**	**
Ethylene/Ethane	**	**	**	**	**	**	**	0.20	0.29	0.29	0.30	**	**	**	**	**	**
CO2/CO	***	***	***	***	***	***	***	364.16	315.60	376.28	479.31	0.29	0.35	0.37	0.24	0.29	0.29

*: Large amounts of H₂ observed in the products.

**: C₂s and C₃'s too low for meaningful results.

***: CO too low for meaningful results.

Table B23. Methane Coupling Activity of 14.7 wt% Li₂CO₃/LaCaMnCoO₆
[Sequential Mode]

CATALYST: 14.7 wt% Li ₂ CO ₃ /LaCaMnCoO ₆		NOTEBOOK: 8-KDC-X-45											
CH ₄ /O ₂ /N ₂ : Pure CH ₄	Weight (g): 10.064	Volume (cc): 11.4											
		Pressure (psig): 0											
Temperature (°C)		800	800	800	800	800	800	800	850	850	850	850	850
Flow (cc/min)		50	50	50	50	50	50	50	50	50	150	150	150
GHSV (h ⁻¹)		263	263	263	263	789	789	789	263	263	789	789	789
Time (h)		0-2	2-5	5-10	0-2	2-5	5-10	0-2	2-5	5-10	0-2	2-5	5-10
CH ₄ Conv., %		9.83	5.18	1.89	8.49	3.50	1.84	10.11	4.94	3.14	7.88	3.84	1.79
C ₂ Selectivity, %		88.20	92.50	91.60	89.29	95.82	93.06	89.72	90.63	89.61	91.21	94.47	89.97
C ₃ Selectivity, %		3.15	2.79	2.25	3.65	0.00	1.33	3.74	5.38	4.73	4.23	3.68	2.43
C ₂ Yield, %		8.67	4.80	1.73	7.58	3.35	1.72	9.08	4.48	2.81	7.19	3.63	1.61
Ethylene/Ethane		1.44	0.89	0.56	1.01	0.58	0.41	1.36	1.03	0.86	1.15	0.78	0.45
CO ₂ /CO		***	***	***	6.03	***	***	22.30	***	***	3.05	***	***

***: CO too low for meaningful results.

Table B23. Methane Coupling Activity of 14.7 wt% Li2CO3/LaCaMnCoO6 (Continued)
[Sequential Mode]

CATALYST: 14.7 wt% Li2CO3/LaCaMnCoO6			NOTEBOOK: 8-KDC-X-45									
CH4/O2/N2: Pure CH4	Weight (g): 10.064	Volume (cc): 11.4	Pressure (psig): 0									
			750	750	750	750	750	700	700	700	700	725
Temperature (°C)			750	750	750	750	750	700	700	700	700	725
Flow (cc/min)			50	50	50	150	150	50	150	150	150	150
GHSV (h-1)			263	263	263	789	789	263	263	789	789	789
Time (h)			0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	0 - 2	2 - 5	0 - 2	2 - 5	5 - 10
CH4 Conv., %			7.59	4.59	2.56	2.75	2.12	5.53	2.80	1.98	1.26	2.58
C2 Selectivity, %			88.95	92.25	94.68	91.00	92.95	70.14	72.45	63.19	46.69	50.29
C3 Selectivity, %			5.57	3.96	1.77	1.49	1.11	1.09	0.82	0.59	0.35	0.28
C2 Yield, %			6.75	4.24	2.43	2.50	1.97	3.88	2.03	1.25	0.59	1.30
Ethylene/Ethane			1.15	0.79	0.51	0.36	0.32	0.61	0.39	0.28	0.13	0.23
CO2/CO			***	***	***	***	***	***	***	***	***	11.63
												26.76

***: CO too low for meaningful results.

Table B23. Methane Coupling Activity of 14.7 wt% Li₂CO₃/LaCaMnCoO₆ (Continued)
[Sequential Mode]

CATALYST: 14.7 wt% Li ₂ CO ₃ /LaCaMnCoO ₆			NOTEBOOK: 8-KDC-X-45											
Weight (g): 10.064		Volume (cc): 11.4												
CH ₄ /O ₂ /N ₂ : 20% CH ₄ / 80% N ₂			Pressure (psig): 0			CH ₄ /O ₂ /N ₂ : Pure CH ₄								
Temperature (°C)	725	725	725	725	725	725	725	800	800	800	800	800	800	800
Flow (cc/min)	50	50	50	50	50	50	150	50	50	50	150	150	150	150
GHSV (h ⁻¹)	263	263	263	263	263	263	789	263	263	263	789	789	789	789
Time (h)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	2 - 5	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	2 - 5
CH ₄ Conv., %	29.98	20.41	5.91	18.17	12.35	8.14	12.35	11.33	8.23	6.25	6.80	3.80	6.80	3.80
C ₂ Selectivity, %	48.17	55.15	65.56	48.75	50.61	66.54	50.61	83.33	85.28	88.31	84.52	82.93	84.52	82.93
C ₃ Selectivity, %	1.88	2.01	2.36	0.84	0.73	0.77	0.73	5.93	6.18	5.92	4.00	3.50	4.00	3.50
C ₂ Yield, %	14.44	11.26	3.88	8.86	6.25	5.41	6.25	9.44	7.02	5.52	5.75	3.15	5.75	3.15
Ethylene/Ethane	1.69	1.36	1.15	0.75	0.53	0.44	0.53	1.91	1.52	1.15	0.87	0.88	0.87	0.88
CO ₂ /CO	371.46	***	***	31.27	361.32	***	361.32	12.57	***	***	***	***	***	***

***: CO too low for meaningful results.

Table B2.4. Methane Coupling Activity of 20 wt% Na₂CO₃/ (80 mole% Pr - 20 mole% Ce oxide)

CATALYST: 20 wt% Na ₂ CO ₃ / (80 mole% Pr - 20 mole% Ce oxide)				NOTEBOOK: 9-KDC-X-60			
Weight (g): 4.001		Volume (cc): 4.7		CH ₄ /O ₂ /N ₂ : 7.78/1/3.69			
CH ₄ /O ₂ /N ₂ : 2.04/1/3.69		Pressure (psig): 5					
Temperature (°C)	779	779	779	779	779	779	779
Flow (cc/min)	100	100	100	100	100	100	100
GHSV (h ⁻¹)	1277	1277	1277	1277	1277	1277	1277
Time (h)	1	3	13	23	43	63	79
CH ₄ Conv., %	27.80	27.53	27.64	27.84	27.39	28.18	9.85
O ₂ Conv., %	94.91	94.92	94.93	94.93	94.93	94.98	94.83
C Balance, %	100.51	100.86	100.41	100.20	100.04	99.40	100.70
C ₂ Selectivity, %	29.34	29.17	28.49	28.07	27.02	28.30	47.41
C ₃ Selectivity, %	1.60	1.59	1.50	1.62	1.43	1.48	3.26
C ₂ Yield, %	8.20	8.10	7.91	7.83	7.40	7.93	4.70
Ethylene/Ethane	0.59	0.59	0.58	0.58	0.57	0.61	0.34
CO ₂ /CO	131.10	130.83	127.65	129.49	113.57	115.25	47.86

Table B24. Methane Coupling Activity of 20 wt% Na₂CO₃/ (80 mole % Pr - 20 mole % Ce oxide) (Continued)

CATALYST: 20 wt% Na ₂ CO ₃ / (80 mole % Pr - 20 mole % Ce oxide)				NOTEBOOK: 9-KDC-X-60			
Weight (g): 4.001	Volume (cc): 4.7			CH ₄ /O ₂ /N ₂ : 3.99/1/3.69			
CH ₄ /O ₂ /N ₂ : 7.78/1/3.69	Pressure (psig): 5						
Temperature (°C)	779	779	779	779	779	779	779
Flow (cc/min)	100	100	100	100	100	100	100
GHSV (h-1)	1277	1277	1277	1277	1277	1277	1277
Time (h)	81	83	85	95	97	99	103
CH ₄ Conv., %	10.10	9.58	9.70	15.32	12.87	12.96	13.06
O ₂ Conv., %	94.94	95.00	94.94	94.91	94.88	94.92	94.90
C Balance, %	100.39	101.00	100.84	102.24	104.97	104.87	104.66
C ₂ Selectivity, %	47.06	47.49	47.33	38.16	39.73	39.81	39.67
C ₃ Selectivity, %	3.26	3.21	3.29	2.45	2.48	2.58	2.55
C ₂ Yield, %	4.77	4.64	4.63	5.98	5.37	5.41	5.42
Ethylene/Ethane	0.34	0.35	0.34	0.46	0.47	0.47	0.47
CO ₂ /CO	49.35	47.77	48.54	76.96	60.44	71.48	64.38
							69.47

Table B25. Methane Coupling Activity of 20 wt% Na₂CO₃/(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide): [Run 1]

CATALYST: 20 wt% Na2CO3/(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)													NOTEBOOK: 9-KDC-X-46																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																		
Weight (g): 4.003		Volume (cc): 4.1																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
CH4/O2/N2: 2.04/1/3.69		Pressure (psig): 5																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
Temperature (°C)	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	699	

Table B25. Methane Coupling Activity of 20 wt% Na₂CO₃(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide): [Run 1] (Continued)

CATALYST: 20 wt% Na ₂ CO ₃ (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)			NOTEBOOK: 9-KDC-X-46											
Weight (g): 4.003	Volume (cc): 4.1													
CH ₄ /O ₂ /N ₂ : 2.04/1/3.69	Pressure (psig): 5													
Temperature (°C)	706	737	737	737	737	737	737	737	737	737	737	737	737	759
Flow (cc/min)	100	100	100	100	100	100	100	100	100	100	100	100	100	100
GHSV (h ⁻¹)	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463
Time (h)	58	66	69	72	75	78	81	84	87	90	93	96	96	96
CH ₄ Conv., %	30.41	33.55	32.98	32.95	33.04	33.11	33.28	33.75	33.11	33.66	33.70	33.81	33.81	33.81
O ₂ Conv., %	94.77	94.78	94.78	94.79	94.80	94.84	94.84	94.78	94.77	94.83	94.82	94.82	94.82	94.82
C Balance, %	98.49	98.25	98.70	98.50	98.10	97.58	97.59	98.44	99.09	98.30	98.14	97.82	97.82	97.82
C ₂ Selectivity, %	33.40	40.59	40.88	40.79	40.87	40.77	40.86	42.59	42.63	42.64	42.64	42.57	42.57	42.57
C ₃ Selectivity, %	2.41	2.59	2.88	2.87	2.72	2.76	2.84	2.93	2.70	2.67	2.79	2.77	2.77	2.77
C ₂ Yield, %	10.00	13.38	13.30	13.24	13.25	13.17	13.27	14.15	13.99	14.11	14.10	14.08	14.08	14.08
Ethylene/Ethane	0.79	0.97	0.89	0.88	0.88	0.87	0.86	0.92	0.92	0.92	0.91	0.91	0.91	0.91
CO ₂ /CO	123.23	112.69	98.64	94.13	91.65	110.77	111.67	80.52	86.71	101.04	288.99	283.74	283.74	283.74

Table B.25. Methane Coupling Activity of 26 wt% Na₂CO₃/(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide): [Run 1] (Continued)

CATALYST: 20 wt% Na2CO3/(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)										NOTEBOOK: 9-KDC-X-46			
Weight (g): 4.003		Volume (cc): 4.1											
CH4/O2/N2: 2.04/1/3.69		Pressure (psig): 5											
Temperature (°C)	780	780	780	780	780	780	780	755	755	755	755	755	755
Flow (cc/min)	100	100	100	100	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463	1463
Time (h)	102	108	111	114	117	120	123	126	129	132	135	138	138
CH4 Conv., %	34.06	33.75	33.52	33.59	33.77	32.64	32.59	32.59	32.62	32.53	32.74	32.93	32.93
O2 Conv., %	94.79	94.78	94.78	94.80	94.80	94.79	94.78	94.79	94.79	94.80	94.80	94.80	94.80
C Balance, %	98.42	99.03	99.07	98.62	98.29	98.87	98.95	98.75	98.79	98.63	98.22	97.99	97.99
C2 Selectivity, %	43.58	42.99	43.16	43.28	43.05	40.65	40.53	40.58	40.58	40.70	40.68	40.37	40.37
C3 Selectivity, %	2.72	3.11	2.64	2.48	2.46	2.37	2.49	2.35	2.51	2.36	2.33	2.35	2.35
C2 Yield, %	14.61	14.37	14.33	14.34	14.29	13.12	13.07	13.06	13.08	13.06	13.08	13.03	13.03
Ethylene/Ethane	0.99	0.99	0.99	0.99	0.98	0.89	0.88	0.88	0.88	0.88	0.88	0.88	0.88
CO2/CO	88.22	85.31	65.13	62.08	61.50	82.10	95.53	73.95	85.14	71.70	70.28	80.04	80.04

Table B26. Methane Coupling Activity of 20 wt% Na₂CO₃/ (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide); [Run 2]

CATALYST: 20 wt% Na ₂ CO ₃ / (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)				NOTEBOOK: 9-KDC-X-55										
Weight (g): 4.001		Volume (cc): 4.7												
CH ₄ /O ₂ /N ₂ : 2.04/1/3.69		Pressure (psig): 5												
Temperature (°C)	580	580	580	580	580	580	580	580	580	580	580	580	580	580
Flow (cc/min)	100	100	100	100	100	100	100	100	100	100	100	100	100	100
GHSV (h ⁻¹)	1277	1277	1277	1277	1277	1277	1277	1277	1277	1277	1277	1277	1277	1277
Time (h)	1	3	4	5	6	7	8	9	10	11				
CH ₄ Conv., %	1.58	1.64	1.04	1.08	2.22	2.63	2.80	10.71	10.19	10.32				
O ₂ Conv., %	4.60	4.58	5.04	5.18	10.63	9.43	9.40	41.32	40.54	40.97				
C Balance, %	98.86	98.74	99.33	99.30	99.74	99.33	98.92	98.26	98.77	98.89				
C ₂ Selectivity, %	**	**	**	**	**	**	**	***	***	***				
C ₃ Selectivity, %	**	**	**	**	**	**	**	0.00	0.00	0.00				
C ₂ Yield, %	**	**	**	**	**	**	**	***	***	***				
Ethylene/Ethane	**	**	**	**	**	**	**	***	***	***				
CO ₂ /CO	**	**	**	**	**	**	**	623.10	676.38	1009.24				

** : Conversion too low for meaningful results.

*** : C₂'s too low for meaningful results.

Table B26. Methane Coupling Activity of 20 wt% Na₂CO₃/ (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide): [Run 2] (Continued)

