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**Catalytic Conversion of Light Alkanes
Phase III**

**Topical Report
January 1990 - December 1992**

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ABSTRACT

This Topical Report on the Catalytic Conversion of Light Alkanes, reviews the project mission, the technical background, the preliminary work done at Sun and the progress made between January 1, 1990 and December 31, 1992 on Phase III of the Cooperative Agreement. The mission of this work is to devise a new catalyst which can be used in the first simple, economic process to convert the light alkanes in natural gas to an alcohol-rich oxygenated product which can either be used as an environmentally friendly, high-performance liquid fuel, or a precursor to a liquid hydrocarbon transportation fuel.

We have focused on preparing and testing catalysts designed to form metal oxo (MO) intermediates directly by reaction with air or oxygen and have found that the catalysts which we have made are able to promote the conversion of light alkanes to alcohols under relatively mild conditions. It is our thesis that if a catalytic entity MO can homolytically cleave the carbon hydrogen bond of a light alkane, RH, to form an intermediate, MOH(R•), that this intermediate could either directly produce the alcohol, ROH, or could produce the radicals R• and OH• which would yield alcohols by low temperature radical reactions. We investigated three molecular environments which appeared to be hospitable ones for the active catalytic species that we were

trying to generate: highly halogenated porphyrinic macrocycles (PHASE I), polyoxoanions or heteropolyacids, (PHASE II), and regular oxidic lattices such as zeolites and related structures (PHASE III).

Work in our laboratories has shown that a new perhaloporphyrinatometal complex is the most active homogeneous catalyst for isobutane oxidation which has yet been found. Rapid oxidations take place at temperatures as low as room temperature to give tert-butyl alcohol in over 90% selectivity at conversions in excess of 30%. Framework substituted metallozeolites have been synthesized which allow methanol to be produced from methane in greater than 70% selectivity at 7% conversion in the vapor phase. Both of these catalysts may operate through the same general reaction mechanism which involves the initial interaction of a high oxidation state metal oxo intermediate with the hydrocarbon to produce free or coordinated hydrocarbon radicals which go on to form oxygenate products. The metal oxo intermediate may be regenerable with molecular oxygen closing the catalytic cycle.

We have entered the proof-of-concept stage for converting isobutane to tert butyl alcohol in a practical process and are preparing to enter proof-of-concept of a propane to isopropyl alcohol process in the near future. Methane and ethane are more refractory and thus more difficult to oxidize than the C_3 and C_4 hydrocarbons. Nonetheless, advances made in this area indicate that further research progress could achieve the goal of their direct conversion to alcohols. Progress in Phase III catalytic vapor phase methane and ethane oxidations over metals in regular oxidic lattices are the subject of this topical report.

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1.0 INTRODUCTION

We have found a family of new catalytic materials which, if successfully developed, will be effective in the conversion of light alkanes to alcohols or other oxygenates. Catalysts of this type have the potential to convert natural gas to clean-burning high octane liquid fuels directly without requiring the energy-intensive steam reforming step. In addition they also have the potential to upgrade light hydrocarbons found in natural gas to a variety of high value fuel and chemical products. In order for commercially useful processes to be developed, increases in catalytic life, reaction rate and selectivity are required. Recent progress in the experimental program geared to the further improvement of these catalysts is outlined in Section 5.

2.0 PURPOSE

The mission of the work presented in this report is to generate novel catalytic technology which will permit the development of a simple, efficient and economical process for the direct conversion of natural gas to liquid transportation fuels. This process should be simple enough to liquify natural gas economically even at a remote reservoir site. It is a further mission of this work to find new routes from natural gas or its components to high value oxygenates by direct air-oxidation using these new catalysts.

The technical objective of the research is to design the first effective molecular catalyst for the direct air-oxidation of the hydrocarbons found in natural gas to an alcohol-rich oxidate which can either be used directly or converted into gasoline via known technology. The development of an efficient catalyst for the smooth and selective oxidation of light alkanes to alcohols will not only provide a solution to the problem of liquifying natural gas, but will create new opportunities to utilize the relatively inexpensive and abundant light alkanes for the production of a variety of valuable fuel and chemical products. Processes for converting natural gas or its components (methane, ethane, propane, and the butanes) to alcohols for use as motor fuels, fuel additives or fuel precursors will not only add a valuable alternative to crude oil but will produce a clean-burning, high octane alternative to conventional gasoline.

3.0 TECHNICAL BACKGROUND

The First Quarterly Report of 1992 for Catalytic Conversion of Light Alkanes Cooperative Agreement, Section 3.0, can be consulted for details of the technical background relating to this project.

4.0 METHODOLOGY

Details of the suprabiotic methodology to be used to conduct research on the Catalytic Conversion of Light Alkanes can be found in Section 4.0 of the First Quarterly Report of the Cooperative Agreement.

5.0 RESULTS AND DISCUSION

The three major thrusts of the research program are catalysis by A) metals in electron deficient macrocycles (PHASE I), B) Polyoxometallates (PHASE II), and C) metals in regular oxidic matrices (PHASE III). This Topical Report reviews work done on Phase III during the period from January 1, 1990 through December 31, 1992.

EXECUTIVE SUMMARY

OBJECTIVE

The objective of this research is to develop new, efficient catalysts for the selective transformation of light alkanes to alcohols for use as fuels, fuel precursors and chemical products. There currently exists no DIRECT one-step catalytic air-oxidation process to convert these substrates to chemical or fuel products. Such a one-step route to fuels or chemicals would represent superior useful technology for the utilization of natural gas and similar refinery-derived light hydrocarbon streams. The mission of this work is to devise a new catalyst which can be used in a simple economic process to convert the light alkanes in natural gas to oxygenated products which can either be used as clean-burning, high octane liquid fuels, as fuel components, or as precursors to liquid hydrocarbon transportation fuel.

APPROACH

We have devised a new catalytic approach to the direct production of alcohols from light

alkanes which grew out of the recognition that metal oxo complexes like those that are intermediates of enzymatic alkane hydroxylations might be generated directly from reaction of air or oxygen with metals in certain supportive molecular environments. We have prepared and tested catalysts designed to form metal oxo intermediates directly by reaction with air or oxygen and find that they are able to convert light alkanes to alcohols under relatively mild conditions.

RESULTS OF WORK CARRIED OUT FROM JANUARY, 1990 THROUGH DECEMBER, 1992

We have investigated three molecular environments which appear to be hospitable ones for the active species that we are trying to generate: A) highly halogenated porphyrinic macrocycles (PHASE I), B) polyoxoanions or heteropolyacids, (PHASE II), and C) regular oxidic lattices such as zeolites and related structures (PHASE III). Work on Phase I has uncovered the most active liquid phase oxidation catalysts yet known for oxidizing isobutane to tert-butyl alcohol. Unprecedented rates and high selectivities have been achieved. We are approaching commercially interesting rates and selectivities in this reaction. Work in PHASE II has shown that two oxidation-active metal centers seem to be able to work cooperatively in the framework of a polyoxometallate to give good rates of propane oxidation. Even the difficult substrates: methane and ethane are oxidized using this catalyst in the liquid phase but rates and selectivities are not yet high. PHASE III studies on metals in zeolitic lattices shows evidence for the need for metal cooperativity in active catalysts. Methane is oxidized to methanol in 70% selectivity and a superior kinetic model provided insight into reaction

mechanisms. Though much progress has been made, catalyst synthesis and reactor design problems are still formidable here. It is with PHASE III that this Topical Report deals.

PHASE III PROGRESS

Progress has been made in four major areas of this work. First, a superior kinetic model was developed to determine the rates, yields and selectivities for methanol formation from methane by gas phase autoxidation. It was essential to know what to expect from homogeneous gas phase oxidations both as a base-line for catalytic studies and to assess literature claims relative to a potential new methane-to-methanol process.

Secondly, catalysts capable of converting methane to methanol were designed synthesized and characterized. Thirdly, suitable reactor systems were designed, built, and lined out as catalyst test units. Finally, the catalytic materials were tested for their activity on methane, ethane, and mixed light gases.

While we have achieved considerable success and have generated the best available catalysts for oxidizing methane directly to methanol, additional design criteria must be incorporated in order to produce materials capable of reaching commercially acceptable targets. We have identified these design criteria and are proceeding to synthesize superior catalysts system.

METHANE OXIDATION KINETIC MODEL

We developed a kinetic model to determine the conditions at which methane and light alkanes oxidize and the expected products as a function of reaction conditions.

We have kinetically modelled vapor phase reactions which are uncatalyzed and those in which gas phase radicals are catalytically produced by homolytic C-H bond cleavage over solid oxidic surfaces. Increased methanol selectivity up to about 65% at ~10% conversion is achieved by catalysis of methyl radical generation. Higher yields of methanol will require participation of a non-radical pathway. Kinetic modelling, therefore, seems to indicate that significant contributions from a selective non-radical pathway are probably required for methanol selectivity over 70%.

CATALYST SYNTHESIS CHARACTERIZATION AND TESTING

We synthesized, characterized and tested new zeolite catalysts which have iron substituted into their siliceous frameworks for vapor phase oxidation of methane to methanol. We have found that the higher the iron content of a framework-substituted zeolite the higher is its catalytic activity for methanol formation. In addition, we have discovered that in a series of iron sodalites, catalysts which have iron in BOTH the framework AND in the proximate extraframework exchange sites are the most active of the iron sodalite catalysts that we have tested. Using these catalysts in a reactor designed to limit contact of products and intermediates with the surface, we produce methanol in

over 70% selectivity at 7% conversion. This is the the most productive direct catalytic synthesis of methanol from methane that we are aware of.

We have also studied the oxidation of ethane over iron exchanged iron sodalite, Fex[Fe]SOD , and compared these results to the known uncatalyzed gas phase oxidation of ethane reported by H. Gesser. Using our active iron sodalite catalyst we have achieved carbon selectivities to liquid oxidate of from 40-60% at ethane conversions of from 6-11% at temperatures below 300. Methanol/ethanol ratios of from 3-9 were observed. Using the molar selectivity calculation of Gesser our selectivities range from 40-70% and seem comparable with his results under similar conditions of temperature and pressure. We would expect to operate at lower temperature with a catalyst but iron sodalite does not allow us to go below the thermal ($\sim 250^\circ\text{C}$) oxidation range.

We have prepared and characterized a series of new catalysts which have iron in the framework of the sodalite structure and either iron, chromium or manganese in the exchange site. In addition to substituting iron, we have also attempted to get chromium and manganese into the sodalite framework. We have managed to get only small amounts of chromium into the framework and have failed in many attempts to make a manganese sodalite. We have made framework-substituted pentasil zeolites containing iron, manganese, chromium and ruthenium. The amount of framework metal which will be accepted by the zeolite is low however - generally less than 3%. We have tested the iron exchanged pentasil zeolite for methane oxidation and found that its activity was

quite a bit inferior to sodalite which had a high concentration of framework iron. We also synthesized tested catalysts which have chromium oxo centers incorporated into surface oxidic layers. Silica surfaces containing discrete chromium oxo units were catalytically active for methane oxidations.

During the period of this project, we were also able to generate for the first time an active and selective methane oxidation catalyst having manganese in the framework of a zeolitic material. In past reports we have disclosed that framework substituted iron sodalite can be an active and relatively selective catalyst for converting methane to methanol. All attempts to incorporate large amounts of manganese into the sodalite framework failed. We further found that iron-exchanged, iron substituted sodalite was a superior oxidation catalyst to manganese-exchanged, iron substituted sodalite. Supported manganese catalysts such as manganese oxides on silica or alumina largely gave combustion to carbon oxides with little or no methanol formed.

We have now found a new and as yet uncharacterized crystalline aluminophosphate phase containing over 8% manganese, MnAPO-X, which catalyzes selective oxidation of methane producing significant amounts of methanol below 400°C. At temperatures below 400°C the new manganese catalyst is at least as active as iron sodalite and produces methanol with equivalent selectivity. We have also prepared an unknown iron aluminophosphate by an analogous preparation and will test its catalytic activity. To our knowledge this class of crystalline aluminophosphates

have not been used to oxidize methane under conditions which give high methanol selectivity.

Methanol had also been formed in good selectivity at conversion levels close to those obtained for the MnAPO-X using iron sodalite catalysts. Because of the manganese results we were encouraged to prepare and test an aluminophosphate catalyst containing large amounts of framework exchanged iron. We prepared the known FAPO-11 phase and tested it under mild conditions. It was not nearly as active as MnAPO-X nor was methanol formed in as high selectivity. It should be noted, however, that the structure of MnAPO-X is quite different than that of FAPO-11.

We have also made MnAPO-5, and CoAPSO-5 and compared these materials with highly pure Fe[SOD]. The former compounds are aluminophosphate structures into whose framework manganese and cobalt are substituted. As we have reported in the past, Fe[SOD] does not have activity because of the difficulty of incorporating Fe(II) into the sodalite structure. The effective Fe(III)/Fe(II) reduction potential, therefore, will be low. When Fe(II) is incorporated into the exchange sites an active catalyst: $\text{Fe}_x\text{Fe[SOD]}$ is prepared. In the case of both MnAPO-5 and CoAPSO-5, the metals may be incorporated in both the (II) and (III) oxidation states. This is important since oxygen will be bound and hopefully activated by Mn(II) and Co(II). We have tested MnAPO-5 for oxidation of both methane and ethane. This catalyst is more active than $\text{Fe}_x[\text{Fe}] \text{SOD}$ and nearly as selective. Using MnAPO-5 we can homolyze the C-H bond of methane at temperatures fully 35°C lower than when $\text{Fe}_x[\text{Fe}] \text{SOD}$ is used as catalyst.

Thus, we have identified three important criteria for a methane to methanol catalyst: (1) stability under reaction conditions (2) proximate metal centers to activate dioxygen and (3) high reversible metal redox potential. Two other criteria were identified and will be necessary for higher methanol selectivity- geometric facilitation of "rebound" of methyl radicals to form methanol on the surface and hydrophobicity to release methanol rapidly from the surface as formed.

We completed a study on the effect of reactor design on the selectivity of iron sodalite catalyzed oxidation of methane to methanol. We find that a complex design having a combination of a low-temperature back-mixed zone over a hot catalyst coupled with reactive distillation gives methanol in 70% selectivity at up to 7% methane conversion (oxygen conversion >90%). As we have mentioned in past reports, this system is too complex to extract unambiguous catalyst screening data. We have constructed three simpler systems which separate the catalytic activity from the reactive distillation aspects. One system operates as a simple downflow reactor in the plug flow mode. In this system under conditions of temperature and pressure comparable to those used in the complex reactor, iron sodalite catalyzes methane oxidation to methanol in 50% selectivity. Another system which operates in a the back-mixed mode gives methanol in up to 30% selectivity at similar temperature, pressure and flow rate. Clearly, reactor design is critical in conducting these oxidations and was closely scrutinized. We concluded that, while simple downflow reactor systems are not

designed to optimize methanol productivity, they are probably the most straightforward way to qualitatively differentiate catalytic efficiency. For this reason we have adopted this technique for screening catalysts at the present time. Reactor design considerations are being addressed in a companion developmental project.

CONCLUSIONS

We have designed a family of new catalytic materials which are effective in the conversion of light alkanes to alcohols or other oxygenates. Until now, the chemical reaction needed to produce the desired oxygenates from alkanes could only be accomplished selectively by specialized enzymatic systems operating in vivo. These systems are impractical for commercial fuel production. Aided by computer-assisted molecular design techniques we have created a family of synthetic catalysts which may operate based on fundamental principles similar to those employed by the biological systems. Our new catalysts, however, can be synthesized in the laboratory from inexpensive raw materials. Using these molecular engineering concepts, we have designed, synthesized and tested a group of oxidatively and thermally robust catalysts for both liquid and vapor phase oxidation of light alkanes. More work is needed, however, to increase the $M(III)/(II)$ reduction potentials of these catalysts. We have used both polyoxometallate catalysts and zeolites containing oxidation-active first row metals to oxidize light alkanes in the vapor phase. Not only are these materials oxidatively and thermally stable, but they can accommodate proximate metal centers

within the support environment, a property that may ultimately be important in obtaining high oxidation rates. To date we have achieved over 70% alcohol selectivity at conversions in excess of 7% in the oxidations of both methane and ethane over an iron sodalite catalyst. This is much better than we can achieve when we conduct thermal non-catalytic methane or ethane oxidations. We are beginning a program aimed at synthesizing these active centers in a hydrophilic surface environment for greater activity and selectivity.

A suprabiotic catalyst which oxidizes methane to methanol on the surface must, in addition to being able to homolyze C-H bonds readily, be able to repel methanol from the surface rapidly before it oxidizes further. Thus a major future thrust of this program is to prepare iron (or other oxidation-active metal) species with high $M(III)$ reduction potentials in hydrophobic surface cavities. Work is proceeding toward that end.

5.1 VAPOR PHASE OXIDATIONS OVER SURFACE SUPRABIOTIC SYSTEMS

This project is an experimental approach to the design, synthesis, characterization and testing of oxidation-active transition metal centers for cleaving the dioxygen molecule and producing metal oxo intermediates which react with alkanes to convert them to alcohols. The molecular environment in which the oxidation-active metal center is located is critical in generating active catalysts. It must tune the center electronically to access appropriate oxidation states and should enable two metal centers to participate in the oxygen splitting process. We are investigating three molecular environments which could be hospitable ones for the active species that we are trying to generate: a) perhaloporphyrin, perhalophthalocyanine or related macrocycles, b) polyoxometallates and c) regular oxidic lattices such as zeolites and related structures. We are testing these three sets of catalysts for activity in the mild oxidation of light alkanes (isobutane, propane, ethane and methane).

During the initial phases of this work we have supported metals in macrocyclic environments and in Keggin ions on a variety of carriers for use as heterogeneous catalysts. We have examined the oxidation of methane and natural gas over these systems. While several of these systems are active, the iron-containing catalysts were unique in the amount of methanol that was produced. Even more striking was the yield and selectivity obtained over catalysts in which iron was incorporated into an ordered oxidic matrix such that two irons could communicate either through space or through a μ -oxo ligand. We have achieved oxidation of methane over one of these systems in >70% selectivity

at 90% oxygen conversion, Table 9. We will continue a vigorous program of inorganic synthesis to construct superior heterogeneous catalyst for selective methane oxidation.

As was mentioned earlier, methane monooxygenase has proximate metal sites. On contemplating various roles for the proximate iron atoms in catalytic oxidation, the direct formation of a diiron-peroxo species seemed possible. Using the same principles as discussed for the macrocyclic systems, the μ -peroxo species could cleave to give adjacent iron oxo sites which could activate an alkane, Eq. 3 (schematically).

We have synthesized a Keggin structure with three iron atoms in close proximity separated by only oxide bridges. The triiron structure demonstrated unique catalytic activity in both liquid and vapor phase (1). It may be critical that the metal centers be proximate for vapor phase activity of the type that we envision. In solution, μ -peroxo species are formed readily. On a surface an immobile iron center cannot readily do this unless it is already proximate to another iron center, Eq. 3.

If metal alkyl intermediates are formed from surface oxo species, they probably have quite weak metal alkyl bonds. Homolysis of the metal-carbon bond could well occur under the higher temperature conditions under which the gas phase reactions will be run. It is not unlikely, therefore,

that a significant portion of the reaction products from vapor phase oxidations over surface suprabiotic systems will be formed via subsequent reactions of gas phase methyl radicals. For this reason we set up a kinetic model using available rate constants for all of the major reaction steps in an effort to determine whether gas phase oxidation of methane would be expected to give methanol in yields high enough to be practical. We believe that the component of the reaction which proceeds through gas phase methyl radicals can be reasonably selective at modest conversions. Kinetic modelling work continues in an effort to quantify the results.

5.2 DEVELOPMENT AND APPLICATION OF A KINETIC MODEL FOR OXIDATION OF METHANE

5.2.1 Summary and Conclusions

This section condenses initial work on modeling the homogeneous oxidation of methane, converging the basic 1-carbon set of reactions and expansion to include 2-carbon kinetics in both plug-flow (or batch) and back-mixed reactors. As a general example, we use the reaction of 3:1 methane:air at 400°C and 815 psi, which approximates many of the laboratory experiments. For applying the models, our target was to find a process which converts at least 20% of the methane to methanol at 80% selectivity.

The basic model is a set of 61 equations, updated from work of Bedeneev, et. al., (2) solved for given conditions by SIMUSOLV, a commercial batch (or plug-flow) isothermal process simulator. Calculating all of the predominant 19 species present, the model finds that the oxidation starts slowly and builds up to a high rate which drops off quickly as the oxygen is depleted. Detailed examination of all reactions, Figure 1A, confirms that the main path is oxygen combining with methyl radicals to ultimately make methoxy radical, which abstracts hydrogen from methane to form methanol and make new methyl radical. Branching comes from splitting peroxy compounds into two radicals. Most of the competing oxidation to carbon monoxide and water proceeds by abstracting hydrogen from methanolic carbon. Over the range 380-450°C, methanol selectivity is favored by high temperature, low oxygen, and high methane. The model was adjusted to lower the oxidation rate by solid glass surface: however, it seems to overcorrect for high surface solids.

One accepted path for catalysis of methane oxidation is formation and emission of methyl radicals, the simulation of which is possible by adding that reaction to the model. Adjusting the rate constant to higher and higher values showed methanol selectivity going through a maximum followed first by formaldehyde and finally by ethane. Nearly 80% selectivity to methanol is observed at 4% methane conversion using 2.5 % oxygen, but selectivity drops at higher oxygen (and higher conversion). Thus, our commercial target is not likely to be obtained solely with this type of catalysis in a plug-flow reactor. The model gives good agreement with the few sets of homogeneous conditions reported in the literature. An exception is a 1988 paper by Gesser and coworkers (8);

FIGURE 1A

SIMPLIFIED RADICAL CASCADE TO METHANOL *

* MODEL INCLUDES UP TO 86 INDIVIDUAL REACTIONS: S = SURFACE.

however, these authors subsequently reported reactor instability.

5.2.2 Basic Model for Methane Oxidation

This model, the workhorse of our program, has been used to examine the overall course of the homogeneous oxidation, rank the importance of reactions, look at the effect of variables, check the impact of adding solid surfaces, predict the results of catalysis, and interpret experimental results.

5.2.2.1 The Model Basics

The original set of reactions for this model was taken from a paper by Bedeneev, Gol'denberg, Gorban, and Teitel'boim, Kin & Kat (Trans) 29 7-13 (1988)(2). In the present set, displayed in Table 5.1, only Reactions 14 and 53 have been updated; however, the new rate constant for #14, $\text{CH}_3\text{O}\cdot + \text{CH}_4 = \text{CH}_3\text{OH}\cdot + \text{CH}_3\cdot$, increases the selectivity to methanol from 30 to 58% when charging 25% air in methane at 400RC and 850 psi. The new rate constant for #53 is about 3 times larger than the old but has less effect on the overall production of carbon dioxide.

Simusolv, a commercial modelling and simulation software, was used to solve the 61 differential equations by Gear stiff integration. We have found that running the integration for a very short time, less than 1% of the total run time, serves to initialize all of the species and allow trouble-free operation for the rest of the run. Also, adding an adjustable factor common to all of the rate

TABLE 5-1

RATE CONSTANTS FOR GAS PHASE METHANE OXIDATIONS

	Con	A	E	380 C	390 C	400 C
1. $\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	K1	1E-10	-55972	1.862103E-29	3.568119E-29	6.706309E-29
2. $\text{CH}_3 + \text{HO}_2 = \text{CH}_4 + \text{O}_2$	K2	1E-12	0.00	1E-12	1E-12	1E-12
3. $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{OO}$	K3	2E-12	0.00	2E-12	2E-12	2E-12
4. $\text{CH}_3\text{OO} = \text{CH}_3 + \text{O}_2$	K4	8.9E+13	-31285	3023.030137	4348.175427	6187.018059
5. $\text{OH} + \text{CH}_4 = \text{H}_2\text{O} + \text{CH}_3$	K5*	1.32E-17	-2688	4.226E-13	4.489E-13	4.7821E-13
6. $\text{CH}_3\text{OO} = 2\text{CH}_3\text{O} + \text{O}_2$	K6	1.71E-13	0.00	1.71E-13	1.71E-13	1.71E-13
7. $2\text{CH}_3\text{OO} = \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	K7	7.4E-14	0.00	7.4E-14	7.4E-14	7.4E-14
8. $\text{CH}_3\text{OO} + \text{CH}_3 = 2\text{CH}_3\text{O}$	K8	4.5E-11	0.00	4.5E-11	4.5E-11	4.5E-11
9. $\text{CH}_3\text{OO} + \text{HO}_2 = \text{CH}_3\text{OOH} + \text{O}_2$	K9	7.7E-14	2599	5.704244E-13	5.534565E-13	5.374753E-13
10. $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	K10	3E-11	0.00	3E-11	3E-11	3E-11
11. $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	K11	2.2E-13	1230	5.6757E-13	5.595165E-13	5.518114E-13
12. $2\text{CH}_3 = \text{C}_2\text{H}_6$	K12	4E-11	0.00	4E-11	4E-11	4E-11
13. $\text{CH}_3\text{O} + \text{HO}_2 = \text{CH}_3\text{OH} + \text{O}_2$	K13	1.7E-11	0.00	1.7E-11	1.7E-11	1.7E-11
14. $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$	K14**	1.7E-10	-14863	1.8068E-15	2.1473E-15	2.5309E-15
15. $\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	K15	1E-13	-2599	1.349872E-14	1.391257E-14	1.432624E-14
16. $\text{CH}_3\text{O} = \text{CH}_2\text{O} + \text{H}$	K16	1E+14	-29986	9241.422637	13093.285546	18359.588310
17. $\text{CH}_3\text{OO} + \text{CH}_4 = \text{CH}_3\text{OOH} + \text{CH}_3$	K17	1E-12	-21491	6.433299E-20	8.258052E-20	1.052203E-19
18. $\text{CH}_3\text{OO} + \text{CH}_2\text{O} = \text{CH}_3\text{OOH} + \text{CHO}$	K18	4.7E-13	-11995	4.551899E-17	5.232624E-17	5.990295E-17