CATALYST: 20 wt% Na ₂ CO ₃ / (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)			NOTEBOOK: 9-KDC-X-55		
Weight (g): 4.001	Volume (cc): 4.7				
CH ₄ /O ₂ /N ₂ : 2.04/1/3.69	Pressure (psig): 5				
Temperature (°C)	736	736	736	769	804
Flow (cc/min)	100	100	100	100	100
GHSV (h ⁻¹)	1277	1277	1277	1277	1277
Time (h)	13	23	24	26	27
CH ₄ Conv., %	34.92	31.95	31.81	33.32	32.85
O ₂ Conv., %	94.91	94.90	94.90	94.86	94.91
C Balance, %	99.22	100.40	100.39	100.50	100.65
C ₂ Selectivity, %	44.49	39.98	39.44	43.92	42.78
C ₃ Selectivity, %	2.74	2.79	2.61	3.00	2.68
C ₂ Yield, %	15.42	12.82	12.60	14.71	14.14
Ethylene/Ethane	1.22	0.87	0.86	1.03	0.97
CO ₂ /CO	110.08	117.93	129.73	96.05	99.79
			88.36	91.36	2.67
				2.12	2.03
				6.68	6.66
				6.31	6.42
				5.87	6.51
				0.76	0.73
				19.98	19.71
				100.26	99.93
				94.95	94.94
				33.34	33.84
				31.82	31.31
				94.90	94.90
				100.28	100.26
				20.27	19.71
				0.80	0.73
				6.73	6.66
				6.42	6.51
				2.03	1.95

Table B27 Methane Coupling Activity of 20 wt% Na₂CO₃/ (80 mole% Pr - 20 mole% Ce oxide)

NOTEBOOK: 8-KDC-X-33

CATALYST: 20 wt% Na₂CO₃/ (80 mole% Pr - 20 mole% Ce oxide)

	Weight (g): 10.012		Volume (cc): 14.9		Pressure (psig): 0			
	CH ₄ /O ₂ /N ₂ : Pure CH ₄							
	750	50	201	750	50	201	750	50
Temperature (°C)	750	50	201	750	50	201	800	800
Flow (cc/min)	50	50	201	150	150	201	50	50
GHSV (h-1)	201	201	201	604	604	201	201	201
Collection Interval (min)	0 - 2	2 - 5	0 - 2	2 - 5	0 - 2	2 - 5	2 - 5	5 - 10
CH ₄ Conv., %	27.00	15.27	16.96	0.29	32.93	1.83	1.03	
C ₂ Selectivity, %	46.90	38.45	58.84	**	36.27	88.10	**	**
C ₃ Selectivity, %	3.35	0.00	1.79	**	1.59	2.52	**	**
C ₂ Yield, %	12.66	5.87	9.98	**	11.95	1.61	**	**
Ethylene/Ethane	1.74	0.95	1.20	**	1.98	0.58	**	**
CO ₂ /CO	147.20	126.63	81.05	**	145.53	0.16	**	**

** : Conversion too low for meaningful results.

Table B27. Methane Coupling Activity of 20 wt% Na₂CO₃/ (80 mole% Pr - 20 mole% Ce oxide) (Continued)

NOTEBOOK: 8-KDC-X-33

CATALYST: 20 wt% Na₂CO₃/ (80 mole% Pr - 20 mole% Ce oxide)

Weight (g): 10.012		Volume (cc): 14.9	
CH ₄ /O ₂ /N ₂ : Pure CH ₄		Pressure (psig): 0	
Temperature (°C)	800	800	850
Flow (cc/min)	150	150	150
GHSV (h ⁻¹)	604	604	604
Collection Interval (min)	0 - 2	2 - 5	0 - 2
CH ₄ Conv., %	10.91	0.44	3.85
C ₂ Selectivity, %	51.67	**	64.61
C ₃ Selectivity, %	1.79	**	3.41
C ₂ Yield, %	5.64	**	0.56
Ethylene/Ethane	1.26	**	0.63
CO ₂ /CO	56.59	**	0.27

** : Conversion too low for meaningful results.

Table B28. Methane Coupling Activity of 20 wt % Na₂CO₃/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide)
[Sequential Mode: Run 1]

CATALYST: 20 wt % Na ₂ CO ₃ /(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide)										NOTEBOOK: 8-KDC-X-25	
Weight (g): 10.005		Volume (cc): 14.2		Pressure (psig): 0							
CH ₄ /O ₂ /N ₂ : Pure CH ₄											
Temperature (°C)		750	750	750	800	800	800	800	800	800	800
Flow (cc/min)		50	50	50	50	50	50	150	150	150	150
GHSV (h ⁻¹)		211	211	211	211	211	211	634	634	634	634
Collection Interval (min)		0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	5 - 10
CH ₄ Conv., %		44.52	9.48	1.45	60.88	6.14	1.47	16.02	1.15	0.95	0.95
C ₂ Selectivity, %		28.79	58.04	57.46	16.81	51.61	51.65	42.29	**	**	**
C ₃ Selectivity, %		1.16	1.63	0.00	0.92	2.77	1.57	1.77	**	**	**
C ₂ Yield, %		12.82	5.50	0.84	10.23	3.17	0.76	6.78	**	**	**
Ethylene/Ethane		2.17	1.27	0.56	2.65	1.31	0.99	1.68	**	**	**
CO ₂ /CO		799.79	54.54	6.10	853.25	15.85	0.87	89.65	**	**	**

** : Conversion too low for meaningful results.

Table B28. Methane Coupling Activity of 20 wt% Na₂CO₃/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide) (Continued)
[Sequential Mode: Run 1]

CATALYST: 20 wt% Na2CO3/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide)																	NOTEBOOK: 8-KDC-X-25		
Weight (g): 10.005		Volume (cc): 14.2																	
CH4/O2/N2: Pure CH4		Pressure (psig): 0																	
Temperature (°C)		850	850	850	750	750	750	750	750	750	750	750	750	750	700	700	700		
Flow (cc/min)		150	150	150	50	50	50	50	50	50	50	50	50	50	50	50	50		
GHSV (h-1)		634	634	634	211	211	211	211	211	211	211	211	211	211	211	211	211		
Collection Interval (min)		6-2	2-5	5-10	0-2	2-5	5-10	0-2	2-5	5-10	0-2	2-5	5-10	0-2	2-5	5-10	5-10		
CH4 Conv., %		14.42	6.62	2.59	28.31	8.24	2.78	15.39	1.71	34.30	11.89	6.14	78.78	38.24	69.31	2.91	2.06		
C2 Selectivity, %		30.40	32.62	15.05	44.16	67.40	69.37	66.95	80.03	38.24	69.31	78.78	78.78	38.24	69.31	2.91	2.06		
C3 Selectivity, %		1.77	1.60	0.30	2.60	2.62	1.55	78	0.90	2.18	2.91	2.06	2.06	2.18	2.91	2.06	2.06		
C2 Yield, %		4.38	2.16	0.39	12.50	5.56	1.93	10.30	1.36	13.12	8.24	4.84	4.84	13.12	8.24	2.91	2.06		
Ethylene/Ethane		2.03	1.70	1.03	2.37	1.36	0.71	1.35	0.41	1.88	1.21	0.83	0.83	1.88	1.21	1.21	1.21		
CO2/CO		35.84	5.76	0.08	205.67	22.95	4.63	45.67	2.89	62.94	38.22	15.33	15.33	62.94	38.22	38.22	15.33		

Table B28 Methane Coupling Activity of 20 wt% Na₂CO₃/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide) (Continued)
[Sequential Mode: Run 1]

CATALYST: 20 wt% Na ₂ CO ₃ /(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide)				NOTEBOOK: 8-KDC-X-25			
Weight (g): 10.005		Volume (cc): 14.2					
CH ₄ /O ₂ /N ₂ : Pure CH ₄		Pressure (psig): 0					
Temperature (°C)	700	700	700	650	650	650	600
Flow (cc/min)	150	150	150	50	50	150	50
GHSV (h ⁻¹)	6.1	634	634	211	211	634	211
Collection Interval (min)	0-2	2-5	5-10	0-2	2-5	5-10	0-2
CH ₄ Conv., %	9.70	6.03	4.74	12.39	4.16	2.16	6.17
C ₂ Selectivity, %	70.36	82.97	86.49	61.50	79.32	84.26	55.39
C ₃ Selectivity, %	1.98	1.38	1.23	2.96	1.18	0.44	0.92
C ₃ Yield, %	6.82	5.00	4.10	7.62	3.30	1.82	3.42
Ethylene/Ethane	0.71	0.53	0.48	0.81	0.40	0.17	0.25
CO ₂ /CO	20.86	11.70	***	156.24	45.31	25.03	20.72

***: CO too low for meaningful results.

Table B28. Methane Coupling Activity of 20 wt% Na₂CO₃/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide) (Continued)
[Sequential Mode: Run 1]

CATALYST: 20 wt% Na₂CO₃/(2.9 mole % Ag - 77.7 mole % Pr - 19.4 mole % Ce oxide) NOTEBOOK: 8-KDC-X-25

	Weight (g): 10.005		Volume (cc): 14.2									
	CH ₄ /O ₂ /N ₂ : Pure CH ₄		Pressure (psig): 0									
Temperature (°C)	600	600	600	600	900	900	900	900	900	900	900	900
Flow (cc/min)	50	150	150	150	50	50	50	50	150	150	150	150
GHSV (h-1)	211	634	634	634	211	211	211	211	634	634	634	634
Collection Interval (min)	5 - 10	0 - 2	2 - 5	2 - 5	0 - 2	2 - 5	2 - 5	5 - 10	0 - 2	0 - 2	2 - 5	2 - 5
CH ₄ Conv., %	5.56	2.76	2.41	2.41	33.34	6.68	9.19	16.19	16.19	16.19	4.92	4.92
C ₂ Selectivity, %	62.75	61.49	70.51	70.51	8.91	17.92	8.26	14.67	14.67	14.67	6.85	6.85
C ₃ Selectivity, %	1.12	0.27	0.33	0.33	0.53	1.03	0.25	0.70	0.70	0.70	0.48	0.48
C ₂ Yield, %	3.49	1.70	1.70	1.70	2.97	1.20	0.76	2.37	2.37	2.37	0.34	0.34
Ethylene/Ethane	0.24	0.13	0.12	0.12	3.17	2.46	1.79	2.26	2.26	2.26	0.05	0.05
CO ₂ /CO	166.22	13.51	***	***	20.11	0.38	0.08	7.25	7.25	7.25	0.10	0.10

***: CO too low for meaningful results.

Table B29. Methane Coupling Activity of 20 wt% Na₂CO₃/ (2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)
[Sequential Mode: Run 2]

CATALYST: 20 wt% Na2CO3/(2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide)																			NOTEBOOK: 8-KDC-X-37					
Weight (g): 9.4		Volume (cc): 2																						
CH4/O2/N2: Pure CH4		Pressure (psig): 0																						
Temperature (°C)		725	725	725	725	725	725	725	725	725	725	725	725	725	725	725	725	725						
Flow (cc/min)		150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150						
GHSV (h-1)		4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500						
Time (h)		0 - 2	2 - 5	5 - 10	2 - 5*	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2						
CH4 Conv., %		11.81	6.45	1.26	6.57	16.58	4.56	0.49	15.08	5.86	1.64	17.80	5.79	0.49	17.80	5.79	0.49	17.80						
C2 Selectivity, %		48.25	80.56	84.66	82.52	63.72	78.29	**	65.82	82.93	78.87	58.06	82.23	**	58.06	82.23	**	58.06						
C3 Selectivity, %		0.00	1.08	0.24	0.87	1.69	0.74	**	1.59	0.77	1.39	1.60	0.96	**	1.60	0.96	**	1.60						
C2 Yield, %		5.70	5.19	1.07	5.42	10.56	3.57	**	9.92	4.86	1.29	10.34	4.76	**	10.34	4.76	**	10.34						
Ethylene/Ethane		34.75	0.49	0.24	0.47	0.91	0.44	**	0.86	0.45	0.26	0.95	0.44	**	0.95	0.44	**	0.95						
CO2/CO		***	***	***	***	77.71	***	**	74.87	***	***	91.11	***	**	91.11	***	**	91.11						

*: Sample was ran the first time 40 minutes after taken then repeated 2.5 hours after sampling.

**: Conversion too low for meaningful results.

***: CO too low for meaningful results.

Table B29. Methane Coupling Activity of 20 wt% Na₂CO₃/(2.9 mole% Ag - 77.7 mole% Pt - 19.4 mole% Ce oxide) (Continued)
[Sequential Mode: Run 2]

CATALYST: 20 wt% Na2CO3/ (2.9 mole% Ag - 77.7 mole% Pt - 19.4 mole% Ce oxide)																			NOTEBOOK: 8-KDC-X-37				
Weight (g): 9.4		Volume (cc): 2																					
CH4/O2/N2: Pure CH4		Pressure (psig): 0																					
Temperature (°C)		725	725	725	725	725	725	725	725	725	725	725	725	725	725	725	725	725					
Flow (cc/min)		50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50					
GHSV (h-1)		1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500					
Time (h)		0 - 2	2 - 5	5 - 10	5 - 10	0 - 2	2 - 5	2 - 5	0 - 2	0 - 2	2 - 5	2 - 5	5 - 10	0 - 2	0 - 2	2 - 5	5 - 10	0 - 2					
CH4 Conv., %		51.37	5.38	1.10	1.10	50.15	5.77	17.37	8.05	2.41	2.41	12.74	3.62	2.83	14.96	4.36	200	200					
C2 Selectivity, %		24.20	91.23	**	**	23.92	91.99	61.24	77.84	85.43	85.43	66.77	83.74	84.96	64.21	85.20	**	**					
C3 Selectivity, %		1.05	1.87	**	**	1.23	1.55	1.80	1.11	0.35	0.35	1.63	0.60	0.29	1.57	0.62	**	**					
C2 Yield, %		12.43	4.91	**	**	11.99	5.31	10.63	6.27	2.06	2.06	8.51	3.03	2.41	9.61	3.72	**	**					
Ethylene/Ethane		1.82	0.81	**	**	1.45	0.95	1.06	0.65	0.33	0.33	0.87	0.37	0.31	0.80	0.36	**	**					
CO2/CO		188.80	***	**	**	***	***	91.57	***	***	***	54.86	***	***	63.29	***	***	**					

**: Conversion too low for meaningful results.

***: CO too low for meaningful results.

Table B30. Methane Coupling Activity of 20 wt% Na₂CO₃/Pr6O11
[Sequential Mode]

CATALYST: 20 wt% Na2CO3/Pr6O11			NOTEBOOK: 8-KDC-X-53		
Weight (g): 10.058		Volume (cc): 7.9			
CH4/O2/N2: Pure CH4		Pressure (psig): 0			
Temperature (°C)	800	800	800	800	850
Flow (cc/min)	50	50	50	150	50
GHSV (h-1)	380	380	380	1139	380
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5
CH4 Conv., %	78.43	16.06	1.54	30.33	26.18
C2 Selectivity, %	16.18	52.91	54.36	43.81	35.02
C3 Selectivity, %	1.06	3.20	1.72	2.81	2.31
C2 Yield, %	12.69	8.50	0.83	13.29	9.17
Ethylene/Ethane	3.85	1.70	0.70	2.08	2.25
CO2/CO	186.44	65.70	1.75	77.87	49.65

**: Conversion too low for meaningful results.

Table B30. Methane Coupling Activity of 20 wt% Na₂CO₃/Pr6O11 (Continued)
[Sequential Mode]

CATALYST: 20 wt% Na2CO3/ Pr6O11			NOTEBOOK: 8-KDC-X-53				
Weight (g): 10.058		Volume (cc): 7.9					
CH4/O2/N2: Pure CH4		Pressure (psig): 0					
Temperature (°C)	850	850	850	750	750	750	750
Flow (cc/min)	150	150	150	50	150	150	150
GHSV (h-1)	1139	1139	1139	380	1139	1139	1139
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	0 - 2	2 - 5
CH4 Conv., %	17.61	2.96	4.41	35.82	5.85	19.04	13.32
C2 Selectivity, %	37.47	24.28	10.35	69.11	67.12	79.68	81.94
C3 Selectivity, %	2.12	0.61	0.00	4.88	3.82	5.13	4.02
C2 Yield, %	6.60	0.72	0.46	24.76	3.93	15.17	10.92
Ethylene/Ethane	1.66	0.62	0.53	3.30	1.27	1.52	1.12
CO2/CO	23.52	0.40	0.20	31.94	19.55	45.03	19.00

***: CO too low for meaningful results.

Table B31. Evaluation of barium carbonate on alumina catalyst in Reactor 1.