TABLE 5-1 (Cont'd)

RATE CONSTANTS FOR GAS PHASE METHANE OXIDATIONS

19. $\text{HO}_2 + \text{CH}_2\text{O} = \text{H}_2\text{O}_2 + \text{CHO}$	K19	2E-12	-10994	4.188812E-16	4.75956E-16	5.387589E-16
20. $\text{CH}_3 + \text{CH}_2\text{O} = \text{CH}_4 + \text{CHO}$	K20	1.4E-12	-6952	6.603431E-15	7.158953E-15	7.74266E-15
21. $\text{CH}_3\text{O} + \text{CH}_2\text{O} = \text{CH}_3\text{OH} + \text{CHO}$	K21	1E-12	-3598	6.251666E-14	6.518555E-14	6.7884E-14
22. $\text{OH} + \text{CH}_2\text{O} = \text{H}_2\text{O} + \text{CHO}$	K22	1.25E-11	-174	1.093161E-11	1.095373E-11	1.097524E-11
23. $\text{H} + \text{CH}_4 = \text{H}_2 + \text{CH}_3$	K23	1.3E-10	-11921	.33291E-14	1.530927E-14	1.751139E-14
24. $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	K24	1E-32	909	2.014559E-32	1.993394E-32	1.973071E-32
25. $\text{H} + \text{CH}_2\text{O} = \text{H}_2 + \text{CHO}$	K25	3.27E-11	-3667	1.938447E-12	2.022822E-12	2.108199E-12
26. $\text{CHO} + \text{O}_2 = \text{CO} + \text{HO}_2$	K26*	5.5E-11	0.00	4.1149E-12	4.0899E-12	4.0655E-12
27. $\text{CHO} + \text{M} = \text{CO} + \text{H} + \text{M}$	K27	4E-10	-16992	8.2414E-16	1.004021E-15	1.21601E-15
28. $\text{CH}_3\text{OOH} = \text{CH}_3\text{O} + \text{OH}$	K28	4E+15	-42979	16.593244	27.340345	44.384696
29. $\text{H}_2\text{O}_2 = 2\text{OH}$	K29	3E+14	-48958	0.012423	0.021942	0.038105
30. $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	K30*	1.06E-17	-1488	1.4369E-12	1.5070E-12	1.5791E-12
31. $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$	K31	5.6E-12	-22289	1.947986E-19	2.523809E-19	3.244782E-19
32. $\text{CH}_3\text{OO} + \text{H}_2 = \text{CH}_3\text{OOH} + \text{H}$	K32	3.6E-12	-22289	1.252277E-19	1.622448E-19	2.085931E-19
33. $\text{CH}_3\text{O} + \text{H}_2 = \text{CH}_3\text{OH} + \text{H}$	K33	3.6E-12	-9986	1.639351E-15	1.841033E-15	2.060411E-15
34. $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$	K34	3.6E-12	-10789	8.830044E-16	1.000931E-15	1.13039E-15
35. $\text{CH}_3\text{OO} + \text{CH}_3\text{O} = \text{CH}_3\text{OOH} + \text{CH}_2\text{O}$	K35	1.5E-12	0.00	1.5E-12	1.5E-12	1.5E-12
36. $\text{CH}_4 + \text{HO}_2 = \text{CH}_3 + \text{H}_2\text{O}_2$	K36	3E-12	-21491	1.92999E-19	2.477416E-19	3.156609E-19
37. $\text{CH}_3 + \text{CH}_3\text{OH} = \text{CH}_4 + \text{CH}_2\text{OH}$	K37	3.3E-13	-9795	1.740997E-16	1.95085E-16	2.178618E-16
38. $\text{CH}_3\text{OO} + \text{CH}_3\text{OH} = \text{CH}_3\text{OOH} + \text{CH}_2\text{OH}$	K38	5E-13	-14393	7.631648E-18	9.020812E-18	1.060999E-17

TABLE 5-1 (Cont'd)

RATE CONSTANTS FOR GAS PHASE METHANE OXIDATIONS

39. $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	K39	2E-12	0.00	2E-12	2E-12	2E-12
40. $\text{HO}_2 + \text{CH}_3\text{OH} = \text{H}_2\text{O}_2 + \text{CH}_2\text{OH}$	K40	1.5E-12	-14393	2.289494E-17	2.706244E-17	3.182998E-17
41. $\text{OH} + \text{CH}_3\text{OH} = \text{H}_2\text{O} + \text{CH}_2\text{OH}$	K41	5.7E-12	-1400	1.938175E-12	1.96995E-12	2.001288E-12
42. $\text{OH} + \text{CH}_3\text{OH} = \text{H}_2\text{O} + \text{CH}_3\text{O}$	K42	1.7E-11	-3299	1.338134E-12	1.390421E-12	1.443107E-12
43. $\text{CH}_3\text{O} + \text{CH}_3\text{OH} = \text{CH}_3\text{OH} + \text{CH}_2\text{OH}$	K43	6.6E-13	-5296	1.115155E-14	1.18593E-14	1.258893E-14
44. $\text{H} + \text{CH}_3\text{OH} = \text{H}_2 + \text{CH}_2\text{OH}$	K44	2.16E-11	-5256	3.763834E-13	4.00085E-13	4.245083E-13
45. $\text{H} + \text{H}_2\text{O}_2 = \text{OH} + \text{H}_2\text{O}$	K45	3E-10	-6297	2.34394E-12	2.521862E-12	2.707397E-12
46. $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$	K46	3.7E-12	-516	2.486176E-12	2.501126E-12	2.515718E-12
47. $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2 + \text{HO}_2$	K47	1.7E-11	-4998	3.61377E-13	3.829839E-13	4.05183E-13
48. $\text{CH}_3\text{OO} + \text{H}_2\text{O}_2 = \text{CH}_3\text{OOH} + \text{HO}_2$	K48	2.5E-13	-12993	1.122206E-17	1.305075E-17	1.510951E-17
49. $\text{CH}_3\text{O} + \text{H}_2\text{O}_2 = \text{CH}_3\text{OH} + \text{HO}_2$	K49	2.5E-13	-3990	1.155474E-14	1.210302E-14	1.265987E-14
50. $\text{CH}_3 + \text{H}_2\text{O}_2 = \text{CH}_4 + \text{HO}_2$	K50	2.5E-13	-2797	2.897181E-14	2.99288E-14	3.088757E-14
51. $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$	K51*	2.5E-17	764	2.0565E-13	2.0790E-13	2.1016E-13
52. $\text{HO}_2 + \text{CO} = \text{OH} + \text{CO}_2$	K52	1.7E-10	-22981	3.469618E-18	4.531522E-18	5.871665E-18
53. $\text{CH}_3\text{O} + \text{CO} = \text{CH}_3 + \text{CO}_2$	K53**	1.83E-12	-6939	8.718522E-15	9.450552E-15	1.021954E-14
54. $2\text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{CH}_2\text{O}$	K54	3E-11	0.0	3.8E-11	3.8E-11	3.8E-11
55. $\text{CH}_3 + \text{CH}_3\text{O} = \text{CH}_4 + \text{CH}_2\text{O}$	K55	2.8E-11	0.00	2.8E-11	2.8E-11	2.8E-11
56. $\text{CH}_3 + \text{Solid} = (1.5\text{H}_2 + x\text{CO} + y\text{CO}_2)$	K56	0.005z	0.00			
57. $\text{CH}_3\text{OO} + \text{Solid} = (1.5\text{H}_2\text{O} + x\text{CO} + y\text{CO}_2)$	K57	0.005z	0.00			
58. $\text{HO}_2 + \text{Solid} = (.5\text{H}_2\text{O} + \text{O}_2)$	K58	0.005z	0.00			

TABLE 5-1 (Cont'd)

RATE CONSTANTS FOR GAS PHASE METHANE OXIDATIONS

59. $\text{CH}_3\text{OOH} + \text{Solid} = (1.5\text{H}_2\text{O} + x\text{CO} + y\text{CO}_2)$	K59	$0.005z$	0.00
60. $\text{H}_2\text{O}_2 + \text{Solid} = (\text{H}_2\text{O} + .5\text{O}_2)$	K60	$0.0015z$	0.00
61. $\text{H}_2\text{O}_2 + \text{Solid} = (\text{H}_2\text{O} + .5\text{O}_2)$	K61	$0.0015z$	0.00

where $z = (3.23\text{E}11 \exp(-31600/\text{RT}))(1.574/\text{DIA} + [\text{SA}]1.4\text{E}4)$ for DIA = diameter of quartz reactor in inches, SA = surface area of quartz packing in sq. meters/cc.

(1) Bedeneev et al, Transl. from Kin & Kat 29 7-13 (1988).

* Factor T^x in rate constant where for K5, $x = 1.92$; K26, $x = -0.4$; K30, $x = 2$; K51, $x = 1.3$.

** K14 from Los Alamos: Wantuck et al, 22nd Int. Symp. on Comb. Seattle, 8/14/88. TIC Abst. 1582580 of TIC Report LA-UR-88-186. K53 calculated from Wantuck, et al, Chem Phys Let 138 548-52 (1987).

NOTE: IN THIS TABLE E MEANS THE EXPONENTS OF 10; THUS, $\text{E-14} = 10^{-14}$. EXP IS USED TO DESIGNATE THE NATURAL BASE; THUS, EXP-14 MEANS NATURAL BASE e^{-14} .

constants allows the time scale to be shifted to smaller units, thereby enabling operations at extremes of variables including run time and temperature.

5.2.2.2 Air Oxidation of Methane

The simple model is batch, starting from zero time with a premixed, preheated gas at constant temperature and pressure. (Because expansion or contraction of volume is always less than 2%, the same data can be used for a plug-flow reactor at various residence times.) Typically, the test reaction in this report will be 3:1 methane:air at 400°C and 815 psi. Figures 5-1, 5-2 and 5-3 illustrate the course of the oxidation according to the model:

1. The oxygen curve in Figure 5-1 shows that oxidation is quite slow at first and increases rapidly as the radicals build up, so that only 15% of the oxygen is used up in the first 8 seconds and then completely exhausted in the next 8 seconds. This means that, in the final stages, the experimenter cannot easily stop the reaction reproducibly short of completion. Most of the published data are taken at very long residence times, presumably where the results can be repeated. Only recently has there been a report (3) (Ritz and Baiker, I.E.C. Res. 30 2287 [1991]) where space velocities have been sufficiently high to examine the early stages of the reaction. Unfortunately, the preheated gases were not premixed, so that their initially high ethylene yield cannot be compared to our model.

FIGURE 5-1

METHANE OXIDATION (mole/cc)
3:1 METH:AIR, 400C, 815psi

2. An interesting feature of the model reaction is the long "tail" which keeps on going long after the oxygen has been exhausted. The reason for this behavior is hydrogen peroxide which builds up and then decays to produce radicals. Experimentally, little or no peroxide is observed, perhaps because of:

- a. Very long residence times so that the peroxide decomposes before the reaction is quenched.
- b. Error in some of our rate constants.
- c. Catalyzed decomposition of the peroxide by surfaces either in or after the reactor. Many solids are known to be active.

3. Figures 5-1 and 5-2 illustrate what happens to all species in the reaction. When the oxygen is being consumed, the products increase while intermediates generally rise and then decline. After oxygen is gone (about 16.5 sec), the reaction changes dramatically. Peroxides decline, methanol and formaldehyde are consumed, and the important products become ethylene, hydrogen, and $\bullet\text{CH}_2\text{OH}$. During regular oxidation, concentrations of H and OH are very low; $\bullet\text{CH}_3$, $\bullet\text{CHO}$ and $\bullet\text{CH}_2\text{OH}$ low; $\text{HO}_2\bullet$ is higher; and $\text{CH}_3\text{O}\bullet$ is very high. Upon depletion of the oxygen, $\bullet\text{CH}_2\text{OH}$ becomes the most stable intermediate.

4. Variation of the product distribution with time appears in Figure 5-3, along with the methane conversion, which with 3:1 methane:air grows to about 6.7%. Note that the post-oxygen

FIGURE 5-2

METHANE OXIDATION - FORMATION OF INTERMEDIATES WITH TIME

FIGURE 5-3

METHANE OXIDATION - % CARBON SELECTIVITY OF PRODUCTS

3:1 METH:AIR, 400C, 815PSI

reaction drops methanol selectivity from an encouraging 55% to 44%, so that the existence of a 'tail' becomes an important consideration. Experimentally, one generally sees lower methanol, low hydrogen peroxide, low formaldehyde and high carbon dioxide; so, perhaps the 'tail' is taking place at the very long residence times customarily employed. It is interesting that formaldehyde starts out as 30% of the product and drops continuously to 1% or less.

5.2.2.3 Important Reactions In the Oxidation

The step-wise single-electron oxidation of methane to methanol requires Removal of one hydrogen to $\bullet\text{CH}_3$, conversion somehow to $\text{CH}_3\text{O}\bullet$, followed by abstraction of H to produce methanol. Working backwards, we looked at the important sources of $\text{CH}_3\text{O}\bullet$ which are $\text{CH}_3\text{OO}\bullet$ and CH_3OOH . These, inturn, are made from $\bullet\text{CH}_3$ by addition of an oxygen molecule. To get a precise picture, we asked Simusolv to calculate the % contribution of all the reactions which make or destroy CH_3OH , $\text{CH}_3\text{O}\bullet$, $\text{CH}_3\text{OO}\bullet$, CH_3OOH , and $\bullet\text{CH}_3$. The simplified Table 5-2 lists the predominant reactions.

As expected, the model pictures the familiar autoxidation model for oxidation of methane to methanol:

TABLE 5-2

RELATIVE IMPORTANCE OF REACTIONS, PER CENT
3:1 Methane:Air

<u>Reaction</u>	<u>815#</u> <u>380C</u>	<u>815#</u> <u>400C</u>	<u>815#</u> <u>420C</u>	<u>1015#</u> <u>400C</u>
<u>Make Methanol</u>				
14. $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$	66	81	63	72
7. $2\text{CH}_3\text{OO} = \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	8	14	7	11
43. $\text{CH}_3\text{O} + \text{CH}_3\text{OH} = \text{CH}_3\text{OH} + \text{CH}_2\text{OH}$	12	2	13	6.1
<u>Destroy Methanol</u>				
40. $\text{HO}_2 + \text{CH}_3\text{OH} = \text{H}_2\text{O}_2 + \text{CH}_2\text{OH}$	29	28	25	28
43. $\text{CH}_3\text{O} + \text{CH}_3\text{OH} = \text{CH}_3\text{OH} + \text{CH}_2\text{OH}$	27	18	29	24
38. $\text{CH}_3\text{OO} + \text{CH}_3\text{OH} = \text{CH}_3\text{OOH} + \text{CH}_2\text{OH}$	17	38	14	24
41. $\text{OH} + \text{CH}_3\text{OH} = \text{H}_2\text{O} + \text{CH}_2\text{OH}$	16	10	22	14
<u>Make Methoxy</u>				
28. $\text{CH}_3\text{OOH} = \text{CH}_3\text{O} + \text{OH}$	51	28	67	48
6. $2\text{CH}_3\text{OO} = 2\text{CH}_3\text{O} + \text{O}_2$	34	44	26	47
<u>Destroy Methoxy</u>				
14. $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$	65	72	49	68
15. $\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	4	21	4	17
21. $\text{CH}_3\text{O} + \text{CH}_2\text{O} = \text{CH}_3\text{OH} + \text{CHO}$	9	3	27	7
43. $\text{CH}_3\text{O} + \text{CH}_3\text{OH} = \text{CH}_3\text{OH} + \text{CH}_2\text{OH}$	12	2	10	6
<u>Make Methyl Peroxy</u>				
3. $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{OO}$	100	100	100	100
<u>Destroy Methyl Peroxy</u>				
4. $\text{CH}_3\text{OO} = \text{CH}_3 + \text{O}_2$	*	*	*	*
6. $2\text{CH}_3\text{OO} = 2\text{CH}_3\text{O} + \text{O}_2$	33	48	32	40
9. $\text{CH}_3\text{OO} + \text{HO}_2 = \text{CH}_3\text{OOH} + \text{O}_2$	30	17	31	25
7. $2\text{CH}_3\text{OO} = \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	14	21	13	17

TABLE 5-2 (Cont'd)

<u>Make Methyl Hydrogen Peroxide</u>				
9. $\text{CH}_3\text{OO} + \text{HO}_2 = \text{CH}_3\text{OOH} + \text{O}_2$	60	96	60	59
18. $\text{CH}_3\text{OO} + \text{CH}_2\text{O} = \text{CH}_3\text{OOH} + \text{CHO}$	12	2	11	14
38. $\text{CH}_3\text{OO} + \text{CH}_3\text{OH} = \text{CH}_3\text{OOH} + \text{CH}_2\text{OH}$	15	1	14	12
48. $\text{CH}_3\text{OO} + \text{H}_2\text{O}_2 = \text{CH}_3\text{OOH} + \text{HO}_2$	10	0.4	12	7
<u>Destroy Methyl Hydrogen Peroxide</u>				
28. $\text{CH}_3\text{OOH} = \text{CH}_3\text{O} + \text{OH}$	100	100	100	100
<u>Make Methyl</u>				
4. $\text{CH}_3\text{OO} = \text{CH}_3 + \text{O}_2$	*	*	*	*
14. $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$	55	50	58	55
5. $\text{OH} + \text{CH}_4 = \text{H}_2\text{O} + \text{CH}_3$	38	43	35	38
<u>Destroy Methyl**</u>				
3. $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{OO}$	87	88	97	98

*Equations 3 and 4 represent an equilibrium favoring the formation of CH_3OO ; therefore, equation 4 does not give any net formation of CH_3 or removal of CH_3OO .

**Since the equilibrium favors formation of CH_3OO , the rate of equation 3 is greater than 4 and the net rate of removal of CH_3 is equation 3 minus equation 4. This difference was used in comparing the various rates of destroying methyl.

Propagation:

Side reactions are the abstraction of hydrogen from both $\text{CH}_3\text{O}\cdot$ and methanol to yield formaldehyde and $\cdot\text{CH}_2\text{OH}$, followed by further oxidation to carbon oxides and water. Modest changes in temperature and/or pressure can have significant effect on the competitive reactions.

5.2.2.4 Effect of Reaction Variables

Temperature, pressure, and initial reagent concentrations are adjustable parameters:

1. The effect of temperature on reaction of 3:1 methane: air mixtures is shown in Figures 5-4 (a) and (b). As expected, the rate of oxidation increases with temperature. Also, selectivity to methanol goes up, especially as long residence times when reaction after oxygen depletion is allowed to occur. (At higher temperature, less peroxide builds up so the tail is less.)

2. Increasing the pressure from 615 to 1015 psi raises the rate somewhat but has little effect on product distributions in Figures 5-4 (c) and (d).

3. Figure 5-5 a,b,c, and d show how raising initial concentration of pure oxygen from 2 to 20% changes methanol selectivity from 70% down to 11-26%, depending on residence time. The time for complete consumption of oxygen increases simply because there is more to use up. Formaldehyde increases during the oxidation but, by the time all oxygen is gone, has dropped off to about the same low levels in all cases.

4. Methane-lean mixtures yield low selectivities to methanol. In Figures 5-6a and 5-6b the MeOH:CO ratio is about 1.1 at 3:1 methane:air and 430°C, but goes down to about 0.25 when the methane concentration is dropped to 10% by substituting nitrogen. Even lower methane concentrations, 5% in oxygen in Figure 5-6c reacts very slowly to carbon oxides and water. The over-riding reason is that lowering methane allows much more hydrogen abstraction from other species, including methanol, and results finally in their complete oxidation. This is clearly illustrated in Figure 5-6d where, as methane is depleted, intermediates first grow and then drop rapidly as they in turn are oxidized.

5.2.2.5 Inhibition by Solid

A unique feature of the Bedenev et.al. model is inclusion of equations 56-61 to adjust

FIGURE 5.4

EFFECT OF TEMPERATURE AND PRESSURE ON METHANOL SELECTIVITY

FIGURE 5.5

EFFECT OF OXYGEN PRESSURE ON METHANE SELECTIVITY

EFFECT OF LOW METHANE CONCENTRATION ON METHANE SELECTIVITY

for quartz surface. In U.S. Patent 4,918,249 to Sun (4), we report some data for oxidation of methane over glass beads. We modified the Russian reactions to make oxidized products shown in Table 5-3a and used proportionality constants to adjust an inhibition rate constant Z which in turn, was adjusted so that oxygen was consumed in the same time as the experiment. Matching experimental and calculated ratios of $\text{CO}_2:\text{CO}$ yielded a value of 56:44. Table 5-3b summarizes these numbers and shows the averaging of the preexponential factors to give the final expression: $Z = 9.8\text{E}13 \exp(-31,600/\text{RT})$. If Z is proportional to glass surface area (we used $.03\text{m}^2/\text{gm}$ beads in a .5 inch I.D., 10 cc reactor), this corresponds to $Z=1$ in an empty reactor at 313°C . Bedeneev et. al., used data at 341 and 313°C , so the agreement is excellent. Also, note in Table 5-3b that selectivity to methanol by model and experiment agree precisely at the two low oxygen conversions but not at the two higher.

If inhibition is proportional to surface area, one can calculate the effect of a high-surface solid catalyst (assuming the same reativity as glass surface). Inhibition by methyl has little effect and can be ignored in our system. But, in Table 5-3c, even a $1\text{ m}^2/\text{gm}$ solid quenches the reaction completely. On closer scrutiny, the culprit is the MeOOH (and $\text{MeOO}\bullet$). Either the Russian rate constants for destruction of MeOO are too high or the peroxide is broken into radicals which continue the chain. HOOH and $\text{HOO}\bullet$ removal slows the reaction at $100\text{ m}^2/\text{gm}$, so that the oxidation proceeds only to 97% oxygen consumed and then levels off. Destruction by a surface prevents build-up of peroxide and thus eliminates the post-oxygen reaction 'tail' and the accompanying drop in methanol yield.

TABLE 5-3(a)

Modified Solid Reactions

Assume all adsorbed carbon goes to carbon oxides.

Y=fraction of adsorbed carbon to CO₂.

	<u>Reaction</u>	<u>Rate Constant</u>
56.	$\text{CH}_3 + (1.25 + .5Y)\text{O}_2 = 1.5\text{H}_2\text{O} + Y\text{CO}_2 + (1-Y)\text{CO}.$	.005Z
57.	$\text{CH}_3\text{OO} + (.25 + .5Y)\text{O}_2 = 1.5\text{H}_2\text{O} + Y\text{CO}_2 + (1-Y)\text{CO}.$	.005Z
58.	$\text{HO}_2 = .5\text{H}_2\text{O} + .75\text{O}_2.$	.005Z
59.	$\text{CH}_3\text{OOH} + (.5 + .5Y)\text{O}_2 = 2\text{H}_2\text{O} + Y\text{CO}_2 + (1-Y)\text{CO}.$	.005Z
60.	$\text{H}_2\text{O}_2 = \text{H}_2\text{O} + .5\text{O}_2.$	.0015Z
61.	$\text{H}_2\text{O}_2 = \text{H}_2\text{O} + .5\text{O}_2.$	.0015Z

TABLE 5-3(b)

Calculation of the Preexponential Factor of Z
 3:1 Methane:Air, 815 psi

<u>Run</u>	<u>T.C</u>	<u>Time</u> <u>Sec</u>	<u>% O₂</u> <u>Conv</u>	<u>Calc*</u> <u>Z</u>	<u>Alc Sel</u>		<u>CO₂/CO*</u>		<u>Preexp</u> <u>Factor</u>
					<u>Exp</u>	<u>Calc</u>	<u>Exp</u>	<u>Calc</u>	
29	407	39.2	7	6802	47	46	1.0	.45	9.7xE13
31	418	38.6	11	10700	44	45	.61	.45	10.5xE13
32	422	38.4	26	10721	56	46	.35	.32	9.2xE13
33	430	37.9	38	14946	56	44	.29	.33	9.9xE13
Average									9.8xE13

*Z calculated by matching the model reaction time to that seen experimentally (US patent 4,918,249). Plotting log Z versus 1/T gives E_{act} = 31.6 kcal. Forcing a match of experimental versus calculated CO₂:CO ratios gives a value of 56:44.