Run Reference: 33NEK36

Catalyst: 33NEK34-1 4.77 wt% BaCO₃ on Al₂O₃ (Norton 5451,30/60 mesh)

Pressure, psig Inlet =22.6 Outlet =11.3

75 ppm ethyl chloride

Feed Composition (mole %)

Oxygen	5.97	6.00	5.98	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99
Nitrogen	0.74	0.77	0.75	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Methane	10.80	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81

HOS 0.75 2.25 3.75 5.25 6.75 8.25 9.75 11.25 12.75 14.25 15.75 17.25

Temp (°C) 750 750 750 750 750 750 750 750 750 750 750 750

GHSV(l/l/hr) 2224 2224 2224 2224 2224 2224 2224 2224 2224 2224 2224 2224

CH₄ Conv.,% 29.97 26.32 26.71 26.11 26.04 25.01 24.47 22.88 24.34 21.99 23.25 21.75

O₂ Conv.,% 72.75 68.88 66.89 65.03 63.83 61.94 60.69 58.95 58.42 56.23 55.97 54.39

C Balance,% 92.59 109.2 95.61 93.82 91.7 93.73 94.84 93.49 94.5 97.5 91.54 93.18

C₂ Sel.,% 18.44 12.29 18.67 20.36 22.04 20.43 19.45 22.75 18.97 18.49 23.36 23.10

C₃ Sel.,% 0.12 0.08 0.12 0.14 0.15 0.14 0.14 0.17 0.14 0.14 0.18 0.18

C₂ Yield,% 5.12 3.53 4.77 4.99 5.26 4.79 4.51 4.87 4.36 3.96 4.97 4.68

Ethene/Ethane 1.16 1.21 1.22 1.23 1.22 1.21 1.20 1.20 1.18 1.17 1.15 1.14

CO₂/CO 2.92 4.63 2.17 1.58 1.20 1.36 1.49 0.99 1.44 1.47 0.79 0.79

Table B31. Evaluation of barium carbonate on alumina catalyst in Reactor 1 (continued).

<u>Feed Composition (mole %)</u>												
Oxygen	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99
Nitrogen	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Methane	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81
HOS	18.75	20.25	21.75	23.25	24.75	26.25	27.75	29.25	30.75	32.25	33.75	35.25
Temp (°C)	750	750	750	750	750	750	750	750	750	750	750	750
GHSV(l/l/hr)	2224	2224	2224	2224	2224	2224	2224	2224	2224	2224	2224	2224
CH ₄ Conv.,%	22.33	22.71	21.1	20.46	20.27	20.51	20.62	20.28	19.51	19.8	19.15	19.42
O ₂ Conv.,%	53.83	53.73	51.65	50.5	49.7	48.86	48.53	47.53	46.47	46.26	45.54	45.33
C Balance,%	92.42	90.59	92.2	92.87	92.65	92.23	92.12	92.24	93.14	92.71	94.07	93.49
C ₂ Sel.,%	22.78	24.64	24.47	24.31	24.66	24.64	24.41	24.65	24.38	24.2	22.92	23.21
C ₃ Sel.,%	0.18	0.20	0.21	0.21	0.21	0.21	0.21	0.22	0.22	0.22	0.21	0.21
C ₂ Yield,%	4.70	5.07	4.76	4.62	4.63	4.66	4.64	4.61	4.43	4.44	4.13	4.21
Ethene/Ethane	1.13	1.12	1.11	1.10	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.02
CO ₂ /CO	0.82	0.60	0.60	0.55	0.51	0.52	0.55	0.52	0.50	0.59	0.56	0.59

Table B31. Evaluation of barium carbonate on alumina catalyst in Reactor 1. (continued).

Feed Composition (mole%)

Oxygen	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99
Nitrogen	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Methane	10.81	10.81	10.81	10.81	10.81	10.81	10.81	10.81

HOS	36.75	38.25	39.75	41.25	42.75	44.25	45.75	47.25
Temp (°C)	750	750	750	750	750	750	750	750
GHSV(l/l/hr)	2224	2224	2224	2224	2224	2224	2224	2224

CH4 Conv.,%	17.85	15.04	18.23	19.27	99.47	17.23	20.11	19.73
O2 Conv.,%	43.93	42.26	43.1	43.39	95.51	41.92	45.94	45.44

C Balance, %	95.25	99.33	95.91	93.93	2.402	96.2	94.04	94.51
--------------	-------	-------	-------	-------	-------	------	-------	-------

C2 Sel.,%	23.09	21.61	20.98	21.83	13.25	21.48	22.30	21.94
C3 Sel.,%	0.21	0.20	0.20	0.20	0.13	0.21	0.21	0.21
C2 % Yield	3.93	3.23	3.67	3.95	0.32	3.56	4.22	4.09

Ethene/Ethane	1.01	1.03	1.01	1.00	1.00	0.99	1.05	1.04
CO2/CO	0.60	0.62	0.79	0.72	0.30	0.72	0.78	0.77

Table B32. Evaluation of barium carbonate on alumina catalyst in Reactor 2.

Run Reference: 33NEK38

Catalyst: 33NEK34-1 4.77 wt% BaCO₃ on Al₂O₃, Norton SA5451,30/60 mesh

Pressure, psig Inlet =17.3 Outlet =10.9

92 ppm ethyl chloride

Feed Composition (mole%)

Oxygen	5.95	5.91	5.93	5.92	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93
Nitrogen	0.93	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
Methane	11.21	11.20	11.21	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20

HOS	0	1.5	3	4.5	6	7.5	9	10.5	12	13.5	15	16.5
-----	---	-----	---	-----	---	-----	---	------	----	------	----	------

Temp (°C)	750	750	750	750	750	750	750	750	750	750	750	750
-----------	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

GHSV(l/l/hr)	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228
--------------	------	------	------	------	------	------	------	------	------	------	------	------

CH ₄ Conv.,%	26.89	32.66	28.98	26.76	25.33	23.69	24.87	23.93	23.85	22.77	21.46	21.95
-------------------------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

O ₂ Conv.,%	93.58	82.73	70.75	63.86	59.13	55.29	54.13	52.23	51.28	49.88	48.64	47.81
------------------------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

C Balance, %	99.01	104.98	95.68	94.19	91.84	95.69	90.46	90.95	90.95	92.03	93.26	93.02
--------------	-------	--------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

C ₂ Sel.,%	30.93	17.64	26.99	30.97	36.75	31.80	37.91	38.11	37.32	36.69	36.57	34.80
-----------------------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

C ₃ Sel.,%	0.33	0.20	0.32	0.37	0.46	0.41	0.51	0.53	0.53	0.36	0.00	0.35
-----------------------	------	------	------	------	------	------	------	------	------	------	------	------

C ₂ Yield, %	8.23	6.05	7.48	7.81	8.55	7.21	8.53	8.29	8.10	7.69	7.32	7.11
-------------------------	------	------	------	------	------	------	------	------	------	------	------	------

Ethene/Ethane	1.51	1.43	1.34	1.31	1.28	1.26	1.23	1.22	1.19	1.18	1.16	1.15
---------------	------	------	------	------	------	------	------	------	------	------	------	------

CO ₂ /CO	3.97	6.70	2.46	1.54	0.81	1.14	0.61	0.58	0.57	0.57	0.58	0.61
---------------------	------	------	------	------	------	------	------	------	------	------	------	------

Table B32. Evaluation of barium carbonate on alumina catalyst in Reactor 2 (continued).

Feed Composition (mole%)												
Oxygen	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93
Nitrogen	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
Methane	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20
HOS	18	19.5	21	22.5	24	25.5	27	28.5	30	31.5	33	34.5
Temp (°C)	750	750	750	750	750	750	750	750	750	750	750	750
GHSV(l/l/hr)	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228	2228
CH ₄ Conv.,%	20.92	21.68	14.70	16.58	21.97	23.21	20.93	21.88	21.50	21.06	21.50	21.89
O ₂ Conv.,%	46.94	46.95	51.53	47.73	48.62	48.33	46.76	46.88	46.28	45.53	45.48	45.28
C Balance, %	95.01	93.57	104.48	98.66	92.62	92.17	95.02	93.38	94.05	93.82	93.27	93.01
C ₂ Sel.,%	32.43	32.97	32.54	36.72	34.75	31.72	30.58	31.26	30.46	31.59	31.51	30.54
C ₃ Sel.,%	0.33	0.34	0.47	0.37	0.36	0.34	0.33	0.34	0.34	0.36	0.36	0.35
C ₂ Yield, %	6.44	6.69	5.00	6.01	7.07	6.78	6.08	6.39	6.16	6.24	6.32	6.22
Ethene/Ethane	1.13	1.13	1.26	1.18	1.16	1.15	1.14	1.13	1.12	1.11	1.10	1.10
CO ₂ /CO	0.85	0.76	0.91	0.53	0.59	0.79	0.84	0.80	0.69	0.77	0.77	0.73

Table B32. Evaluation of barium carbonate on alumina catalyst in Reactor 2 (continued).

Feed Composition (mole%)								
Oxygen	5.93	5.93	5.93	5.93	5.93	5.93	5.93	5.93
Nitrogen	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
Methane	11.20	11.20	11.20	11.20	11.20	11.20	11.20	11.20
HOS	36	37.5	39	40.5	42	43.5	45	46.5
Temp (°C)	750	750	750	750	750	750	750	750
GHSV(l/l/hr)	2228	2228	2228	2228	2228	2228	2228	2228
CH4 Conv.,%	21.61	21.64	18.97	20.06	21.97	19.59	16.58	18.74
O2 Conv.,%	45.10	44.24	43.35	42.90	44.03	50.14	44.17	44.59
C Balance, %	93.18	93.03	96.21	94.58	92.56	95.42	98.66	95.68
C2 Sel.,%	30.61	30.49	30.08	30.18	31.33	36.68	34.65	34.96
C3 Sel.,%	0.35	0.36	0.36	0.18	0.20	0.40	0.40	0.41
C2 Yield, %	6.16	6.14	5.49	5.72	6.37	6.86	5.67	6.27
Ethene/Ethane	1.09	1.09	1.08	1.07	1.06	1.16	1.11	1.10
CO2/CO	0.75	0.75	0.74	0.76	0.77	0.60	0.57	0.59

Case A1.1b - Nitrogen Diluent

Table B33. Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMpppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H2			0.6	0.3		0.3		2.2		2.2
N2	2.4	2082.9	3260.2	3260.2		3260.2		3260.2		3260.2
O2		629.2	629.2							
CO			35.3	91.6		91.6		91.7		91.7
CO2	1.0		1.0	275.9		275.9		275.8		
CH4	338.2		630.8	351.4		351.4		353.1		353.1
C2H4			2.5	97.5		97.5		124.0		124.0
C2H6	3.4		3.7	32.1		32.1		58.0		58.0
C3H6				5.4		5.4		8.1		8.1
C3H8				1.8		1.8		1.9		1.9
C4s +								1.6		1.6
H2O				447.3	374.1	73.2	64.4	10.3		
Total	345.0	2712.1	4563.3	4563.5	374.1	4189.4	64.4	4186.9	286.1	3900.8

Component	11	12	13	14	15	16	17	18	19	20	21
H2	0.6	1.6							1.9		1.9
N2	1174.9	2085.2									
O2											
CO	35.3	56.3							0.1		0.1
CO2											
CH4	292.6	60.6							1.7		1.7
C2H4	2.5		121.5		121.5	121.0	0.5		26.6		26.6
C2H6	0.4		57.7	0.1	57.6	0.1	57.5		25.9		25.9
C3H6			8.1	5.9	2.2		2.2		2.7		2.7
C3H8			1.9	1.5	0.4		0.4		0.1		0.1
C4s +			1.6	1.6					1.6		1.6
H2O								10.8	10.7	8.0	2.7
Total	1506.3	2203.7	190.8	9.1	181.7	121.1	60.6	10.8	71.3	8.0	63.3

Table B34. Methane Coupling System Investment
Nitrogen Diluent Cases

	<u>Case A1.1d</u> <u>CH4/O2=1</u>	<u>Case A1.1b</u> <u>CH4/O2=2</u>	<u>Case A1.1c</u> <u>CH4/O2=4</u>
Coupling Reaction System	203.0	130.5	111.3
Steam Cracking System	20.5	25.2	30.3
Compression System	119.2	149.1	128.3
Acid Gas Removal System	30.6	30.6	23.6
Cold Box System	58.2	48.6	70.8
Refining System	30.6	31.0	31.5
Refrigeration System	30.5	39.4	54.4
Acetylene Hydrogenation System	1.3	1.4	1.4
Air Compression System	115.0	65.5	48.8
Total ISBL Investment	\$608.9MM	\$521.3MM	\$500.4MM

All Figures are $\pm 25\%$ for a Unit producing 1,000 MMpppy of ethylene.

28-Nov-89
JLMatherne

Table B35. Methane Coupling Economics
Nitrogen Diluent Cases

	Case A1.1d CH4/O2=1			Case A1.1b CH4/O2=2			Case A1.1c CH4/O2=4		
	Price \$/Unit	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr	Value \$MM/Yr
Investment									
ISBL		1000	609	1000	521	1000	500		
Oxygen Plant		0	0	0	0	0	0		
OSBL			100		92		90		
Total Fixed Investment			709		613		590		
Working Capital			29		23		22		
Total Utilized Investment			738		636		612		
Ethylene Sales	\$0.320	1000	320	1000	320	1000	320		
Variable Cost									
Methane, Lb	\$0.049	3892	190	2847	139	2508	123		
Ethane, Lb	\$0.064								
By-Product Credit									
Fuel Gas, MMBTU	\$2.050	0	0	0	0	0	0		
Propylene, Lb	\$0.205	39	-8	49	-10	80	-16		
Propane, Lb	\$0.077	1	0	12	-1	23	-2		
Crude C4s +, Lb	\$0.139	1	0	13	-2	16	-2		
Total By-Product Sales			-8		-13		-20		
Utilities, MMBTU	\$2.050	5	10	11	23	16	34		
Catalyst & Chemicals			1		1		1		
Total Variable Cost			193		151		137		
Fixed Cost			53		46		45		
Total Cash Cost			246		197		181		
Operating Income			74		123		139		
Depreciation (10%)			71		61		59		
NIAT (37% Tax Rate)			2		39		50		
ROIAT			0%		6%		8%		

Case A1.2a - Methane Diluent

Table B36. Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMpppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H2			3.9	1.9		1.9		4.1		4.1
N2	1.6	4.3	117.0	117.0		117.0		117.0		117.0
O2		187.6	187.6			0.0				
CO			5.6	5.9		5.9		5.9		5.9
CO2	0.7		0.7	27.8		27.8		27.8		
CH4	228.1		1626.2	1464.8		1464.8		1466.6		1466.6
C2H4			2.8	94.9		94.9		124.3		124.3
C2H6	2.3		2.5	35.4		35.4		64.2		64.2
C3H6				6.9		6.9		9.7		9.7
C3H8				2.8		2.8		2.9		2.9
C4s +								1.8		1.8
H2O				189.0	139.8	49.2	44.3	6.4		
Total	232.7	191.9	1946.3	1946.4	139.8	1806.6	44.3	1830.7	34.2	1796.5

Component	11	12	13	14	15	16	17	18	19	20	21
H2	3.9	0.2							2.1		2.1
N2	111.1	5.8									
O2											
CO	5.6	0.3							0.1		0.1
CO2											
CH4	1398.1	68.4							1.9		1.9
C2H4	2.8		121.5		121.5	121.0	0.5		29.5		29.5
C2H6	0.2		64.0	0.1	63.9	0.1	63.8		28.8		28.8
C3H6			9.7	7.5	2.2		2.2		2.8		2.8
C3H8			2.9	2.4	0.5		0.5		0.1		0.1
C4s +			1.8	1.8					1.8		1.8
H2O								11.8	11.8	8.9	2.9
Total	1521.7	74.7	199.9	11.8	188.1	121.1	67.0	11.8	78.9	8.9	70.0

Table B37. Methane Coupling System Investment
Methane Diluent Cases

	Case A1.2a <u>Rx O2 = 11%</u>	Case A1.2b <u>Rx O2 = 5%</u>
Coupling Reaction System	86.8	115.9
Steam Cracking System	28.1	28.0
Compression System	80.7	118.4
Acid Gas Removal System	13.6	21.9
Cold Box System	44.9	64.8
Refining System	30.7	30.7
Refrigeration System	45.1	59.4
Acetylene Hydrogenation System	1.4	1.4
Total ISBL Investment	\$331.3MM	\$440.5MM

All Figures are $\pm 25\%$ for a Unit producing 1,000 MMpppy of ethylene.

28-Nov-89
JLMatherne

Table B38. Methane Coupling Economics
Methane Diluent Cases

<u>Methane Diluent Cases</u>			Case A1.2a	Case A1.2b	
			<u>O2 = 11%</u>	<u>O2 = 5%</u>	
	Price \$/Unit	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr	Value \$MM/Yr
Investment					
ISBL		1000	330	1000	439
Oxygen Plant		3297	62	2280	50
OSBL			83		110
Total Fixed Investment			475		599
Working Capital			16		19
Total Utilized Investment			491		618
Ethylene Sales	\$0.320	1000	320	1000	320
Variable Cost					
Methane, Lb	\$0.049	2185	107	1941	95
Ethane, Lb	\$0.064				
By-Product Credit					
Fuel Gas, MMBTU	\$2.050	14	-28	12	-25
Propylene, Lb	\$0.205	62	-13	62	-13
Propane, Lb	\$0.077	20	-2	20	-2
Crude C4s +, Lb	\$0.139	15	-2	15	-2
Total By-Product Sales			-44		-41
Utilities, MMBTU	\$2.050	13	27	26	54
Catalyst & Chemicals			1		1
Total Variable Cost			90		108
Fixed Cost			37		45
Total Cash Cost			127		154
Operating Income			193		166
Depreciation (10%)			47		60
NIAT (37% Tax Rate)			92		67
ROIAT			19%		11%

28-Nov-89
JLMatherne

Table B39. Methane Coupling Process Material Balance Case A1.3b - Steam Diluent

Mlb/hr for a process producing 1,000MMpppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10	11
H2				3.1	1.6		1.6		3.5		3.5
N2	2.1	15.2		172.7	172.7		172.7		172.7		172.7
O2		665.5		665.5							
CO				122.3	135.4		135.4		135.4		135.4
CO2	0.9			0.9	344.5	1.4	343.1		343.1	343.1	
CH4	305.4			630.4	350.3	0.1	350.2		351.9		351.9
C2H4				13.0	108.2	0.1	108.1		134.5		134.5
C2H6	3.1			4.2	32.6		32.6		58.4		58.4
C3H6					5.4		5.4		8.1		8.1
C3H8					1.8		1.8		1.9		1.9
C4s +									1.6		1.6
H2O								18.7	5.3	5.3	
Total	311.5	680.7	2034.0	3646.1	3646.2	2472.8	1173.4	18.7	1216.4	348.4	868.0

Component	12	13	14	15	16	17	18	19	20	21	22
H2	3.1	0.4							1.9		1.9
N2	155.4	17.3									
O2											
CO	122.3	13.2							0.1		0.1
CO2											
CH4	325.0	27.0							1.7		1.7
C2H4	13.0	0.1	121.5		121.5	121.0	0.5		26.4		26.4
C2H6	1.2		57.2	0.1	57.1	0.1	57.0		25.8		25.8
C3H6			8.1	5.9	2.2		2.2		2.7		2.7
C3H8			1.9	1.5	0.4		0.4		0.1		0.1
C4s +			1.6	1.6					1.6		1.6
H2O								10.7	10.6	8.0	2.6
Total	620.0	58.0	190.3	9.1	181.2	121.1	60.1	10.7	70.9	8.0	62.9

Table B40. Methane Coupling System Investment
Steam Diluent Cases

	Case A1.3d <u>CH4/O2=1</u>	Case A1.3b <u>CH4/O2=2</u>	Case A1.3c <u>CH4/O2=4</u>
Coupling Reaction System	176.9	129.6	108.0
Steam Cracking System	19.9	25.0	29.6
Compression System	54.5	47.7	62.2
Acid Gas Removal System	16.1	13.0	14.8
Cold Box System	23.5	26.2	31.8
Refining System	30.3	31.0	32.6
Refrigeration System	32.6	38.3	45.4
Acetylene Hydrogenation System	1.3	1.4	1.4
Total ISBL Investment	\$355.1MM	\$312.2MM	\$325.8MM

All Figures are $\pm 25\%$ for a Unit producing 1,000 MMpppy of ethylene.

28-Nov-89
JLMatherne

Table B41. Methane Coupling Economics
Steam Diluent Cases

	Case A1.3d CH4/O2=1		Case A1.3b CH4/O2=2		Case A1.3c CH4/O2=4	
	Price \$/Unit	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr	Value \$MM/Yr	Volume Units/Yr
Investment						
ISBL		1000	354	1000	311	1000
Oxygen Plant		14530	144	8088	103	5907
OSBL			90		82	
Total Fixed Investment			588		496	
Working Capital			35		24	
Total Utilized Investment			623		520	
Ethylene Sales	\$0.320	1000	320	1000	320	1000
Variable Cost						
Methane, Lb	\$0.049	3562	174	2570	126	2375
Ethane, Lb	\$0.064					
By-Product Credit						
Fuel Gas, MMBTU	\$2.050	3	-7	5	-11	8
Propylene, Lb	\$0.205	39	-8	49	-10	81
Propane, Lb	\$0.077	10	-1	12	-1	23
Crude C4s +, Lb	\$0.139	10	-1	13	-2	16
Total By-Product Sales			-17	26	-24	19
Utilities, MMBTU	\$2.050	42	85		53	
Catalyst & Chemicals			1		1	
Total Variable Cost			243		156	
Fixed Cost			44		38	
Total Cash Cost			287		194	
Operating Income			33		126	
Depreciation (10%)			59		50	
NIAT (37% Tax Rate)			-17		48	
ROIAT			-3%		9%	
			170			

28-Nov-89 JL Matherne

Table B42. Methane Coupling Process Material Balance Case A1.4b - Sequential Feed

Mlb/hr for a process producing 1,000MMpppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10	11
H ₂		3.3			1.7		1.7		3.6		3.6
N ₂	2.0	93.6	1178.8	1170.6	101.8		101.8		101.8		101.8
O ₂			356.1								
CO		68.4			75.9		75.9		76.0		76.0
CO ₂	0.9	0.9			119.8		119.8		119.7		
CH ₄	287.2	930.4			707.9		707.9		709.6		709.6
C ₂ H ₄		1.8			95.9		95.9		123.3		123.3
C ₂ H ₆	2.9	3.0			33.0		33.0		59.8		59.8
C ₃ H ₆					9.0		9.0		11.7		11.7
C ₃ H ₈					3.1		3.1		3.2		3.2
C ₄ s +					18.8		18.8		20.5		20.5
H ₂ O					298.8	270.3	28.5	26.1	3.9	3.9	
Total	293.0	1101.4	1534.9	1170.6	1465.7	270.3	1195.4	26.1	1233.1	123.6	1109.5

Component	12	13	14	15	16	17	18	19	20	21	22
H ₂	3.3	0.4							2.0		2.0
N ₂	91.6	10.1									
O ₂											
CO	68.4	7.6							0.1		0.1
CO ₂											
CH ₄	643.2	66.2							1.8		1.8
C ₂ H ₄	1.8		121.5		121.5	121.0	0.5		27.4		27.4
C ₂ H ₆	0.1		59.7	0.2	59.5	0.1	59.4		26.8		26.8
C ₃ H ₆			11.7	9.5	2.2		2.2		2.7		2.7
C ₃ H ₈			3.2	2.9	0.3		0.3		0.1		0.1
C ₄ s +			20.5	20.5					1.7		1.7
H ₂ O								11.1	11.0	8.3	2.7
Total	808.4	84.3	216.6	33.1	183.5	121.1	62.4	11.1	73.6	8.3	65.3

Table B43. Methane Coupling System Investment
Sequential Feed Cases

	<u>Case A1.4c</u> <u>CII4/O2=2</u>	<u>Case A1.4b</u> <u>CII4/O2=5</u>	<u>Case A1.4d</u> <u>CII4/O2=7</u>	<u>Case A1.4e</u> <u>CII4/O2=10</u>
Coupling Reaction System	112.5	95.4	99.7	104.4
Steam Cracking System	26.6	26.0	25.9	25.8
Compression System	70.9	77.0	84.9	93.7
Acid Gas Removal System	15.3	13.7	15.6	16.9
Cold Box System	39.1	51.4	52.3	58.3
Refining System	30.5	30.5	30.5	30.5
Refrigeration System	46.9	48.7	51.6	54.8
Acetylene Hydrogenation System	1.4	1.4	1.4	1.4
Air Compression System	75.4	35.8	31.9	26.7
Total ISBL Investment	\$418.6MM	\$379.9MM	\$393.8MM	\$412.5MM

All Figures are $\pm 25\%$ for a Unit producing 1,000 MMpppy of ethylene.

28-Nov-89
JLMatherne

Appendix C. FIGURES

Figure C1. IR Reactor System

Figure C2. Vapor Phase Quartz Reactor

Figure C3. IR Ovens in Series

Heavy cast aluminum construction
Ovens containing four reflector
array with lamps

Figure C4. Reactor System, NEK Laboratory

Figure C5. Valco Valves for simultaneous injection of one gas stream onto two GC columns.

Figure C6. BaCO₃/TiO₂, 33-BKW-85

Figure C7. BaCO₃/TiO₂, 33-BKW-85, Rates to Products

Figure C8. BaCO₃ Catalysts on Al₂O₃ (33-BKW-74) and TiO₂ (33-BKW-85)

Times are shown for 33-BKW-85. Add 317.1 to these times for the times for 33-BKW-74.

Figure C9. BaCO₃ Catalysts on Al₂O₃ (33-BKW-74) and TiO₂ (33-BKW-85)

Times are shown for 33-BKW-85. Add 317.1 to these times for the times for 33-BKW-74.

Figure C10. 17% BaCO₃/TiO₂, 33-BKW-114

Figure C11. 5% BaCO₃/TiO₂, 33-BKW-115

Figure C12. Effect of Space Velocity on Methane Coupling Over a BaCO₃/TiO₂ Catalyst

Figure C13. $\text{SrCO}_3/\text{Al}_2\text{O}_3$, 34-BKW-18

Figure C14. $\text{SrCl}_2/\text{Al}_2\text{O}_3$, 34-BKW-19

Figure C15. Relative Rates to Products
SrCO₃/Al₂O₃, 34-BKW-18

Figure C16. 34-BKW-1

Figure C17. 34-BKW-2

Figure C18. Temperature profiles of tubular furnaces.

Figure C19. Methane Coupling Process Simplified Block Diagram
Case A1.1 - Nitrogen Diluent

Figure C20. Methane Coupling Process Simplified Block Diagram
Case AL2 - Methane Diluent

Figure C21. Methane Coupling Process Simplified Block Diagram
Case A1.3 - Steam Diluent

Figure C22. Methane Coupling Process Simplified Block Diagram
Case A1.4 - Sequential Feed