TABLE 5-3(c)

High Surface Area Silica
 3:1 Methane:Air, 440 C, 815 psi

SA, m ² /gm	0	1	1	100
Quench COO		Yes	No	No
Seconds	4.0	N.R.	15	29
GHSV	2E4		5E3	3E3
%O left	None		None	3**
Sel, %Alc	52.7		51.6	53.1
CO	38.5		38.3	34.5
CO ₂	2.2		2.0	1.0
Formald	6.4		8.1	11.4
Meth Conv	7.2		7.4	7.5

**At the end of reaction time, oxygen levels off and oxidation stops.

This brings up a problem with using a single model to predict catalyzed reactions. Generally, catalysts are high surface area solids supporting transition metals, like iron, which are known to be very active peroxide decomposers, perhaps a million times more potent than silica, and should quench the homogeneous oxidation completely. Since methane is oxidized, the model would predict that either the peroxide is broken into radicals which are emitted into the vapor phase, or the catalyzed oxidation occurs completely on the surface.

5.2.2.6 Decomposition of Methanol

The decomposition of methanol to CO and H₂ is catalyzed by some metals, for example copper, particularly under reducing conditions. As expected, the model shows a large increase in hydrogen when this reaction becomes important. Also, methanol should continue to drop at longer residence times. This reaction is not a part of the model at this time.

5.2.2.7 Catalysis of Methyl Radicals

One way to catalyze oxidation of methane to methanol is to create methyl radicals on a solid surface and eject them into the vapor phase. Such a situation can be modelled by adding the catalytic reaction and adjusting its rate constant. As the reaction, we chose:

A careful check of all species in reaction of 3:1 methane:Air at 400°C showed that a moderate quantity level of catalysis has no effect on most of them. Methanol:CO ratio goes up a little, methyl peroxide increases while hydrogen peroxide goes down, and CHO becomes more favored. Overall, however, the oxidation looks much the same, except for the expected rate increase.

Next, the rate constant was increased gradually to a very high value, with the results listed in Table 5-4a and pictured in Figure 5-7. The carbon oxides decrease while methanol goes through a maximum. Formaldehyde goes up gradually at first and then jumps to become the major product. The numbers in parentheses at the bottom of the graph are the fraction of methyls supplied by the catalyst, indicating that, at the large rate constant, very few are being made in the vapor phase. Raising the temperature gives much the same overall picture, except that the rate constant does not have to be so large to make maximum methanol. Changing the catalytic reaction to produce methyl and hydroxyl radicals has only minor effect on product distributions.

In practice, catalyst activity would probably be adjusted to achieve maximum methanol; therefore, we settled on that point to make the variable comparisons displayed in Tables 5-4b and 5-4c. Methanol selectivity is favored by high temperature, low oxygen, and independent of pressure (from 15 to 55 atm). The highest methanol in these Tables is a little less than 80% at 2.5% oxygen charged--and only 4% methane conversion. Thus, the model predicts that our target of high selectivity at high conversions is unlikely by this type of catalysis.

METHANE OXIDATION
CATALYZED $\text{CH}_4 + \frac{1}{4} \text{O}_2 \rightarrow \text{CH}_3 + \frac{1}{2} \text{H}_2\text{O}$
815 psi, M: AIR = 3:1, 400° C

FIGURE 5.7

TABLE 5-4(a)

Catalyzed $\text{CH}_4 + .25 \text{O}_2 = \text{CH}_3 + .5 \text{H}_2\text{O}$
 815 psi, M:Air = 3:1, Complete Conv. of O_2 , Packed Bed, SA=.03, 400C

K Catal	E-8	E-7	E-6	E-5	E-4	E-3	E-2	E-1	1
Seconds	26	4.4	.6	.08	.01	.001	2E-4	2E-5	3E-6
GHSV	3100	2E4	13E4	1E6	8E6	8E7	4E8	4E9	3E10
Select, %									
MeOH	44.1	52.8	59.0	61.8	60.4	57.9	50.7	39.3	23.6
CO	41.5	32.9	25.6	18.3	12.9	10.4	8.5	4.9	1.7
CO ₂	9.3	6.6	4.8	3.2	1.0	0.3	.08	.02	.002
Formal	5.0	7.6	10.4	13.6	15.2	19.4	28.2	36.3	33.9
C ₂ H ₆		.01	.15	.07	0.4	.09	4.0	15.0	39.3
Meth Conv		7.3	8.0	8.4	9.0	9.1	9.2	9.8	11.8
% Me Cat.(Av)	35	43	46	65	72	82	90		

TABLE 5-4(b)

Conditions for Maximizing Methanol
 815 psi, Complete Oxygen Conversion, Packed Bed (SA=.03)

Temp, C	400	400	400	400	440	440	440	440
Oxidant	.25air	.25air	.05 O ₂	.10 O ₂	.25air	.25air	.05 O ₂	.10 O ₂
Catalyze	Me	Me&OH	Me	Me	Me	Me&OH	Me	Me
K Catal	E-5	E-10	E-5	E-5	E-4	E-10	E-5	E-4
GHSV	1E6	1E6	15E5	81E4	96E5	16E5	17E5	69E5
Select, %								
Alc	61.8	59.5	64.3	55.9	67.0	68.5	69.6	62.4
Ald	13.6	12.7	13.7	12.1	14.6	12.7	13.0	14.1
Meth Conv	8.4	8.0	6.9	12.1	9.4	9.0	7.4	14.4

TABLE 5-4(c)

Methane-Oxygen Mixtures
Catalyzed $\text{CH}_4 + .25 \text{O}_2 = \text{CH}_3 + .5 \text{H}_2\text{O}$
 Max. Methanol, Comp. Conv. O_2 , 440 C (S.A.=0)

P, atm	55	30	30	30	15
% Oxygen	10	10	15	2.5	10
K Catal	E-4	E-4	E-5	E-5	E-5
GHSV	7E6	6E6	5E5	4E6	6E5
Sel, %					
Alc	62.6	62.5	57.1	78.1	62.6
CO	17.8	17.5	30.5	6.2	23.0
CO ₂	2.3	2.3	1.8	.08	1.0
Ald ²	13.9	14.8	10.5	13.2	12.9
Meth Conv	13.6	13.6	18.3	4.12	13.9

5.2.2.8 Comparison With Reported Homogeneous Oxidations

Among others, five groups of workers have reported work on oxidizing methane to methanol recently:

1. Work by Gesser et.al. Most of the recent reports of homogeneous oxidation of methane have come from Gesser and coworkers Pet Div Prep 36 160 (1991) (5); App Cat 57 45 (1990) (6); Comb Flame 79 216 (1990) (7); and IEC Res 27 252 (1988) (8). Their most recent results and the model agree, at least to some extent.

- a. The 1991 paper concerns the effect of reactor packing, but lists runs for empty reactor and glass beads. As Table 5-5a shows, the conversions per unit time are in good agreement. If formaldehyde is removed from the product, the model predicts somewhat less methanol in the empty reactor versus somewhat more over glass beads.
- b. In the first 1990 paper, Gesser et.al., report about 43% methanol at 380-410°C and 10% oxygen at 10 atm. in an empty glass-lined reactor, stopping the reaction at "minimum" time of 160 sec on the average. Considering the difficulty in finding that minimum time, we think the model prediction, plotted in Figure 5-8 is in excellent agreement at 60 seconds and 43% methanol. (The 90% methanol from natural gas reported in the same paper is far above model predictions and must be either an experimental aberration or reflect a very beneficial "sensitizer" in the gas.)

TABLE 5-5(a)

Comparison of Gesser* Data and Model
882 psi, GHSV=2200

Source	Gesser	Model	Gesser	Model
Temp, C	364	364	381	381
% Oxy Chrg	3.0	3.0	2.5	2.5
Packing	None	—	Glass	—
Res t, sec	42.3	43.4	24.9	20-25
% Oxy left	(26)	20	(0)	0
% Meth conv	2.7	2.7	3.0	3.07
Selectivity, %				
MeOH	74.7	66.0	70.0	68-66
CO	19.3	27.7	25.7	23-27
CO ₂	6.3	.005	4.5	.64
Ald ²	—	5.81	—	8.1-6.5

*Gesser et al, Pet Div Prep 36 160(1991).

TABLE 5-5(b)

Sun Data (Gesser Apparatus) Vs Model
Charge 4.2% O₂ in Methane, 815 psi

°C	GHSV	Selectivity, mol %				H ₂ : MeOH	Calculated from Model(1) Selectivity, Mol % (2)				
		MeOH	CO	CO ₂	Eth		GHSV	MeOH	CO	CO ₂	CH ₂ O
412	666	44	44	11	—	.12	1E4	59	34	1.5	5.4
411	816	49	42	9	—	.14		62	36	1.6	
412	1449	40	51	10	—	.19					
422	660	40	45	15	—	.25	E4	60	33	1.4	5.6
	to	to	to	to	to	to		64	35	1.5	
	6613	23	61	9	7.1	1.27					
431	533	45	42	13	—	.19	1.9E4	62	31	1.3	
	to	to	to	to	to	to		66	33	1.4	
	6579	23	61	8	8.2	1.29					
441	1832	43	49	8	—	.35	2.5E4	63	29	1.2	6.0
	to	to	to	to	to	to		67	31	1.3	
442	6679	20	63	9	9.1	1.4					
452	633	24	60	13	3.1	.80	3.8E4	65	28	1.1	6.2
	to	to	to	to	to	to		70	30	1.2	
452	6613	20	63	9	8.8	1.7					
Preheater											
500	666						666	41	39	2.0	17.52
								50	47	2.4	
								(9.0% Oxygen used)			

(1) The model always produces low ethane and hydrogen.

(2) **Bold numbers** calculated assuming formaldehyde is not observed.

FIGURE 5.8

- c. The data reported in the 1988 paper(8) are difficult to rationalize. Compared with the model, residence times used by Gesser et.al. are high by a factor of 100 or more. Many times, temperatures were so high as to give complete reaction in less than 2 seconds and tend to generate hot spots. In fact, those same workers measured temperature oscillations during reaction (7). Only in two cases of low oxygen at moderate temperature did the model predict about the same product distribution.

2. Work at Sun. A very thorough attempt was made to reproduce the 1988 Gesser paper(8) in a replica of their apparatus with the yields summarized in Table 5-5(b). None of the reported high methanol yields were ever observed; in fact, methanol selectivities were generally lower than model predictions, especially at higher temperatures. Undoubtedly, oscillating reactions, back-mixing, and hot spots were occurring. Also Sun workers saw high CO₂ and ethane, the latter at high temperatures and space velocities where hot spots are more likely.

3. Burch et.al. Their paper in J. Chem Soc Far Trans 85 3561 (1989)(9) is so constructed that insufficient input was given for us to make model comparisons, but these British workers apparently could not reproduce the Gesser 1988 yields.

4. Huang and Huang. The preprint, withdrawn before presentation in the fall 1989 ACS meeting, reports 77% selectivity to methanol from methane oxidation over a chromia-zirconium sulfate-silica catalyst at 250°C where little if any homogeneous reaction should take place.

5. Rytz and Baiker. In IEC Res 30 2287 (1991)(3) these Swiss workers studied the early stages of methane oxidation at 450°C. As shown in Table 5-6 they found much ethylene where our model sees none. However, they preheated oxygen and methane separately, and mixed in the packed bed reactor where they calculate laminar flow. We believe that their product distributions are good evidence that considerable reaction had taken place before the gases had completely mixed.