Figure C23. Results of Methane Coupling Sensitivity Studies

Figure C24. Results of Methane Coupling Sensitivity Studies

Appendix D. CATALYST COMPOSITIONS AND PREPARATION PROCEDURES

Ref. (Reactor)	Catalyst	Wt. % Components	Moles/g Support	g/cc Catalyst	Mesh Prepared	Reference of Preparation	Date Run	Wt. % Metals	Preparation Procedure	g Support or g Cat.
33-BKW-81(R#4)	BaCl ₂ / Al ₂ O ₃ , Norton SA5451 (850 °C, 4 hrs)	5.033	0.000254	1.11	60/100	33-BKW-79A	3/30/89	3.5	A(*)	(* 6 g of 31-BKW-48F)
33-BKW-85(R#4)	BaCO ₃ / TiO ₂ , Norton 88-55-004 (850 °C, 4 hrs)	4.77	0.000254	1.32	30/100	33-BKW-79B(#1)	4/4/89	3.49	B#4(*)	(* 24 g of 33-BKW-79B)
33-BKW-91(R#3)	BaCO ₃ / TiO ₂ , Norton 88-55-004 (850 °C, 4 hrs)	16.7	0.001	1.32	30/100	33-BKW-79C(#1)	4/18/89	13.95	B#4(*)	(* 24 g of 33-BKW-79C)
33-BKW-101(R#4)	33-BKW-85(R#4) - Used catalyst									
33-BKW-114(R#3)	BaCO ₃ / TiO ₂ (850 °C, 4 hrs)	16.7	0.001	1.61	3/60	33-BKW-107B	4/28/89	13.95	B#3	18
33-BKW-115(R#4)	BaCO ₃ / TiO ₂ (850 °C, 4 hrs)	4.77	0.000254	1.61	30/60	33-BKW-107A	4/28/89	3.49	B#3	18
33-BKW-120(R#3)	Ag / BaCO ₃ (800 °C, 4 hrs)	16.9		1.22	30/60	33-BKW-119	5/5/89	20.33	Z	15.64
33-BKW-121(R#4)	50/50 BaCl ₂ / BaCO ₃ mixture (850 °C, 2 hrs)	99.999, 99.997		2.375	30/100	33-BKW-15A	5/5/89		B#2 (melted when calcined)	
34-BKW-1(R#3)	32-BKW-63(R#4) - used catalyst			1.33	60/100		5/16/89			
34-BKW-2(R#4)	32-BKW-63(R#4) - used catalyst			1.33	60/100		5/16/89			
34-BKW-6(R#3)	Pr(NO ₃) ₃ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	0.307, 20	0.000007	1.22	30/60	33-BKW-136A(#1)	5/19/89	0.133, 25.0	Y + A	(* 6 g of 33-BKW-87)
34-BKW-7(R#4)	Pr(NO ₃) ₃ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	0.031, 20	0.000007	1.22	30/60	33-BKW-136B(#1)	5/19/89	0.013, 25.0	Y + A	(* 6 g of 33-BKW-87)
34-BKW-10(R#3)	Bi(NO ₃) ₃ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	0.23, 20	0.0000047	1.22	30/60	33-BKW-136C(#1)	5/23/89	0.133, 25.0	Y + A#5	(* 6 g of 33-BKW-87)
34-BKW-11(R#4)	Ba(NO ₃) ₂ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	0.19, 20	0.0000072	1.22	30/60	33-BKW-136D(#1)	5/23/89	0.133, 25.0	Y + A	(* 6 g of 33-BKW-87)
34-BKW-14(R#3)	Ba(NO ₃) ₂ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	1.87, 20	0.0000728	1.22	30/60	33-BKW-136E(#1)	5/23/89	1.36, 25.0	Y + A#5	(* 6 g of 33-BKW-87)
34-BKW-15(R#4)	KNO ₃ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	2.52, 20	0.000255	1.22	30/60	33-BKW-136F(#1)	5/23/89	1.36, 25.0	Y + A	(* 6 g of 33-BKW-87)
34-BKW-18(R#3)	SnCO ₃ / Al ₂ O ₃ , Norton SA5451 (850 °C, 4 hrs)	6.97	0.000508	1.25	60/100	34-BKW-16A(#1)	5/26/89	4.45	B(*)	(* 6 g of 34-BKW-16A)
34-BKW-19(R#4)	SnCl ₂ ·6H ₂ O / Al ₂ O ₃ , SA5451 (850 °C, 4 hrs)	11.94	0.0005086	1.14	60/100	34-BKW-16B	5/26/89	4.45	A(*)	(* 6 g of 31-BKW-122H#1)
34-BKW-32(R#3)	Ag / Al ₂ O ₃ , Norton SA5451 (800 °C, 4 hrs)	20		1.22	30/60	33-BKW-87A	6/16/89	25	Y	
34-BKW-37(R#4)	BaCl ₂ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	5.29, 19.2	0.000268	1.32	30/60	34-BKW-24A(#1)	6/21/89	4.83, 23.76	Y + A	(* 5 g of 33-BKW-87)
34-BKW-44(R#3)	BaCl ₂ , La ₂ O ₃ , Ag / Al ₂ O ₃ , SA5451 (800 °C, 4 hrs)	5.29, 0.43, 19.2	0.00268, 0.0000134	1.32	30/60	34-BKW-24D(#1)	6/21/89	4.83, 0.485, 23.76	Y + B#1	(* 6 g of 34-BKW-23)
34-BKW-45(R#4)	CaCl ₂ ·xH ₂ O, Ag / Al ₂ O ₃ , Norton SA5451	5.29, 4.18, 19.2	0.00268, 0.000134	1.32	30/60	34-BKW-24C(#1)	6/21/89	4.84, 4.91, 23.76	Y + B#1	(* 6 g of 34-BKW-23)
34-BKW-50(R#3)	BaCl ₂ , Ag / Al ₂ O ₃ , SA5502 (800 °C, 4 hrs)	5.29, 19.13	0.000268	1.32	30/60	34-BKW-41C	6/23/89	1.411, 23.76	Y + A	(* 6 g of 34-BKW-23)
34-BKW-51(R#4)	BaCl ₂ , La ₂ O ₃ , Ag / Al ₂ O ₃ , SA5502 (800 °C, 4 hrs)	5.29, 19.13	0.000268	1.22	30/60	34-BKW-41B(#1)	6/26/89	4.90, 10.05	X + A	(* 6 g of 30-BKW-115)
34-BKW-59(R#3)	SnCO ₃ / Al ₂ O ₃ , SA5451 (850 °C, 4 hrs)	6.97	0.000508	1.25	30/60	34-BKW-57A(#1)	7/7/89	4.91, 4.96, 10.05	X + B#1	(* 6 g of 30-BKW-115)
34-BKW-61(R#4)	BaCO ₃ / Al ₂ O ₃ , SA5451 (850 °C, 4 hrs)	9.107	0.000508	1.25	30/60	34-BKW-57B(#1)	7/7/89	4.45	B#3(*)	(* 3.5 g of 34-BKW-57A)
34-BKW-63(R#3)	BaCO ₃ / Al ₂ O ₃ , SA5451 (850 °C, 4 hrs)	9.107	0.000508	1.25	30/60	34-BKW-57B(#2)	7/11/89	6.98	B#3(*)	(* 3.5 g of 34-BKW-57B)

A) The loading of the catalyst is expressed as wt. % support (e.g. Al₂O₃, Ga₂O₃).

B) Mesh size shown refers to the mesh size of the catalyst when prepared and is not necessarily that which was run.

C) Refer to the Experimental Section and appropriate Appendices for descriptions of preparation procedures in the Catalyst Preparation column.

E) Grams/cc shown refers to the measured grams/cc of catalyst at the beginning of each run and after catalyst preparation.

F) Listed below are catalyst preparations referred to in the last column.

30-BKW-123	Ag / Al ₂ O ₃ , Norton SA5502	9.13		1.14	cylindrical	30-BKW-115	6/16/88	10.05	X	300
	BaCl ₂ / Al ₂ O ₃ , Norton SA5451	5.033	0.000254	1.09	60/100	31-BKW-48F		3.5	A	15
	SnCl ₂ ·6H ₂ O / Al ₂ O ₃ , Norton SA5451	11.94	0.0005086	1.09	60/100	31-BKW-122H(#1)		4.45		15
32-BKW-63(R#4)	BaCO ₃ / Al ₂ O ₃ , Norton SA5451	4.77	0.000254	1.09	60/100	32-BKW-20H	11/1/88	3.49	B	15
	BaCO ₃ / TiO ₂ , SN-88-55-004	4.77	0.000254		30/100	33-BKW-79B		3.49	B#4	24
33-BKW-91	BaCO ₃ / TiO ₂ , SN-88-55-004	16.7	0.001		30/100	33-BKW-79C		13.95	B#4	24
	Ag / Al ₂ O ₃ , Norton SA5451	20		1.28	30/60	33-BKW-87		25	Y	50
34-BKW-18	SnCO ₃ / Al ₂ O ₃ , Norton SA5451	6.97	0.000508		60/100	34-BKW-16A		4.45	B	15
	Ag / Al ₂ O ₃ , Norton SA5451	19.2		1.28	30/60	34-BKW-23		23.76	Y	50
34-BKW-59	SnCO ₃ / Al ₂ O ₃ , Norton SA5451	6.97	0.000508		30/60	34-BKW-57A		4.45	B#3	10
34-BKW-63	BaCO ₃ / Al ₂ O ₃ , Norton SA5451	9.107	0.000508		30/60	34-BKW-57B		6.98	B#3	10

Appendix E. CATALYST PREPARATION PROCEDURES

General Procedures

Procedure A

In Procedure A, supported catalysts are prepared using the incipient wetness technique. In this procedure, the amounts of components required to give the desired loading are dissolved in a quantity of deionized, distilled water necessary to just fill the pores of the support. The solution is then added to the support particles. In some cases, if the dopants are not easily soluble, suspensions of the components are added to the support. The resulting material is dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (usually 18-20 hours). Most dried catalysts are tested without further treatment. Several were first calcined in air. In most cases, these are marked in Appendix D as procedure A(*). These were prepared in 15 gram batches prior to calcining, and 5.3 to 6 grams of material was calcined, as indicated in Appendix D. Metal or inorganic compound loadings are expressed as weight percent based on 100 weight percent of the support.

Procedure A#5 is the same as Procedure A except that the metal salt was dissolved in the aqueous solution or suspension while heating slightly over hotplate until a clear aqueous solution or suspension of metal salt was observed. This was then added to the support.

Procedure B

In Procedure B, supported catalysts were prepared by adding the proper amount of component(s) to a mixture of water which was stirred with the support, while heating in a glass container on a hotplate for 2 to 3 hours (or until almost no water left), to distribute the material in and on the support. If the dopants were not easily soluble, they were finely ground first. Deionized, distilled water was used (50 mL unless stated otherwise). The resulting material was dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (usually 18-20 hours). The dried catalysts were then calcined in air. Metal or inorganic compound loadings are expressed as weight percent based on the weight of the support, except for catalysts containing silver. Components on silver catalysts are described by weight percent, based on the total catalyst weight.

Procedure B#1 is the same as Procedure B except that 30 mL of deionized, distilled water were used.

Procedure B#3 is the same as Procedure B except that 40 mL of deionized, distilled water were used.

Procedure B#4 is the same as Procedure B except that 70 mL of deionized, distilled water were used.

Preparation of Silver Catalysts

Silver catalysts are made by putting silver on a support by one of three general procedures, Procedure X, Procedure Y, or Procedure Z. Additional components are added to small portions of silver on alpha alumina from General Procedures X or Y as described below.

In Procedure X, a 9 weight percent silver on alpha aluminum oxide catalyst is made as follows. 600 grams of 88% aqueous lactic acid are added to a glass beaker and heated to 80 °C with stirring (30 minutes). Silver oxide (220 grams available from either Ames Goldsmith Corporation, Glens Falls, New York) is slowly added, with stirring. The mixture is stirred an additional 30 minutes at 80-85 °C, then 10 milliliters of CP grade hydrogen peroxide from J. T. Baker are added. The clear solution is slowly added from a 1000 milliliter glass separatory funnel over a period of 5 minutes to 300 grams of Norton SA5502 (Sample number 82343) hollow cylinder supports. These are first evacuated under a vacuum of from less than 1kPa to 70 kPa pressure at 80 °C for 120 minutes in a 5.7 cm i. d.(5.9 o. d.) glass tube, which is 36 cm long. This tube is fitted with a stopcock on the bottom and on the top, through a two-hole, black rubber, size 12 stopper, with a separatory funnel and a vacuum adapter. The glass tube is heated with a 6 foot Thermolyne heat tape, controlled by a Variac. The impregnating solution remains in the tube with the support at 81 °C for 60 minutes, then is drained. Recovered catalysts are placed in an oven at 60 °C and atmospheric pressure for 2 hours, then roasted on a moving belt at 500 °C using a forced air flow. The procedure for belt roasting catalysts which is used in General Procedures X and Y is described in M. M. Bhasin and G. H. Warner, "Silver Catalyst for the Manufacture of Ethylene Oxide and a Process for Preparing the Catalyst," U. S. Patent 4,419,276 to Union Carbide Corporation. Hollow spheres are then ground to 30 to 60 mesh (U. S. Sieve Series) prior to evaluation or addition of other components.

In procedure Y, a 20 weight percent silver on an alpha aluminum oxide catalyst is made using the procedure described in M. M. Bhasin and G. H. Warner, "Silver Catalyst for the Manufacture of Ethylene Oxide and a Process for Preparing the Catalyst," U. S. Patent 4,419,276 to Union Carbide Corporation. The silver oxide is available from either Ames Goldsmith Corporation, Glens Falls, New York, or Metz Metallurgical Co. Norton 5451 alpha aluminum oxide, 50 grams, Sample number 8883119, 30 to 60 mesh (U. S. Sieve Series) is used as support.

In Procedure Z, a 16.9 weight percent silver/barium carbonate catalyst is made using Procedure Y except that barium carbonate is used instead of alpha aluminum oxide.

For those catalysts with additional components, these are added by one of two general procedures, Procedure A or Procedure B, described above. Individual catalyst preparation procedures for silver catalysts follow. The first reference is that of the experiment testing the catalyst for methane coupling. The second reference (in parenthesis) is that of the catalyst preparation. Note that the percentages of components below are weight percentages based on the total catalyst weight. In Appendix D, weight percentages of metals are expressed as weight percent against 100 weight percent support (so they are higher, since the weight of the support is less than the weight of the total catalyst).

(30-BKW-115) A catalyst of 9 weight percent silver (calculated as elemental silver) on aluminum oxide is prepared by General Procedure X. Approximately 330.16 grams of catalyst are obtained.

34-BKW-32 (33-BKW-87) A catalyst of 20 weight percent silver (calculated as elemental silver) on aluminum oxide is prepared by General Procedure Y. Approximately 62.5 grams of catalyst are obtained. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

33-BKW-120 (33-BKW-119) A catalyst of 16.9 weight percent silver (calculated as elemental silver) on barium carbonate (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S97090R, 99.997 weight percent) is prepared by General Procedure Z. The catalyst is calcined at 800 °C for 4 hours. Approximately 18.82 grams of catalyst are obtained. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-6 (33-BKW-136A#1) A catalyst of 0.10 weight percent hydrated praseodymium nitrate (calculated as elemental praseodymium) and 20 weight percent silver on aluminum

oxide is prepared by General Procedure Y followed by General Procedure A using 0.0185 grams of hydrated praseodymium nitrate (6 waters of hydration, from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number 11240A, 99.99 weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst VII. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-7 (33-BKW-136B#1) A catalyst of 0.01 weight percent hydrated praseodymium nitrate (calculated as elemental praseodymium) and 20 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.00185 grams of hydrated praseodymium nitrate (6 waters of hydration, from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number 11240A, 99.99 weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst VII. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-10 (33-BKW-136C#1) A catalyst of 0.10 weight percent bismuth nitrate (calculated as elemental bismuth) and 20 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.0139 grams of bismuth nitrate (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S96494, 99.999 weight percent) in 2.17 grams of deionized water and 6 grams of Catalyst VII except that the solution is at a slightly elevated temperature such that it remains clear. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-11 (33-BKW-136D#1) A catalyst of 0.10 weight percent barium nitrate (calculated as elemental barium) and 20 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.011 grams of barium nitrate (J. T. Baker Chemical Co., Phillipsburg, NJ, Lot number 43774, 99.3 weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst VII. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-14 (33-BKW-136F#1) A catalyst of 1.0 weight percent barium nitrate (calculated as elemental barium) and 20 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.11 grams of barium nitrate (J. T. Baker Chemical Co., Phillipsburg, NJ, Lot number 43774, 99.3

weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst VII except that the solution is at a slightly elevated temperature such that it remains clear. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-15 (33-BKW-136I#1) A catalyst of 1.0 weight percent potassium nitrate (calculated as elemental potassium) and 20 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.1551 grams of potassium nitrate (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S95682, 99.999 weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst VII. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

(34-BKW-23) A catalyst of 19 weight percent silver (calculated as elemental silver) on aluminum oxide is prepared by General Procedure Y. Approximately 61.89 grams of catalyst are obtained.