5.2.2.9 Modeling Studies

We have constructed a kinetic model of the homogeneous vapor phase reactions involved in methane partial oxidation utilizing published rate constants and activation parameters for individual steps. The model enables us to derive the influences of temperature and pressure on the concentrations of intermediates or products or on global rates. We have used specific rate parameters published by Bedeneev (2) in most cases except for the more recent values (10) for the key reaction (4), which is larger than previously reported by several orders of magnitude:

We have further modified the Bedeneev scheme to include reactions of radicals derived from some higher hydrocarbons present in natural gas up through propane (11), and to include methanol decomposition pathways. Results from calculations using the empty tube version of our model were

TABLE 5-6

Comparison With Rytz and Baiker(1)
450 C, 750 psi, 5% Oxygen

	<u>Exp</u>	<u>Model</u>	<u>Exp</u>	<u>Model</u>	<u>Exp</u>	<u>Model</u>
Oxygen Used	0.4	0.4	1.0	1.0	1.0	1.0
Time, sec	1.0	.76	2.51*	1.9*	3.14	4.0
Select, %						
MeOH	7.6	74.9	27.9	67.1	27.9	60.7
CO	27.6	5.7	61.3	22.9	61.3	33.2
CO ₂	8.2	0	9.2	2.1	9.2	2.3
C=C	43.2	0	1.6	0	0	0
CH ₂ O	(10)	20.4	(0)	9.1	(0)	3.6
Meth Conv	1.71	.68	6.8	6.12	6.92	6.36

*Time when oxygen is just completely consumed.

compared to the experimental findings of Yarlagadda et. al (8) who have reported significant methanol yields in an experimental study without the use of an apparent catalyst. The model gives reasonable agreement with the experimental findings of Yarlagadda for runs at low temperature and oxygen partial pressure, but it cannot mathematically reproduce the very high methanol selectivities exceeding 80% reported at relatively high (ca. 8%) methane conversions without additional assumptions. Based on our kinetics simulations, we conclude that selective surface catalysis or cooxidation (12) is probably required to achieve simultaneously high selectivities and conversions needed for a practical process.

Finally, we further modified the model to include more extensive peroxide radical quenching believed to occur in the presence of reactor packing or on reactor walls (13) which results in significant rate inhibition and loss of methanol selectivity. The empty reactor calculation shows a slight drop in the methanol yield (and selectivity) beginning at the point at which oxygen concentration is depleted. In the packed bed, methanol selectivity is generally invariant once 100% oxygen conversion is achieved. We used the packed bed version of the model (with quenching included) to explore the effects of methyl radicals resulting from a hypothetical catalyzed hydrogen abstraction eq. (5), added to the non-catalyzed homogeneous reaction:

Variation of the rate constant for (5) arbitrarily to give 11% of the total methyl radical flux expected at 400°C, 815 psig, 3:1 methane:air mixture, for example, resulted in an increase in the reaction rate, lowering the time for oxygen depletion from 15.5 to 5.6 seconds, in an increase in methanol selectivity from 65 to 67%, and in no effect on CO₂.

5.2.3 Applications of the Methane Oxidation Model

We have described Sun's kinetic model for studying gas phase methane oxidation. Figure 5.10 outlines the major features of this model. The initial use of this model was to determine how well it fit the observed gas phase oxidation data. Tables 5.7 and 5.8 compare the results of the model with experimental findings from the literature and from our laboratory. Figures 5.11 through 5.14 indicate the expected results in methanol yield and selectivity from thermal gas phase oxidation of methane. It is interesting that this model predicts that at a conversion of 20% (at the low end of what might be commercially feasible) non-catalytic gas phase methane oxidation produces methanol in less than 30% selectivity. It appears, therefore, that a catalytic approach is necessary to combine the features of high conversion AND high selectivity.

FIGURE 5.10

FEATURES OF METHANE OXIDATION MODEL

- Isothermal or adiabatic, plug flow or batch, homogeneous.
- No. fluid dynamics or heat transport.
- Built on Simusolv (Dow) using GEAR and others; runs on VAX mainframe cluster; checks material balance.
- Works well (300-700°C); 5-100 atm., residence times ≤ 1000 sec.
- Basic model (61 eqns.) is a modification of the Bedeneev scheme (1988).
- Modified to include recent rate constant and T dependence determinations: $\text{CH}_3\text{O}^\bullet + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3^\bullet$. (Wantuck, 1988 - Los Alamos) (Rate $\gg$ than previously believed).
- An expanded version includes peroxy quenching over solids.
- An expanded version includes 44 reactions of C_2 species after inclusion of 77 reactions (Baerns, 1990; Lignola, 1987; Tsang, 1986) and eliminating 33 very slow reactions ($\times 10^6$) after sensitivity study - all reactions used at long rxn times; C_3 expansion problematic.
- Expanded to include catalyzed formation of radicals.
- Separate version for fast reactions.
- Compared to other models; published data, and in-house data.

TABLE 5-7

**COMPARISON OF EMPTY TUBE MODEL WITH EXPERIMENTS OF
YARLAGADDA AND GESSER[‡]**

T(°C)	-OBSERVED- MOL. % SELECTIVITY						-CALCULATED- MOL. % SELECTIVITY				
	% O ₂	SEC.	CH ₃ CO	CO	CO ₂	CH ₄ CONV.	SEC.	CH ₃ OH	CO	CO ₂	CH ₄ CONV.
411	2.8	144	76.8	23.2	VS	5.9	13	66.2	26.1	0.9	3.8
448	2.8	110	68.3	31.7	VS	4.5	3	71.6	19.0	0.6	4.1
500	2.8						1	73.4	15.3	0.4	4.5
550	2.8						0.3	67.5	16.2	0.4	4.7
456	5.1	232	83	10.7	6.4	6.6	1.5	61.1	3.14	1.6	6.7
500							0.3	66.9	24.3	1.1	7.4

[‡] Yarlagadda, et. al., I&EC (1988) 27, 252

TABLE 5-8

COMPARISON OF EMPTY TUBE MODEL WITH EXPERIMENTS OF THIS WORK[‡]

T(°C)	-OBSERVED- MOL. % SELECTIVITY					-CALCULATED- MOL. % SELECTIVITY				
	GHSV	CH ₃ OH	CO	CO ₂	CH ₄ CONV.	SEC	CH ₃ OH	CO	CO ₂	CH ₄ CONV.
412	666	44	44	11	4.3	8	59	34	1.5	5.1
411	816	49	42	9	3.3					
412	1449	40	51	10	5.1					
422	660	40	45	15	4.8					
421	816	49	41	10	4.3	6	60	33	1.4	5.3
422	1449	38	52	11	3.9					
421	1816	44	48	8	4.2					
422	3165	31	51	10	3.9					
423	6613	23	61	9	4.1					
452	849	22	65	10	3.6	2	65	28	1.1	5.6
	3248	24	61	11	3.8					
	6613	20	63	9	4.1					

[‡] 4.2% O₂ in Methane, 815 psi, quartz lined downflow reactor.

FIGURE 5.11

SELECTIVITY VERSUS OXYGEN CONCENTRATION

410° C, 520 psia, LONG RESIDENCE TIME

EFFECT OF METHANE CONCENTRATION ON SELECTIVITY TO METHANOL

5.25 % O₂ , 815 psi , 430 °C

METHANE OXIDATION IN EMPTY REACTOR SELECTIVITY vs TEMPERATURE

$\text{CH}_4 : \text{O}_2 = 95.3 : 2.8, 36.8 \text{ ATM.}$
LONG RESIDENCE TIME

FIGURE 5.14

METHANE OXIDATION

815 psia, 430° C, METHANE : AIR MIXTURES

EMPTY REACTOR

COMPLETE CONSUMPTION OF OXYGEN

Two of the ways that a solid catalyst can act to produce methanol are (1) by reactions in which bonds are made and broken on the surface to produce methanol which is then desorbed from the catalyst surface, or (2) to split the carbon hydrogen bond in methane to produce a gas phase methyl radical which is converted to products by homogeneous gas phase reactions. In order to evaluate a catalyst which only acts in the second sense, we used the Sun model to attempt to gain insight into how the methanol yield would vary with methyl radical flux from a catalyst surface in a packed bed reactor.

5.2.3.1 Effect of Methyl Radical Flux

We have investigated the effect of methyl radical flux on methanol yield and selectivity in both simulated empty and packed reactors. Figure 5.15 indicates the assumptions used to model packed reactors. Figure 5.16 shows the two different catalytic reactions which were used to generate methyl radicals and Table 5.9 shows the variation of methanol yield with the mode of methyl radical generation. Figures 5.17 and 5.18 indicate that selectivities in excess of 60% can be expected from high methyl radical flux generated by very active solid catalysts.

QUENCHING ON SOLIDS

- Assumed stoichiometry, then fit to our experimental data over silica compared to empty reactor.
- Assumed all solids behave as does silica in a quartz reactor but adjust for surface area.

$$\text{Z} = 3.23\text{E}11 \exp (-31600/\text{RT})(1.574/\text{D} + \text{E4} \cdot \text{SA})$$

Where D is reactor diameter in inches assuming a cylinder
SA is surface area of solid

- Destruction of peroxy species affects selectivity and reaction rate.
- Destruction of CH_3 makes little difference in selectivity.

FIGURE 5.16

SIMULATE CATALYSIS BY CONTINUOUS DISCHARGE OF METHYLS AND HYDROXYLS INTO THE GAS PHASE

ADD ANOTHER EQUATION:

OR

FIND MAXIMA IN METHANOL, FORMALDEHYDE, AND THEN ETHANE.

TABLE 5-9

INCREMENTAL CATALYSIS OF METHANE OXIDATION

Make OH	NO	NO	NO	YES	YES	NO	NO	YES	YES	YES
TEMP, °C	400	400	400	400	400	430	430	426	426	426
K62	E-13	E-8	E-7	3E-8	5E-8	E-13	E-7	E-13	E-8	3E-8
SEC. TO COMPLETION										
	250	26	4.5	7	4.5	60	3	65	10+	5
SELECTIVITY, %										
METHANOL										
ACTUAL	32.8	44.1	52.4	49.2	50.7	40.7	55.2	39.8	47.8	51.4
APPARENT	33.9	46.4	56.8	52.8	54.6	42.6	60.3	44.6	50.9	55.2
CO	49.1	41.5	32.6	36.3	35.1	42.5	30.4	43.3	37.8	34.7
CO ₂	14.7	9.3	6.6	7.5	7.1	12.3	6.1	12.6	8.4	7.1
CH ₂ O	3.3	5.0	7.8	6.9	7.1	4.4	8.4	4.3	6.0	6.8
CH ₄ CONV., %										
	5.7	6.3	7.1	7.0	7.4	6.2	6.8	6.2	6.8	7.2
MAX CH ₃ RATE										
x E-18	0.1	1	9	4	8	1	11	1	4	7
MAX OH RATE										
x E-18	-	-	-	2	3	-	-	0.4	1	2

Apparent methanol selectivity is that if formaldehyde is not observed.
Packed reactor, 815 psi, 3:1 methane:air, complete consumption of oxygen.

FIGURE 5.17

METHANE OXIDATION
CATALYZED $\text{CH}_4 + \frac{1}{4} \text{O}_2 \rightarrow \text{CH}_3 + \frac{1}{2} \text{H}_2\text{O}$
815 psi, M: AIR = 3:1, 400° C

FIGURE 5.18

METHANE OXIDATION

CATALYZED $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3 + \text{OH}$

815 psi, M:AIR = 3:1, 440 °C, PACKED REACTOR

5.2.3.2 Effect of Feed Complexity

Another goal we had set for the model during the past quarter was to get an indication of the effect of ethane in the feed. Natural gas has significant quantities of hydrocarbons other than methane which could affect reaction by cooxidative processes. Table 5.10A shows the effect that adding ethane can have on increasing methanol make from methane in gas phase oxidation reactions.

5.2.3.3 Methane Oxidation Model For Backmixed Reactor

In this report, we have considered reactions run in a tubular reactor and compared homogeneous gas phase reactions with an hypothetical catalytic reaction which generated increased amounts of methyl radicals in the gas phase. The Sun model predicts that at methane conversions of from 5 to 20%, methanol can be made in 65 to 30% selectivity at high oxygen conversions. Our model was unable to generate commercially acceptable methanol yields over a hypothetical catalyst whose only function was to generate gas phase methyl radicals.

In this Section we show simulated operations in a completely back-mixed reactor and obtained similar findings in the laboratory. The back-mixed reactor allows much more flexibility in oxygen usage than the tubular reactor and provides a number of interesting differences relative to the tubular reactor, but we have not found operating regimes which suggest that we could get the methanol selectivity (>80%) at the conversion level (> 20%) which we would find interesting from a practical

TABLE 5-10A
METHANE OXIDATION WITH ADDED ETHANE
Methane: Air 3:1, 815 psi

<u>°C</u>	<u>C₂H₆</u>	<u>Sec[•]</u>	<u>C₁ Conv.</u>	CH ₃ OH From <u>CH₄ %</u>
400	0	20	6.7	47
	1	23	6.3	50
	5	32	5.0	53
	10	36	4.1	59
700	0	.011	9.5	26
	1	.008	8.9	28
	5	.004	7.2	30
	10	.003	5.7	32

• To "complete" oxygen use.

standpoint by merely increasing methyl radical flux. Figure 5-19 shows the relationship between methanol selectivity and temperature as a function of space velocity in a back mixed reactor.