34-BKW-36 (34-BKW-24A#1) A catalyst of 3.5 weight percent barium chloride (calculated as elemental barium) and 18 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.335 grams of barium chloride (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94730, 99.9999 weight percent) in 1.17 grams of deionized water and 6 grams of Catalyst XV. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-44 (34-BKW-24C#1) A catalyst of 3.4 weight percent barium chloride (calculated as elemental barium), 3.4 weight percent lanthanum oxide (calculated as elemental lanthanum) and 18 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure B using 0.335 grams of barium chloride (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94730, 99.9999 weight percent) and 0.262 grams of lanthanum oxide (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number R3677, 99.99 weight percent) in 30 milliliters of deionized water and 6 grams of Catalyst XV. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-37 (34-BKW-24D#1) A catalyst of 3.5 weight percent barium chloride (calculated as elemental barium), 0.35 weight percent lanthanum oxide (calculated as elemental lanthanum) and 18 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure B using 0.335 grams of barium chloride (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94730, 99.9999 weight percent) and 0.0262 grams of lanthanum oxide (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number R3677, 99.99 weight percent) in 30 milliliters of deionized and 6 grams of Catalyst XV. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-51 (34-BKW-41A#1) A catalyst of 4.1 weight percent barium chloride (calculated as elemental barium), 4.1 weight percent lanthanum oxide (calculated as elemental lanthanum) and 9 weight percent silver on aluminum oxide, Catalyst I, is prepared by General Procedure X followed by General Procedure B using 0.335 grams of barium chloride (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94730, 99.9999 weight percent) and 0.262 grams of lanthanum oxide (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number R3677, 99.999 weight percent) in 30 milliliters of deionized water and 6 grams of Catalyst I. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-50 (34-BKW-41B#1) A catalyst of 4.3 weight percent barium chloride (calculated as elemental barium) and 9 weight percent silver on aluminum oxide, Catalyst I, is prepared by General Procedure X followed by General Procedure A using 0.335 grams of barium chloride (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94730, 99.9999 weight percent) in 1.21 grams of deionized water and 6 grams of Catalyst I. The catalyst is calcined at 800 °C for 4 hours. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

34-BKW-45 (34-BKW-41C) A catalyst of 1.1 weight percent hydrated calcium chloride (calculated as elemental calcium) and 19 weight percent silver on aluminum oxide is prepared by General Procedure Y followed by General Procedure A using 0.353 grams of hydrated calcium chloride (XH_2O waters of hydration, from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number LV01629KV, 99.99+ weight percent) in 1.17 grams of deionized water and 6 grams of silver catalyst. The catalyst particle size is 30 to 60 mesh (U. S. Sieve Series).

Sources of Materials

Alpha-alumina supports were obtained from Norton, unless otherwise specified. Sample numbers are shown in tables, designating the type of alpha-alumina support. Alkaline earth salts and others salts, unless specified, were obtained from Johnson Matthey (JM) or AESAR, and are greater than 99.99% pure, unless specified. Metal oxides, unless specified, are also obtained from Johnson Matthey or AESAR, and are greater than 99.99% pure.

See Appendix E of the Fourth²¹ and Fifth⁴ Quarterly Reports for sources of most materials. Norton TiO₂, sample number 88-55-004, 30/100 mesh, 0.6 m²/g surface area, was used in catalysts for reactions 33-BKW-85 and 33-BKW-91. JM TiO₂, 30/60 mesh, 0.82 m²/g surface area, lot #S96579, 99.995%, was used in catalysts for reactions 33-BKW-114 and 115.

BaCO₃ was JM powder, 99.997% pure, lot #S96252B (for 33-BKW-85) and lot #S97090R for 33-BKW-91, 114, 115, 120, and 34-BKW-61 and 63. SrCO₃ was from JM, 99.999% pure, lot #S96275. BaCl₂ was from JM (Aesar) that was used for all reactions except 33-BKW-81 was from lot #S94730, 99.999% pure.

Barium nitrate was from Baker, lot #43774, 99.3%. Bismuth nitrate was from JM (Aesar), 99.999% pure, lot #S96494. Potassium nitrate was from JM (Aesar), 99.999%. Praseodymium nitrate was from JM (Aesar), lot #11240A, 99.99% pure.

Appendix F. DETAILED EXPERIMENTAL AND SUMMARY OF VAPOR PHASE REACTIONS

In reaction 35-BKW-23, no catalyst and no volatile component are used. Some oscillating reactions may be occurring, especially at temperatures of 700 °C and above.

In reaction 35-BKW-26, the effect of volatilized component is shown. In the cup in the upper part of the reactor, 5 grams of cesium hydroxide (from Johnson Matthey/Aesar Group, Seabrook, NH, Lot number 1403, 99.9 weight percent salt with 15-20% water) are used. The cesium hydroxide particle size is 100+ mesh (U. S. Sieve Series). At the completion of the experiment, cesium hydroxide (about 3.9 grams) covers the walls of the reactor. The experiment demonstrates the reduction in vapor phase alkane conversion due to the presence of a volatilized compound of cesium hydroxide.

In reaction 35-BKW-29, 1.4 grams of lithium hydroxide (from Johnson Matthey/Aesar Group, Seabrook, NH, Lot number GO9E, 99.3 weight percent) is placed in the reactor cup. The catalyst particle size is 100+ mesh (U. S. Sieve Series). Most of the lithium hydroxide is volatilized out of the catalyst cup during the reaction.

In reaction 35-BKW-32, 5 grams cesium chloride (from Johnson Matthey/Aesar Group, Seabrook, NH, Lot number S94942, 99.999 weight percent, particle size is 100+ mesh, U. S. Sieve Series) are placed in the reactor cup, and are observed after the experiment to have melted. The effect of the volatilized component is readily observed when the temperature of the upper oven is decreased to 226 °C when little cesium chloride is volatilized.

In reaction 35-BKW-35, 2 grams of lithium chloride (from Johnson Matthey/Aesar Group, Seabrook, NH, Lot number S94408, 99.999 weight percent) are placed in the cup. The catalyst particle size is 100+ mesh (U. S. Sieve Series). After the reaction, the reactor cup contains less than 1.73 grams of lithium compound. This example shows that the vapor phase alkane conversion reactions are altered by the addition of the volatile lithium component.

In reaction 35-BKW-37, cesium chloride (5 grams, particle size 100+ mesh, U. S. Sieve Series, from Johnson Matthey/Aesar Group, Seabrook, NH, Lot number S94942, 99.999 weight percent) are placed in the cup and 38.23 grams of alpha aluminum oxide (14 to 30 mesh, U. S. Sieve Series, from Norton Company, Akron, OH, Sample number 8883119, Type SA 5451, B. E. T. surface area 0.27 square meters per gram, measured with a nitrogen flow method) are placed in the reaction zone. About 4.9 grams of cesium compound are present in the reactor cup after the reaction.

Appendix F. DETAILED EXPERIMENTAL AND SUMMARY OF VAPOR PHASE REACTIONS (continued)

In reaction 35-BKW-41, 4 grams of ruthenium dioxide (100+ mesh, U. S. Sieve Series, from Alfa Products, Danvers, MA, Lot number B24H, 99.9 weight percent) are placed in the reactor cup. After the reaction, 3.95 grams of ruthenium compound are present in the reactor cup.

In reaction 35-BKW-44, 5 grams cesium chloride (100+ mesh, U. S. Sieve Series, from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94942, 99.999 weight percent) are placed in the reactor cup. The vapor phase alkane conversion reactions are depressed.

In reaction 35-BKW-47, cesium chloride (5 grams, 100+ mesh, U. S. Sieve Series, from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S94942, 99.999 weight percent) is placed in the reactor cup, and 4 grams of a used catalyst (used in 34-BKW-63 described in the Task 1 Section of this report), 30 to 60 mesh (U. S. Sieve Series), consisting of 9.1 weight percent barium carbonate (4.5 weight percent barium) on alpha aluminum oxide (from Norton Company, Akron, OH, Sample number 8883119, Type SA 5451, B. E. T. surface area 0.27 square meters per gram) are placed in the reaction zone. The barium catalyst is made by stirring a mixture of 40 milliliters of water, 10 grams of alpha alumina, and 1.0 grams of barium carbonate (from Johnson Matthey/AESAR Group, Seabrook, NH, Lot number S97090R, 99.997 weight percent) until most of the water is evaporated. The material is then dried further in a 130 °C oven under a vacuum of 16-84 kPa for 20 hours, then it is calcined at 850 °C for 4 hours at atmospheric pressure in air. Five grams of this catalyst is reacted with 80 volume percent methane, 10 volume percent oxygen, 10 volume percent nitrogen, and from 5 to 20 ppmv ethyl chloride for 151 hours at 750 °C in a 7 mm i.d. quartz reactor. At the end of this time, the methane conversion is 7 percent and the C₂ selectivity is 70 percent (prior to use in this reaction).

Approximately 20 ppmv (parts per million by volume) of ethyl chloride are added to the methane inlet stream of the reactor initially, and the flow rate is 160 sccm. After 1290 minutes, the total flow rate is changed to 80 sccm and the ethyl chloride level is changed to 40 ppmv. After 2665 minutes, the ethyl chloride level is changed to 10 ppmv. After 1900 minutes, the ethyl chloride level is changed to 20 ppmv.

**Appendix G. SELECTED LITERATURE REFERENCES,
CATALYSTS FOR METHANE COUPLING CONTAINING
ALKALINE EARTH METALS**

(Numbers refer to References Section in this Quarterly)

31. K. Aika, T. Moriyama, T. Takasaki, and E. Iwamatsu, *J. Chem. Soc. Chem. Comm.*, 1210 (1986).
- Kh. M. Minachev, N. Ya. Usachev, V. N. Udit, and Yu. S. Khodakov, *Russ. Chem. Rev.*, 57, 221 (1988) refer to this reference as showing that activities and selectivities to C_2 's increase with increasing atomic weight of alkaline earths in the alkaline earth metal oxides. At 750 °C, methane conversion and C_2 selectivity with BaO are reported to be 15.2% and 45.4%, respectively. The lack of CO_2 during initial operation of alkaline earth oxide catalysts is attributed to the uptake of CO_2 in converting oxides to carbonates. Highest yields for alkaline earth oxides or carbonates referred to was 16.3% to C_2 's (52.7% C_2 selectivity) for SrO (800 °C, CH_4 :air:He=1:2.5:33.3, 55.2 mL/min flow rate), 16.6% to C_2 's (44.6% C_2 selectivity) for BaO (800 °C, CH_4 : O_2 =5, 0.074 mol g⁻¹ s⁻¹), and 18.2% to C_2 's (48.4% C_2 selectivity) for BaCO₃ (800 °C, CH_4 :air:He=1:2.5:33.3, 55.2 mL/min flow rate).
34. A. I. Suleimanov, S. V. Akiev, and V. D. Sokolovskii, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No. 7220-V.
6. D. E. Driscoll, W. Martin, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, 107, 58 (1985).
35. E. Iwamatsu, T. Moriyama, N. Takasaki, and K. Aika, *J. Chem. Soc. Chem. Comm.*, 19 (1987).
- Kh. M. Minachev, N. Ya. Usachev, V. N. Udit, and Yu. S. Khodakov, *Russ. Chem. Rev.*, 57, 221 (1988) refer to this reference as showing that heat treatment of

MgO at 1000 °C (with reduction of surface area) was reported to increase activity and selectivity to C₂'s.

36. E. Yamagata, K. Tanaka, S. Sasaki, and S. Okazaki, *Chem. Lett.* 81 (1987).
37. M. Ya. Sinev, V. N. Korchak, and O. V. Krylov, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reactsii" (Abstracts of the Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p.27.
32. R. F. Hicks, WO 86/07351 to W. R. Grace & Co., Dec. 18, 1986 (priority June 14, 1985).

This patent claims a process and catalysts for conversion of methane to ethane, ethylene, and higher hydrocarbon products from contacting a gas mixture of methane and oxygen with a catalyst, the improvement comprising a catalyst with one or more of the following oxides:

IIA (Be, Mg, Ca, Sr, Ba)

IIIA (Sc, Y or La)

Lanthanide series excluding Ce (Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

Mixtures of these

Also claimed are these catalysts promoted with IA, IIA, IIIA, lanthanides, IVB, VB, IB or mixtures of these, from a catalytically effective amount to 50% by weight. Conditions are 1-50 atm., methane to oxygen ratios of 0.5-50, and 500-1000 °C. Preferred catalysts are implied (by claims and discussion) to be Li₂O on MgO, CaO, or SrO, and Y₂O₃ or La₂O₃ with a variety of promoters including the alkaline earth compounds. Also preferred is a mixture of rare earth oxides with a lot of the Ce removed, promoted with a variety of compounds. The patent distinguishes this process from prior art because methane and oxygen are cofed, basic and ionic metal oxides can be used, catalysts can be improved by promoters, and an inert support is not necessary (it is not specifically listed in claims). Catalysts are composed of one or more base metal oxides. They may result from metal oxides or metal salts which are decomposed to metal oxides. Salts listed include carbonates, hydroxides, nitrates, and halides, among others. CeO₂ is stated to cause CO and CO₂ formation

from redox of Ce between +3 and +4 states. Catalysts may be made from adsorption, incipient wetness, precipitation, coprecipitation, or dry-mixing. Catalysts may also be made on alumina or silica. Acidic supports require reduction in acidity from high metal loadings, doping with alkalis, or low porosity. Heating can reduce porosity. A fixed bed, a fluidized bed, an ebullating bed, a moving bed, or an entrained bed may be used. Reactors may be in parallel or in series. Examples used a 4 mm OD quartz tube heated in a fluidized sand bath. Catalysts were heated to 900 °C prior to use. Reported conditions included reactions at 1 atm and 700-900 °C with space velocities of 37,500 to 800,000, oxygen of 5 -10%, methane of 30%, catalyst meshes of 20-32 mesh, and Ar as diluent. Hydrogen was observed to be made in an H₂ to C₂'s ratio of 0.4-1. Catalysts were active at temperatures as low as 600 °C (with 100% oxygen conversion). Hydrogen was presented as an advantage. Some results follow:

BaO/La₂O₃: 800 °C, 68.2% C₂'s, C₂H₄/C₂H₆~1, CH₄ conv. 20.3%, 0.5 H₂/C₂'s
 SrO/La₂O₃: 800 °C, 69% C₂'s, C₂H₄/C₂H₆~1, CH₄ conv. 20.9%, 0.6 H₂/C₂'s
 CaO/La₂O₃: 800 °C, 64.32% C₂'s, C₂H₄/C₂H₆~1, CH₄ conv. 26.3%, 0.8 H₂/C₂'s
 BaO/MgO: 850 °C, 57.8% C_n's, C₂H₄/C₂H₆~1, CH₄ conv. 17.4%, 0.9 H₂/C₂'s

33. Ger. Patent No. 3,503,664 to AKZO, GmbH, Wuppertal, appl. Feb. 4, 1985.
= (EP 194425, Australia 86-212857-33.

This reference reports high C₃ and C₄ yields with bivalent metal halides [46.8% of the hydrocarbons (38.6% overall selectivity including carbon oxides) are butenes with BaBr₂/pumice and 24.1% of them (14.3% overall selectivity) are butenes with CaBr₂/MgO].