Two of the ways that a solid catalyst can act to produce methanol are 1) by splitting the C-H bond in methane to produce a gas phase methyl radical which is converted to products by homogeneous gas phase reactions, or 2) by reactions in which bonds are made and broken on the surface to produce methanol which is then desorbed from the catalyst surface. Pathway (1) provides enhancement in methanol selectivity in principal over uncatalyzed gas phase oxidations, Figure 5-20, but it is becoming apparent that pathway (1) alone may not suffice. Pathway (2) may be required to achieve the high selectivity and conversion needed for commercial viability. Pathway (2) would be expected to require low temperature and we may be observing it in our PHASE I studies on C_3 and C_4 substrates. A temperature dependent continuum between paths (1) and (2) is envisioned below:

As the temperature is raised $\text{M}-\text{CH}_3$ bond homolysis would be expected to become increasingly important and radical reactions would predominate. At lower temperatures, selective surface catalysis could produce methanol in high yield.

FIGURE 5.19
 COMPLETE BACK-MIXING
 CONSTANT SPACE VELOCITY
 3:1 METHANE:AIR, 815 PSI

FIGURE 5.20

EFFECT OF METHYL FLUX (CATALYSIS) ON
% METHANE TO METHANOL
CHARGE. 3 : 1 METHANE : AIR , 815 PSI

It is interesting to note that the model indicates that $\text{OH}\bullet$ radicals produced in the gas phase have roughly the same effect as methyl radicals on increasing methanol yields.

5.3 CATALYST SYNTHESIS

Surface oxide catalysts were prepared that aimed at incorporating oxidation-active transition metal centers in a stable oxidic lattice environment such that proximate metal centers could reductively bind and cleave the oxygen molecule to generate active MO centers for vapor phase oxidation of methane, ethane and other light alkanes. Among the catalysts successfully prepared for testing were iron sodalites, metal framework - substituted pentasil zeolites, iron, manganese and cobalt framework substituted aluminophosphates and surface bound chromium oxo catalysts.

We are attempting to use the framework of crystalline aluminosilicates and aluminophosphates as ligand systems for oxidation-active first row transition metals which could have redox properties similar to those of the porphyrin or polyoxometalate species described previously yet would be suitable for use as vapor phase catalysts for methane or ethane oxidations at high temperature. Low oxidation activity of early framework-substituted zeolites has been interpreted as due to apparently low $(\text{Fe(III)}/\text{Fe(II)})$ reduction potentials which may have been due to inaccessibility of important oxidation states. We, therefore, concentrated on the synthesis, characterization and testing of

framework-substituted aluminophosphates with the belief that stability of the M(II) oxidation state may be higher in these catalysts and the hope that Fe(III)/Fe(II) redox process may be more facile within their frameworks. We have prepared and characterized MnAPO-5>47, CoAPSO-5>47, MnAPO-5, MnAPO-11, and FAPO-11 and have tested their oxidation activity. Details of the preparation and characterization of these materials will be reported in the next quarterly report.

5.3.1 Iron Sodalite

A silicoferrate, iron sodalite, was synthesized by a modification of the method of Szostak and Thomas *supra*. A solution of 500 g. sodium silicate solution (Fisher Scientific) and 108 g. sodium hydroxide in 200 g. deionized water was prepared and designated solution A. A second solution, solution B, was prepared by adding 82 g. of 98% sulfuric acid and 80.4g of iron (III) nitrate nonahydrate (Aldrich) to 200 g. deionized water with stirring. Solution A and solution B were mixed by 25 alternate addition of small aliquots of each to a beaker fitted with an overhead stirrer. Solution C was prepared by adding 82.7% tetramethylammonium chloride (Aldrich) to 137 g. deionized water.

Solution C was then rapidly added to the mixture of A and B with vigorous stirring. The resulting tan slurry had a relative molar composition ratio of 1.0 Fe₂O₃: 24.2SiO₂ 20.7Na₂O: 7.6TMACl: 465H₂O and a pH of 11.5. The slurry was stirred without additional cooling for 15 minutes then charged to a Teflon lined 2 liter autoclave, sealed, and purged with argon. The reactor was pressurized to 200 psig with argon and allowed to crystallize with stirring at 168°-172°C. for 68

hours. The reactor product was washed with 1 liter of hot distilled water and 3 liters of room temperature distilled water and dried for 2 days at 125°C in air. The recovered dried product (80.3 g.) was then calcined in an ebullating bed reactor under argon at 540°C for one hour and in air at 540°C for two hours. Chemical analysis indicated 10.6% by weight iron, and BET surface area measurement indicated $2.9 \text{ m}^2\text{g}^{-1}$. A portion of the calcined product (46 g.) was impregnated with a binder consisting of 17 g. sodium silicate solution (Fisher Scientific) in 75 ml of water, dried at 125°C overnight, ground and sized to 18/35 mesh, and calcined in a tube furnace exposed to air at 550°C for one hour.

Chemical analysis indicated that the sample contained 10.11% Fe, 30.23% Si, 0.007% SO_4^{2-} , 0.018% Cl, and 4.03% Na, by weight, somewhat higher than the expected percentage of iron after dilution with the binder, which was 9.5%.

Given in Table 5-10B is a list of the major peaks obtained in the x-ray diffraction pattern of the above calcined sample prior to addition of binder, using CuK radiation and a solid state detector. The diffraction pattern of hydroxysodalite is given for reference. A small amount of a cancrinite phase may be present in the calcined sample.

During the period of this program, we further developed the synthesis of the active iron sodalite [Fe]SOD. We found that the amount of framework iron in the sodalite should be maximized to give high activity. We further determined that

TABLE 5-10B

<u>Calcined Sample</u>		<u>Hydroxysodalite</u> <u>(hydrated, synthetic)</u>	
2-Theta	Relative Intensity	2-Theta	Relative Intensity
14.05	100	34.92	100
24.24	84	24.54	90
24.46	53	24.46	89
19.78	37	24.49	88
34.49	17	14.08	49
31.47	11	31.89	27
69.17	10	43.02	23
11.13	10	43.08	22
31.79	8	58.7	10
31.24	8		
51.88	7		
11.60	7		
27.47	6		
34.65	6		
20.21	5		
20.32	5		
52.39	5		
40.17	5		
17.06	5		
13.42	5		
61.76	4		
58.52	4		
43.12	4		

the catalytic activity was enhanced by adding additional iron(II) to the exchange sites. The best catalyst, therefore, had iron in both the exchange and the framework positions. The iron sodalite catalyst was characterized by a combination of its elemental analysis, its x-ray powder diffraction pattern, its esr spectrum and some ion exchange studies. We chose manganese as the metal to be inserted into the framework of the second [M]SOD catalyst. As we disclosed in an early Quarterly Report we were unable to prepare [Mn]SOD in a manner analogous to [Fe]SOD. Neither direct synthetic methods nor post synthesis substitution were effective at rendering a manganese sodalite phase. We have prepared, however, crystalline reaction products containing substantial amounts of manganese that exhibit an x-ray diffraction pattern, characteristic of porous solids but we have no firm evidence that the manganese is in the framework as of these new materials. Since addition of Fe into the exchange sites of framework substituted [Fe]SOD gave rise to the highest methane oxidation activity and methanol selectivities, we added Mn into the exchange sites of [Fe]SOD. This catalyst, $Mn_x[Fe]SOD$, was tested for methane oxidation activity.

5.3.2 Attempted Synthesis of [Mn]SOD

Attempts to prepare mangano-zeolites by direct synthesis of [Mn]SOD and [Mn]ZSM-5 from aqueous gel preparations were unsuccessful due to decomposition of Mn(III) species more rapidly than their framework - incorporation reaction. Solubilization of the $K_2MnF_5 \cdot H_2O$ reagent in non-aqueous solvents using crown ethers, a procedure which might have reduced the hydrolysis rate and

hence alleviated rapid Mn(III) decomposition, was not successful. Solid state reactions were then attempted to effect the substitution of Mn for Si or Fe in zeolite lattices in the absence of solvents: Using silicalite as a substrate, intimate mixtures were made with potassium pentafluoromanganate hydrate and pressed at high pressure into wafers. These were dried and calcined in air for various times/temperatures between 200-800 degrees. Products were analyzed for crystallinity by PXRD, for surface area by the BET method, and for unit cell volume by PXRD line shifts determination. Reactions conducted at 700 degrees and above yielded a low surface area cristobalite phase, and reactions below this temperature resulted in insignificant shifts in unit cell volume, indicative of little or no substitution by manganese into the structure. The high temperature phases were purple and insoluble, indicative of some manganese incorporation, but of a collapsed structure.

Additional experiments were conducted at 500 and 400 degrees using [Fe]SOD as a substrate in place of silicalite with calcination times up to 68 hours to allow enough time for a slow solid-solid migration process. These reactions resulted in the formation of new unknown amorphous and crystalline phases which were not of a sodalite structure, but of potential interest as catalyst candidates. No characterization was conducted to attempt to measure the number of Mn-Fe pair sites.

Separate DTA experiments indicated a potential reaction between [Fe]SOD and the fluoromanganate between 550-660 degrees, just below the temperature at which [Fe]SOD would

ordinarily deferrate under these conditions in the absence of the manganese reagent. One may infer from this result along with the results of the reactions using silicalite above that there is a narrow temperature window for interaction, and for [Fe]SOD and silicalite this is close to the threshold for structural collapse. Additional experiments were conducted at precisely controlled temperatures with [Fe]SOD and also with [B] zeolites using the MnF_5_2 reagent with the hope of effecting Mn substitution without structural collapse. One or two of the samples prepared as high temperature phases which contain manganese were incorporated into our reactor test program.

We have succeeded in preparing a sample containing Fe-Mn pair sites by ion exchange of (Na⁺, H⁺ [Fe]SOD) under anaerobic conditions with hot Mn(III) acetate solution containing hydrazine to prevent disproportionation of manganese ion. we have not yet analyzed this sample, but we shall examine this sample by ESR in the future and test it as a catalyst candidate for methane oxidation.

5.3.3 Synthesis of Framework Substituted Zeolites

Efforts were aimed at the preparation of the pentasil zeolites which contain framework iron (III) and which have a cavity size large enough to admit both O₂ and CH₄. ESR, PXRD, unit cell volume, ion exchange capacity, elemental analysis and IR measurements were used to determine the proportion of framework and extra framework iron atoms.

Earlier results on iron sodalite (14) in our laboratory indicated the utility of framework iron containing catalysts at promoting methanol synthesis. We speculated that active sites required multiple iron atoms for maximal activity, but that the formation of μ -oxo bridged iron. To be better able to understand the actual nature of the metal-related active sites, we have begun to prepare a series of framework substituted molecular sieves containing different amounts, and types of trivalent framework metal species as well as correspondingly different ion exchanged metal ions. Since the iron exchanged sites are localized in close proximity to the framework metal species, metal pair sites are created with metal-metal distances in the range of μ -O₂ bridging, and are potentially capable of oxygen activation under our reaction conditions. The iron exchange technique also affords the opportunity to vary the initial oxidation state and the ligand environment of the exchanged metal site.

5.3.3.1 Preparation of [Fe]ZSM-5

Four solutions were prepared as follows:

Solution A: 67.59g Ferric nitrate dissolved in distilled water to give 550cc
29.8g Sulfuric acid added

Solution B: 300g N-Brand sodium silicate, PQ
300g distilled water

Solution C: 40.9g Sodium hydroxide in 200cc water

Solution D: 39.0g Tetrapropylammonium Bromide, Aldrich
dissolved in 60cc water

Solution B was added to A with vigorous overhead stirring in a teflon autoclave liner. Some precipitate and a reddish-brown solution resulted. More H_2SO_4 was added to adjust pH to 1.5, giving a murky tan-brown solution. Solution C was added resulting in a hydrogel pH of 8.5 and a heavy brown precipitate. Solution D was added with stirring to give a pH of 9.1.