30. J. B. Kimble and J. H. Kolts, EP 210383 to Phillips, Dec. 12, 1986.
= JP 61,282,322.
= U. S. Appl. 742,335, June 7, 1985

A process is described for halide addition to known methane coupling catalysts (from the literature) with the addition of a gas phase material containing halogen to prevent the depletion of halide. The process is for the oxidative conversion of organic compounds to other organic compounds. Methane and ethane are specifically claimed, and all but two of the examples are for ethane conversion to ethylene. The halide is stated to be important to increase conversion, especially for the conversion

halide is stated to be important to increase conversion, especially for the conversion of saturated to unsaturated materials. Gaseous halogen materials which can be added intermittently to the catalyst or continuously in the feed gas include Cl_2 , CH_3Cl , or CH_2Cl_2 . Catalysts can be prepared with the halides or they can be added later by contacting the catalyst with gaseous material. Types of catalysts listed as good with the addition of halides include group IA or IIA or mixtures (including Li/MgO , Na/CaO , SrO , and BaO), group IA with lanthanides ($\text{Li/Sm}_2\text{O}_3$, $\text{Na/La}_2\text{O}_3$), group IA with zinc (Li/ZnO), group IA with Ti or Zr ($\text{Li}_2\text{O/TiO}_3$), group IA or IIA or a mixture with phosphate anions ($\text{K}_2\text{HPO}_4/\text{supports}$), or many other catalysts such as $\text{Co/ Zr/ S/ P/ Na/ K/ O}$.

The first of two methane coupling examples shows $\text{Li}_2\text{O/MgO}$ as having selectivities to ethylene and ethane and methane conversions of 43%, 31%, and 9.9% respectively for the chlorinated catalyst, and 31%, 42%, and 10.0% for the unchlorinated catalyst. For a $\text{Li}_2\text{O/TiO}_2$ catalyst, selectivities to ethylene and ethane and methane conversions of 48%, 21%, and 14%, respectively were observed for the chlorinated catalyst, and of 37%, 38%, and 9.3% were observed for the unchlorinated catalyst.

Appendix H. ELECTRON MICROSCOPY AND EDS DATA

Table H1. Ba/Al₂O₃ Catalysts, 33-BKW-47B, 49, 64A, 74, 79A and 81

Surface: Weight Percent

<u>Weight %</u>	<u>Element</u>			
	<u>Al</u>	<u>Si</u>	<u>Cl</u>	<u>Ba</u>
1. <u>33-BKW-47B</u> (NO ₃ , fresh)				
Area 1	15.82	0.28	0.00	3.86
Area 2	12.52	0.36	0.00	0.95
Area 3	<u>10.01</u>	<u>0.21</u>	<u>0.00</u>	<u>2.69</u>
	12.78	0.28	0.00	2.50
2. <u>33-BKW-49</u> (NO ₃ , used 47B)				
Area 1	19.49	0.31	0.27	27.41
Area 2	14.14	0.24	0.15	15.64
Area 3	<u>11.63</u>	<u>0.29</u>	<u>0.00</u>	<u>9.19</u>
	15.09	0.28	0.14	17.41
3. <u>33-BKW- 64A</u> (CO ₃ , fresh)				
Area 1	12.63	0.28	0.00	21.54
Area 2	11.53	0.19	0.00	16.56
Area 3	<u>14.08</u>	<u>0.25</u>	<u>0.00</u>	<u>19.00</u>
	12.75	0.24	0.00	19.03
4. <u>33-BKW-74</u> (CO ₃ , used 64A)				
Area 1	14.36	0.30	0.00	11.66
Area 2	11.49	0.13	0.24	12.92
Area 3	<u>15.29</u>	<u>0.20</u>	<u>0.00</u>	<u>13.43</u>
	13.71	0.21	0.08	12.67
5. <u>33-BKW-79A</u> (Cl ₂ , fresh)				
Area 1	15.78	0.28	0.00	5.73
Area 2	18.23	0.34	0.17	5.24
Area 3	<u>14.01</u>	<u>0.25</u>	<u>0.00</u>	<u>5.74</u>
	16.01	0.29	0.06	5.57
6. <u>33-BKW-81</u> (Cl ₂ , used 79A)				
Area 1	13.66	0.23	0.62	9.60
Area 2	19.03	0.40	2.74	18.26
Area 3	<u>23.07</u>	<u>0.64</u>	<u>0.00</u>	<u>7.58</u>
	18.59	0.42	1.12	11.81

Electron Microscopy Skill Center
44PHT56
7/20/89

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H1. Ba/Al₂O₃ Catalysts, 33-BKW-47B, 49, 64A, 74, 79A and 81 (cont.)

Surface: Atom Percent

Atom %	Element			
	Al	Si	Cl	Ba
1. 33-BKW-47B (NO ₃ , fresh)				
Area 1	93.86	1.63	0.00	4.51
Area 2	95.93	2.63	0.00	1.44
Area 3	<u>93.13</u>	<u>1.93</u>	<u>0.00</u>	<u>4.94</u>
	94.31	2.06	0.00	3.63
2. 33-BKW-49 (NO ₃ , used 47B)				
Area 1	76.73	1.18	0.83	21.27
Area 2	80.49	1.30	0.65	17.56
Area 3	<u>84.74</u>	<u>2.06</u>	<u>0.00</u>	<u>13.20</u>
	80.65	1.51	0.49	17.34
3. 33-BKW-64A (CO ₃ , fresh)				
Area 1	73.86	1.57	0.00	24.75
Area 2	77.01	1.21	0.00	21.79
Area 3	<u>77.93</u>	<u>1.34</u>	<u>0.00</u>	<u>20.72</u>
	76.27	1.37	0.00	22.42
4. 33-BKW-74 (CO ₃ , used 64A)				
Area 1	84.72	1.72	0.00	13.55
Area 2	80.09	0.84	1.31	17.75
Area 3	<u>84.36</u>	<u>1.04</u>	<u>0.00</u>	<u>14.60</u>
	83.06	1.20	0.44	15.30
5. 33-BKW-79A (Cl ₂ , fresh)				
Area 1	91.87	1.55	0.00	6.58
Area 2	92.45	1.67	0.65	5.23
Area 3	<u>91.08</u>	<u>1.57</u>	<u>0.00</u>	<u>7.35</u>
	91.80	1.60	0.22	6.39
6. 33-BKW-81 (Cl ₂ , used 79A)				
Area 1	84.03	1.39	2.95	11.63
Area 2	75.75	1.52	8.41	14.33
Area 3	<u>91.63</u>	<u>2.44</u>	<u>0.00</u>	<u>5.93</u>
	83.80	1.78	3.79	10.63

Electron Microscopy Skill Center
44PHT56
7/20/89

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H2. BaCO₃/Al₂O₃ Catalysts, 32-BKW-20 I (fresh) and 32-BKW-62 (used)

<u>Weight %</u>	<u>Surface</u>			
	<u>Element</u>			
<u>32-BKW-20 I (fresh)</u>	<u>Al</u>	<u>Si</u>	<u>Cl</u>	<u>Ba</u>
Area 1	16.33	0.27	0.00	23.05
Area 2	12.68	0.17	0.00	20.73
Area 3	<u>14.79</u>	<u>0.18</u>	<u>0.00</u>	<u>26.59</u>
	14.60	0.21	0.00	23.46
<u>32-BKW-62 (used 20 I)</u>				
Area 1	23.99	0.55	0.00	16.81
Area 2	20.02	0.43	0.00	13.82
Area 3	<u>23.26</u>	<u>0.38</u>	<u>0.00</u>	<u>15.69</u>
	22.42	0.45	0.00	15.44
<u>Atom %</u>	<u>Element</u>			
<u>32-BKW-20 I (fresh)</u>	<u>Al</u>	<u>Si</u>	<u>Cl</u>	<u>Ba</u>
Area 1	77.29	1.22	0.00	21.49
Area 2	74.89	0.98	0.00	24.12
Area 3	<u>73.19</u>	<u>0.88</u>	<u>0.00</u>	<u>25.93</u>
	75.12	1.03	0.00	23.85
<u>32-BKW-62 (used 20 I)</u>				
Area 1	86.20	1.90	0.00	11.90
Area 2	86.44	1.81	0.00	11.75
Area 3	<u>87.05</u>	<u>1.38</u>	<u>0.00</u>	<u>11.57</u>
	86.56	1.70	0.00	11.74

Electron Microscopy Skill Center
43PHT129
7/17/89

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H2. BaCO₃/Al₂O₃ Catalysts, 32-BKW-20 I (fresh) and 32-BKW-62 (used) cont.

Cross-Section

Weight %	Element			
	Al	Si	Cl	Ba
32-BKW-20 I (fresh)				
Particle 1	21.76	0.52	0.00	9.82
Particle 2	9.35	0.10	0.00	3.68
Particle 3	24.47	0.45	0.00	6.85
Particle 4	28.15	0.54	0.00	4.73
Particle 5	25.65	0.34	0.00	11.21
Particle 6	<u>14.05</u>	<u>0.11</u>	<u>0.00</u>	<u>7.34</u>
	20.57	0.34	0.00	7.27
32-BKW-62 (used 20 I)				
Particle 1	8.72	0.11	0.00	5.87
Particle 2	14.47	0.13	0.00	10.02
Particle 3	21.56	0.25	0.06	8.70
Particle 4	21.20	0.18	0.00	13.64
Particle 5	23.70	0.25	0.00	8.77
Particle 6	<u>20.77</u>	<u>0.23</u>	<u>0.00</u>	<u>13.58</u>
	18.40	0.19	0.01	10.10
Atom %	Element			
	Al	Si	Cl	Ba
32-BKW-20 I (fresh)				
Particle 1	89.93	2.07	0.00	8.00
Particle 2	91.01	0.96	0.00	7.13
Particle 3	93.21	1.65	0.00	5.14
Particle 4	95.10	1.75	0.00	3.15
Particle 5	91.00	1.17	0.00	7.84
Particle 6	<u>90.06</u>	<u>0.68</u>	<u>0.00</u>	<u>9.26</u>
	91.72	1.38	0.00	6.75
32-BKW-62 (used 20 I)				
Particle 1	87.33	1.08	0.00	11.58
Particle 2	87.30	0.78	0.00	11.92
Particle 3	91.49	1.04	0.20	7.28
Particle 4	88.10	0.72	0.00	11.17
Particle 5	92.32	0.95	0.00	6.73
Particle 6	<u>87.74</u>	<u>0.95</u>	<u>0.00</u>	<u>11.31</u>
	89.05	0.92	0.03	10.00

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H3. $\text{SrCO}_3/\text{Al}_2\text{O}_3$ Catalysts, 34-BKW-16A (fresh) and 34-BKW-18 (used)
 $\text{SrCl}_2/\text{Al}_2\text{O}_3$ Catalysts, 34-BKW-16B (fresh) and 34-BKW-19 (used)

Weight %	<u>Surface</u>				
	Element				
	<u>Al</u>	<u>Si</u>	<u>Cl</u>	<u>Ba</u>	<u>Sr</u>
1. <u>34-BKW-16A</u> (fresh)					
Area 1	12.72	0.58	0.00	0.00	5.69
Area 2	14.24	0.44	0.00	0.87	11.17
Area 3	<u>12.58</u>	<u>0.23</u>	<u>0.00</u>	<u>0.00</u>	<u>7.10</u>
	13.18	0.42	0.00	0.29	7.99
2. <u>34-BKW-18</u> (used 16 A)					
Area 1	5.81	0.17	1.45	0.00	5.49
Area 2	14.69	0.41	0.73	0.94	4.77
Area 3	<u>11.58</u>	<u>0.32</u>	<u>0.76</u>	<u>0.00</u>	<u>5.23</u>
	10.69	0.30	0.98	0.31	5.16
3. <u>34-BKW-16B</u> (fresh)					
Area 1	9.42	0.37	1.45	0.00	2.91
Area 2	10.27	0.16	2.67	0.46	5.66
Area 3	<u>13.29</u>	<u>0.57</u>	<u>5.53</u>	<u>0.00</u>	<u>10.52</u>
	10.99	0.37	3.21	0.15	6.36
4. <u>34-BKW-19</u> (used 16 B)					
Area 1	14.01	0.48	2.62	0.00	8.58
Area 2	15.98	0.38	3.34	0.00	10.11
Area 3	<u>6.98</u>	<u>0.00</u>	<u>2.30</u>	<u>0.00</u>	<u>5.59</u>
	12.32	0.29	2.75	0.00	8.09

Electron Microscopy Skill Center
44PHT100
7/26/89

Appendix II. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H3. $\text{SrCO}_3/\text{Al}_2\text{O}_3$ Catalysts, 34-BKW-16A (fresh) and 34-BKW-18 (used)
 $\text{SrCl}_2/\text{Al}_2\text{O}_3$ Catalysts, 34-BKW-16B (fresh) and 34-BKW-19 (used) cont.

Atom %	Surface				
	Element				
	Al	Si	Cl	Ba	Sr
1. <u>34-BKW-16A</u> (fresh)					
Area 1	84.66	3.72	0.00	0.00	11.62
Area 2	77.96	2.34	0.00	0.94	18.76
Area 3	<u>83.98</u>	<u>1.47</u>	<u>0.00</u>	<u>0.00</u>	<u>14.55</u>
	82.20	2.51	0.00	0.31	14.98
2. <u>34-BKW-18</u> (used 16 A)					
Area 1	66.19	1.87	12.74	0.00	19.20
Area 2	84.94	2.27	3.26	1.07	8.46
Area 3	<u>82.24</u>	<u>2.18</u>	<u>4.19</u>	<u>0.00</u>	<u>11.39</u>
	77.79	2.11	6.73	0.36	13.02
3. <u>34-BKW-16B</u> (fresh)					
Area 1	79.96	3.10	9.46	0.00	7.57
Area 2	71.76	1.11	14.37	0.63	12.13
Area 3	<u>62.28</u>	<u>2.60</u>	<u>20.00</u>	<u>0.00</u>	<u>15.12</u>
	71.33	2.27	14.61	0.21	11.61
4. <u>34-BKW-19</u> (used 16 B)					
Area 1	73.25	2.42	10.57	0.00	13.76
Area 2	72.56	1.66	11.69	0.00	14.09
Area 3	<u>66.66</u>	<u>0.00</u>	<u>16.94</u>	<u>0.00</u>	<u>16.39</u>
	70.82	1.36	13.07	0.00	14.75

Electron Microscopy Skill Center
44PHT100
7/26/89

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H4. Used Catalysts Containing BaCl₂/Al₂O₃, 30-BKW-52, 30-BKW-93

Weight %

30-BKW-52 BaCl₂/Al₂O₃ (used)

	<u>Al</u>	<u>Si</u>	<u>Ti</u>	<u>Ba</u>	<u>Fe</u>	<u>Mg</u>	<u>S</u>	<u>Cl</u>	<u>Ca</u>	<u>P</u>
Area 1 (200X)	22.57	0.55	0.00	5.26	0.00	0.00	0.00	0.00	0.11	0.00
Area 2 (200X)	17.13	0.43	0.00	3.60	0.00	0.00	0.10	0.00	0.08	0.00
Area 3 (200X)	29.37	0.67	0.09	13.68	0.00	0.00	0.19	1.62	0.00	0.16
Area 4 (200X)	20.67	0.47	0.00	5.15	0.00	0.00	0.00	0.00	0.00	0.14
Area 5 (200X)	12.65	0.22	0.00	7.17	0.00	0.00	0.00	0.59	0.00	0.10
	20.48	0.47	0.02	6.97	0.00	0.00	0.06	0.44	0.04	0.08

30-BKW-93 BaCl₂/Al₂O₃ (used 68 D)

Area 1 (200X)	26.39	0.53	0.00	10.62	0.00	0.00	0.00	0.00	0.18	0.00
Area 2 (200X)	11.76	0.20	0.00	8.40	0.00	0.00	0.00	0.00	0.09	0.00
Area 3 (200X)	19.20	0.48	0.00	6.50	0.00	0.00	0.00	0.00	0.21	0.00
Area 4 (200X)	17.84	0.28	0.00	8.18	0.00	0.00	0.00	0.00	0.00	0.00
Area 5 (200X)	29.33	0.47	0.00	15.83	0.00	0.00	0.18	0.00	0.00	0.00
	20.90	0.39	0.00	9.91	0.00	0.00	0.04	0.00	0.10	0.00

Atom %

30-BKW-52 BaCl₂/Al₂O₃ (used)

	<u>Al</u>	<u>Si</u>	<u>Ti</u>	<u>Ba</u>	<u>Fe</u>	<u>Mg</u>	<u>S</u>	<u>Cl</u>	<u>Ca</u>	<u>P</u>
Area 1 (200X)	93.21	2.20	0.00	4.28	0.00	0.00	0.00	0.00	0.31	0.00
Area 2 (200X)	93.10	2.27	0.00	3.85	0.00	0.00	0.46	0.00	0.31	0.00
Area 3 (200X)	85.72	1.90	0.09	7.87	0.00	0.00	0.48	3.64	0.00	0.40
Area 4 (200X)	92.85	2.05	0.00	4.56	0.00	0.00	0.00	0.00	0.00	0.55
Area 5 (200X)	85.40	1.42	0.00	9.55	0.00	0.00	0.00	3.07	0.00	0.57
	90.06	1.97	0.02	6.02	0.00	0.00	0.19	1.34	0.12	0.30

30-BKW-93 BaCl₂/Al₂O₃ (used 68 D)

Area 1 (200X)	90.64	1.77	0.00	7.19	0.00	0.00	0.00	0.00	0.41	0.00
Area 2 (200X)	86.02	1.44	0.00	12.10	0.00	0.00	0.00	0.00	0.45	0.00
Area 3 (200X)	91.07	2.18	0.00	6.08	0.00	0.00	0.00	0.00	0.67	0.00
Area 4 (200X)	90.47	1.36	0.00	8.18	0.00	0.00	0.00	0.00	0.00	0.00
Area 5 (200X)	88.73	1.37	0.00	9.44	0.00	0.00	0.46	0.00	0.00	0.00
	89.39	1.62	0.00	8.60	0.00	0.00	0.09	0.00	0.31	0.00

Electron Microscopy Skill Center 7/22/88

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H5. Catalysts Containing BaCl₂ or CaCl₂, 30-BKW-68C, 30-BKW-68D, 30-BKW-125H, 31-BKW-13

Weight %

30-BKW-68C BaCl₂/Al₂O₃ (fresh)

	Al	Si	Ti	Ba	Fe	Mg	S	Cl	Ca	P
Area 1 (20X)	8.28	0.13	0.00	5.40	0.08	0.00	0.00	0.87	0.00	0.00
Area 2 (200X)	23.30	0.45	0.00	3.24	0.15	0.00	0.08	0.00	0.00	0.00
Area 3 (200X)	14.19	0.37	0.00	1.52	0.00	0.00	0.00	0.00	0.00	0.00
Area 4 (200X)	17.03	0.43	0.00	1.66	0.00	0.00	0.00	0.00	0.00	0.00
Area 5 (200X)	7.66	0.14	0.00	0.47	0.00	0.00	0.06	0.00	0.00	0.00
Area 6 (200X)	9.54	0.15	0.00	22.76	0.00	0.00	0.00	3.59	0.05	0.00
Area 7 (200X)	15.59	0.32	0.00	1.31	0.17	0.00	0.14	0.00	0.09	0.00
Avg. Areas 2 - 7 =	14.60	0.31	0.00	5.16	0.05	0.00	0.05	0.60	0.02	0.00

30-BKW-68D BaCl₂/Al₂O₃ (fresh)

	Al	Si	Ti	Ba	Fe	Mg	S	Cl	Ca	P
Area 1 (20X)	9.87	0.35	0.00	3.90	0.00	0.00	0.10	0.41	0.00	0.00
Area 2 (1000X)	24.55	0.51	0.00	1.44	0.12	0.00	0.00	0.00	0.00	0.00
Area 3 (200X)	7.64	0.18	0.00	1.30	0.00	0.00	0.00	0.00	0.00	0.00
Area 4 (200X)	8.72	0.15	0.00	4.79	0.09	0.00	0.00	0.52	0.00	0.00
Area 5 (200X)	7.46	0.24	0.00	2.10	0.00	0.00	0.00	0.00	0.00	0.00
Avg. Areas 3 - 5 =	7.94	0.19	0.00	2.73	0.03	0.00	0.00	0.17	0.00	0.00

30-BKW-125H CaCl₂/Al₂O₃ (fresh)

	Al	Si	Ti	Ba	Fe	Mg	S	Cl	Ca	P
Area 1 (20X)	8.39	0.16	0.00	0.56	0.00	0.00	0.00	0.55	0.53	0.00
Area 2 (200X)	12.90	0.17	0.00	0.93	0.21	0.00	0.00	1.51	1.20	0.00
Area 3 (200X)	7.84	0.26	0.00	0.00	0.41	0.00	0.09	0.68	0.51	0.00
Area 4 (200X)	15.95	0.45	0.00	1.38	0.00	0.00	0.07	1.75	0.95	0.10
Area 5 (200X)	13.85	0.32	0.00	0.67	0.00	0.00	0.00	0.86	0.84	0.00
Avg. Areas 2 - 5 =	12.64	0.30	0.00	0.75	0.16	0.00	0.04	1.20	0.88	0.03

31-BKW-13 CaCl₂/Al₂O₃ (used 125 H)

	Al	Si	Ti	Ba	Fe	Mg	S	Cl	Ca	P
Area 1 (20X)	6.19	0.00	0.00	0.39	0.00	0.00	0.13	0.00	0.52	0.00
Area 2 (200X)	19.73	0.31	0.00	0.70	0.17	0.00	0.38	0.00	1.38	0.00
Area 3 (200X)	18.86	0.34	0.00	0.95	0.27	0.00	0.14	0.00	0.96	0.00
Area 4a (200X)	6.54	0.08	0.22	0.00	0.44	0.00	0.17	0.00	0.81	0.00
Area 4b (200X)	10.02	0.29	0.00	0.00	1.01	0.00	0.00	0.00	1.02	0.00
Area 5 (200X)	15.25	0.31	0.00	1.27	0.81	0.00	0.00	0.00	1.27	0.00
Avg. Areas 2 - 5 =	14.08	0.25	0.04	0.58	0.54	0.00	0.14	0.00	1.09	0.00

Appendix H. ELECTRON MICROSCOPY AND EDS DATA (continued)

Table H5. Catalysts Containing BaCl₂ or CaCl₂, 30-BKW-68C, 30-BKW-68D, 30-BKW-125H, 31-BKW-13 (cont.)

	Atom %									
30-BKW-68C BaCl ₂ /Al ₂ O ₃ (fresh)	Al	Si	Ti	Ba	Fe	Mg	S	Cl	Ca	P
Area 1 (20X)	81.31	1.26	0.00	10.46	0.36	0.00	0.00	6.61	0.00	0.00
Area 2 (200X)	95.03	1.78	0.00	2.61	0.30	0.00	0.28	0.00	0.00	0.00
Area 3 (200X)	95.55	2.43	0.00	2.02	0.00	0.00	0.00	0.00	0.00	0.00
Area 4 (200X)	95.85	2.31	0.00	1.84	0.00	0.00	0.00	0.00	0.00	0.00
Area 5 (200X)	96.85	1.65	0.00	1.17	0.00	0.00	0.60	0.00	0.00	0.00
Area 6 (200X)	56.18	0.87	0.00	26.42	0.00	0.00	0.00	16.32	0.21	0.00
Area 7 (200X)	94.97	1.86	0.00	1.57	0.50	0.00	0.71	0.00	0.39	0.00
Avg. Areas 2 - 7 =	89.07	1.82	0.00	5.94	0.13	0.00	0.17	2.72	0.10	0.00
30-BKW-68D BaCl ₂ /Al ₂ O ₃ (fresh)										
Area 1 (20X)	86.77	2.94	0.00	6.76	0.00	0.00	0.73	2.79	0.00	0.00
Area 2 (1000X)	96.71	1.93	0.00	1.12	0.23	0.00	0.00	0.00	0.00	0.00
Area 3 (200X)	94.65	2.17	0.00	3.18	0.00	0.00	0.00	0.00	0.00	0.00
Area 4 (200X)	85.06	1.41	0.00	9.21	0.40	0.00	0.00	3.93	0.00	0.00
Area 5 (200X)	92.06	2.83	0.00	5.11	0.00	0.00	0.00	0.00	0.00	0.00
Avg. Areas 3 - 5 =	90.59	2.14	0.00	5.83	0.13	0.00	0.00	1.31	0.00	0.00
30-BKW-125H CaCl ₂ /Al ₂ O ₃ (fresh)										
Area 1 (20X)	88.89	1.68	0.00	1.16	0.00	0.00	0.00	4.46	3.81	0.00
Area 2 (200X)	84.18	1.10	0.00	1.20	0.66	0.00	0.00	7.59	5.27	0.00
Area 3 (200X)	84.95	2.69	0.00	0.00	2.14	0.00	0.79	5.71	3.71	0.00
Area 4 (200X)	84.90	2.29	0.00	1.45	0.00	0.00	0.30	7.17	3.40	0.48
Area 5 (200X)	89.25	1.98	0.00	0.84	0.00	0.00	0.00	4.29	3.64	0.00
Avg. Areas 2 - 5 =	85.82	2.02	0.00	0.87	0.70	0.00	0.27	6.19	4.00	0.12
31-BKW-13 CaCl ₂ /Al ₂ O ₃ (used 125 H)										
Area 1 (20X)	92.01	0.00	0.00	1.16	0.00	0.00	1.63	0.00	5.20	0.00
Area 2 (200X)	91.74	1.40	0.00	0.64	0.38	0.00	1.49	0.00	4.35	0.00
Area 3 (200X)	93.06	1.61	0.00	0.92	0.64	0.00	0.59	0.00	3.19	0.00
Area 4a (200X)	85.59	1.02	1.61	0.00	2.78	0.00	1.87	0.00	7.14	0.00
Area 4b (200X)	87.31	2.44	0.00	0.00	4.24	0.00	0.00	0.00	6.01	0.00
Area 5 (200X)	89.44	1.76	0.00	1.46	2.30	0.00	0.00	0.00	5.05	0.00
Avg. Areas 2 - 5 =	89.43	1.65	0.32	0.60	2.07	0.00	0.79	0.00	5.15	0.00

Electron Microscopy Skill Center, 41-PHT-101, 7/20/88

Figure H1. Fresh and Used $\text{BaCO}_3/\text{Al}_2\text{O}_3$ Catalysts

33-BKW-64A, $\text{BaCO}_3/\text{Al}_2\text{O}_3$

BEI

33-BKW-74, Used 33-BKW-64A

BEI

Figure H2. Fresh and Used $\text{Ba}(\text{NO}_3)_2/\text{Al}_2\text{O}_3$ Catalysts

33-BKW-47B, $\text{Ba}(\text{NO}_3)_2$

BEI

33-BKW-49, Used 33-BKW-47B

BEI

Figure H3. Fresh and Used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalysts

33-BKW-79A, $\text{BaCl}_2/\text{Al}_2\text{O}_3$

BEI

33-BKW-81, Used 33-BKW-79A

BEI

Figure H4. Fresh $\text{BaCO}_3/\text{Al}_2\text{O}_3$ Catalysts

32-BKW-20IA

SEI

32-BKW-20IA

BEI

Figure H5. BEI Surface Analyses of Fresh and Used $\text{BaCO}_3/\text{Al}_2\text{O}_3$ Catalysts

32-BKW-20I (Fresh)

32-BKW-62 (Used)

BEI

32-BKW-20I (Fresh)

32-BKW-62 (Used)

BEI

Figure H6. Surface BEI Analyses of Fresh and Used $\text{BaCO}_3/\text{Al}_2\text{O}_3$ Catalysts

32-BKW-20I

BEI

32-BKW-62, Used 32-BKW-20I

BEI

Figure H7. Cross Section of Fresh and Used $\text{BaCO}_3/\text{Al}_2\text{O}_3$ Catalysts

32-BKW-20I Cross Section

BEI

32-BKW-62, Used 32-BKW-20I Cross Section

BEI

Figure H8. Fresh and Used $\text{SrCO}_3/\text{Al}_2\text{O}_3$ Catalysts

34-BKW-16A

BEI

$\text{SrCO}_3/\text{Al}_2\text{O}_3$

34-BKW-18, Used 34-BKW-16A

BEI

Figure H9. Fresh and Used $\text{SrCl}_2/\text{Al}_2\text{O}_3$ Catalyst

34-BKW-16B

BEI

$\text{SrCl}_2/\text{Al}_2\text{O}_3$

34-BKW-19, Used 34-BKW-16B

BEI

Figure H10. Used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalysts: Areas for EDS Analyses

30-BKW-52

SEI, EDS

30-BKW-93

SEI, EDS

Figure H11. Used $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalysts

30-BKW-93, Used 30-BKW-68D

SEI

30-BKW-52

SEI

Figure H12. Fresh $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalyst

30-BKW-68D

SEI

30-BKW-68D

SEI

Figure H13. Fresh $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalysts: Areas for EDS Analyses

30-BKW-68D

SEI, EDS

30-BKW-68C

SEI, EDS

Figure H14. Fresh $\text{BaCl}_2/\text{Al}_2\text{O}_3$ Catalyst on Norton 555l Alumina

30-BKW-68C

$\text{BaCl}_2/\text{Al}_2\text{O}_3$ - 555l

SEI

Figure H15. Fresh and Used $\text{CaCl}_2/\text{Al}_2\text{O}_3$ Catalyst

30-BKW-125H

SEI, EDS

31-BKW-13, Used 30-BKW-125H

SEI, EDS

END

DATE FILMED

01 / 29 / 91