After charging to a 2 liter stirred autoclave and flushing with N_2 , the reactor was heated to 153-160°C for 90 hours. The reactor was then cooled and the contents filtered by vacuum and washed repeatedly with 3 liter volumes of distilled water. After drying at 100°C overnight, 104.2g were recovered. This sample was later calcined in a fluidized bed heated at 10°C/minute under N_2 to 500°C followed by 10°C/minute to 530°C under air where it was held for 2 hours. Elemental analysis indicated 7.58% Fe (VF) and 0.070% Al(VF); BET surface area measurement indicated $161\text{m}^2\text{g}^{-1}$; typical infrared spectra of [Fe]ZSM-5 prepared by this technique Figures 5.21 and 5.22. Figure 5.23 is a typical PXRD diffraction pattern observed for these samples characteristic of the MFI (ZSM-5) topology. Horwath-Kawazoe adsorption analysis at low Xe pressures were applied to some samples to confirm the pore size of the zeolite.

Subsequently, Na^+ or K^+ ion exchange capacity measurements, typically 4-5% Na^+ , were made on these type of samples to determine the degree of framework substitution. Unit cell volumes

0387. KBr. 941815-1. (Fe) /ZSM-5, dww. gh1, mdc.

0393, KBr, 941815-2, (Fe)/ZSM-5, dw, gh1, mdc.

941815-2.ras

FIGURE 22 INFRARED SPECTRUM OF A Fe/ZSM-5

ID: 0941815-1 FE-SUB.ZSMS D. WALKER P/N41 SCINTAG/USA
TIME: 22:13 PT: 2.400 STEP: 0.020 WL: 1.54059

substitution. Unit cell volumes were also computed using either the LATCON or LOUER computer programs from x-ray peak shifts relative to aluminum ZSM-5 control sample.

As increasing amounts of iron are added to the framework, the unit cell volume of the dried (125°C) but uncalcined samples increases and is diagnostic of the degree of framework substitution. This is shown in Figure 5.24. Upon rapid heating calcinating in air without first heating under nitrogen, much of the iron is removed from the framework as evidenced by the point indicated in Figure 5.24 showing a decrease in the unit cell volume after air calcination at 530°C. Our calcination procedure under nitrogen to 500° followed by air to 510-520° results in far less removal of framework iron.

5.3.3.2 Synthesis of [V]ZSM-5

Preparation of vanadium-substituted ZMS-5 zeolite using the method of Ghamami & Sand (4).

Ingredients added in order:

200 g. colloidal silica (DuPont Ludox-30, 30% SiO₂)

5.2 g. vanadium(III) chloride, VCl₃

270 g. tetrapropylammonium hydroxide solution, Aldrich 20%

16g. ammonium hydroxide

FIGURE 24

UNIT CELL VOLUME BY LATCON PROGRAM FROM PXRD
MEASUREMENTS OF [Fe]ZSM-5 VS IRON CONTENT

□ UCV, Å³
 — 11.800994 * X + 5357.820834

• SAMPLES DRIED AT 125°C AND STILL CONTAIN TEMPLATE

Ingredients added in order to the Teflon liner of the 2-liter Parr autoclave, the autoclave assembled, and purged with argon.

Hydrothermal Treatment:

The autoclave was heated to 185°C with stirring, and held for 20 hours at 185-189°C.

Product Recovery:

The contents of the reactor were poured onto a filter and the dark green solid was washed once with 500 cc of hot deionized water. It was dried at 120°C in an oven overnight. The product weighed 69.7 g. The product was carefully ground and sieved to obtain 16.7 g. of 14/20 mesh fraction which was labeled 941723-2. The fines were labeled 941723-1. The meshed material (-2) was loaded into a tube furnace, an argon flow passed up through the bed, and heated to 530°C. The temperature was at 530°C in argon for 10 minutes, and the flow was changed to air and the temperature increased to 540°C. The temperature was held at 540°C in air for 20 minutes. The product weighed 14.3 g. after calcining (14% weight loss).

Characterization:

A sample of the calcined product (941723-2) was examined by powder XRD and found to have a pattern characteristic of ZSM-5 zeolites. The unit cell volume was calculated to be 5376 cu. Å by the computer program for determining cell parameters from XRD pattern data. This compares with a similar cell volume for aluminum-containing ZSM-5, and 5351 cu Å for pure silica Silicalite. These numbers indicate that the cell lattice was expanded by incorporation of vanadium ion in a manner similar to that with aluminum ion.

Elemental analysis by X-ray fluorescence indicated the solid product contained 2.51 wt. percent vanadium. After sodium exchange of the solid, elemental analysis by AA indicated the solid to contain 0.21 wt. percent sodium ion evidence for vanadium ion incorporation. BET surface area of the solid product was 152 m²/g. slightly less than half that obtained with a fully crystallized ZSM-5 zeolite.

5.3.3.3 Metals In Regular Oxidic Matrices

MnAPO molecular sieves are a member of the AlPO₄-based materials patented by Union Carbide (UOP). They are synthesized from gels containing the transition metal ions such as Mn²⁺, and it is assumed that the cations are incorporated into tetrahedrally coordinated lattice positions during hydrothermal crystallization of the molecular sieves. There has also been evidence to suggest that some of the manganese cations exist in extraframework sites to balance the negative charge formed by the incorporation of the manganese into the neutral AlPO₄ framework.

5.3.3.4 MnAPO-5,47

MnAPO-5 is a large pore material (0.8nm) with a novel structure that is templated by a number of different organics, including diethylethanolamine. MnAPO-5 has excellent thermal and hydrothermal stability. MnAPO-47 has the same topology as the zeolite chabazite and is a small pore material (0.43nm); diethylethanolamine in high gel concentrations is the most common templating agent for the 47 structure type. MnAPO-47 is not thermally stable when calcined in air to remove the organic template, and calcination is generally done in an inert atmosphere.

The tested sample was prepared following USP 4,567,029 Ex. 66. The starting gel ratio was:

2.0 DEEA : 0.167 MnO : 0.917 Al₂O₃ : 1 P₂O₅ : 45 H₂O

The synthesis was done at 200°C for one day, quiescently under autogeneous pressure. The final product was white. Under the microscope, the sample contained two distinct morphologies: cubes and six-sided rods. The six-sided rod morphology is typical of the 5 structure, and the cubes are typical of the 47 structure.

X-ray diffraction pattern of the as-synthesized material was consistent with that of a mixture of

5 and 47 with the predominant phase being 5 (Figure 5.25). Calcination at 600°C in air for three hours yielded a lavender/gray material. The X-ray diffraction pattern of the calcined material showed that the 47 structure type had completely collapsed and that the 5 structure type was still present (Figure 5.26).

The calcined material was sent for chemical analysis and the final product oxide ratio was:

Al ₂ O ₃	0.40
P ₂ O ₅	0.49
MnO	0.11

It can be seen that the divalent manganese substitutes for the trivalent aluminum and not for the phosphorus, and this is consistent with the MeAPO materials and results in a net negative framework charge.

5.3.3.5 MnAPO-11 and FAPO-11

The eleven structure type in the AlPO₄ system is a 10 membered ring material with elliptical pores. The pores are 3.9 x 6.3 Å in diameter and are arranged in a one dimensional channel system.

Two framework substituted AlPO₄'s were prepared during this quarter for testing: FAPO-11 and MnAPO-11.

FN: BKM996601.NI ID: M1 APO-5 B.K. MARCUS 17.51M SCINIAG/USA
 DATE: 03/30/92 TIME: 16:33 P1: 0.600 STEP: 0.0100 WL: 1.54060

FILE: BKM996501C.NI ID: 9965-01C CHU MAPU-5 1.5PM SCINIAG-USA
 DATE: 03/30/92 TIME: 20:31 PT: 0.600 STEP: 0.0100 WL: 1.54060

5.3.3.6 FAPO-11

FAPO-11 was prepared using the following gel composition:

0.1 Fe_2O_3 , 1 Pr_2NH , 0.9 Al_2O_3 , 1.0 P_2O_5 , 43 H_2O . Digestion was done at 200°C for 24 hours.

The final product was green, probably indicating incomplete insertion of the iron into the framework.

The XRD of the material showed that the material was not fully crystalline and that there were impurity phases present that are probably 5, 11, or 41.

The sample as calcined at 500°C for one hour in air; there was a decrease in crystallinity and the impurity phases were still present. Calcination in nitrogen for two hours gave less of a decrease in crystallinity, but the impurity phases were still present.

A chemical analysis of the calcined material gave an oxide formula of: $\text{Fe}_{0.5} \text{Al}_{.46} \text{P}_{.49}$.

This indicates that the iron is substituting primarily for the aluminum. The bulk analysis was

5.29	weight %	Fe_2O_3
32.87		Al_2O_3
49.03		P_2O_5

Preparation of this material should be repeated to produce a more crystalline material with better iron insertion.

5.3.3.7 MnAPO-11

MnAPO-11 was prepared from a gel with the composition: 0.167MnO, 1 Diisopropylamine, 0.917 Al₂O₃, 1 P₂O₅, 40H₂O.

The gel was digested at 200°C for 3 days. The XRD was consistent with a well-crystallized 11 sample. Calcination at 500°C for one hour in air showed some decrease in crystallinity; calcination for 4 hours in nitrogen gave excellent structure retention.

Chemical analysis of the material gave a framework oxide formula of: [Al₄₂ P₅₅ Mn₀₃]. In this case, the amount of phosphorus is high and could indicate an error in the analysis.

The five structure type in the AlPO₄ system is a 12 ring material with a circular pore that is 7.3 Å in diameter. The material is less dense than the 11 structure type; but it also has a one dimensional pore system.

5.4 Catalyst Testing

An active surface containing metal oxo centers might generate alkyl radicals according to equation (6) (15):

FN: 8KM996691.NI ID: 09966-91 FAPO-11 B.K. MARCUS 06003 SCINTAG/USA
 DATE: 07/01/92 TIME: 10:30 PT: 0.600 STEP: 0.0200 WL: 1.54060

FN: BKM996648.NI

DATE: 05/06/92

ID: MNAPO-II B.K.MARCUS 1/.5MM

TIME: 09:22

PT: 0.300

STEP: 0.0100

SCINTAG/USA

WL: 1.54060

We have synthesized a variety of all-inorganic phases which we thought capable of generating high oxidation state iron oxo species under appropriate conditions and examined them for catalytic activity. Examples are framework substituted iron sodalite (16,17) and amorphous silicoferrates, containing isolated iron atoms or oxo-bridged multi-nuclear iron centers respectively in varying amounts in predominantly siliceous frameworks.

5.4.1 Testing of Iron Sodalite

Early experiments were conducted in barricaded stainless steel packed bed reactors under steady-state conditions using 3:1:2.5 methane:air:water fed continuously over the catalysts at 918 psig. Although methanol selectivities were in general quite low in this reactor (<30%) probably due to reactor induced methanol decomposition (13,18), differences among catalysts were noted. Silica supported bulk iron oxide demonstrated extremely low selectivity to methanol, forming mostly CO₂. In contrast, sodium exchanged iron sodalite containing 13% iron, Figures 5.29, 5.30 gave higher methanol selectivity than either its aluminum analog, hydroxysodalite, or than a lower iron content iron-substituted pentasil of the ZSM-5 structure when each was bound with sodium silicate then calcined in air. Pretreatment of the iron sodalite catalyst by sodium azide decomposition to remove traces of acidity (19) resulted in even higher methanol selectivities; whereas, mild acid exchange resulted in virtually no methanol production. An amorphous iron silicate prepared similarly to the precursor gels for iron sodalite but calcined instead of being allowed to crystallize to the

LIGHT ALKANES TO LIQUID OCTANE

METHANE TO METHANOL

CATALYST = 15 % Fe IN SODALITE
 CONDITIONS : T = 420 °C, G HSV ~ 600,
 3/1 METHANE / AIR

	RESULTS	GOAL
O ₂ CONVERSION	90 %	90 %
METHANE CONVERSION	7 %	20 %
METHANOL SELECTIVITY	70 %	80 %

FIGURE 30 SUPERIMPOSED PXRD'S OF FRESH AND USED
[Fe]SODALITE

zeolite was found to be less active. Iron (II) ion exchange of the iron sodalite resulted in improved performance.

During the course of this work it became apparent that methanol decomposition induced by the stainless steel reactors could result in low methanol yields. In addition, we found that significant backmixing resulted in diffusion of much of the methanol formed at the top of the catalyst bed into the vapor space above the reactor when operating at low flow rates. For this reason we constructed a quartz lined packed bed reactor in which a portion of the gas flow at the head of the reactor bed could be drawn off instead of passing through the entire packed bed. The amount of product drawn from above the bed was controlled by a needle valve and could be either cold trapped or recombined with the main flow exiting the bottom of the catalyst bed prior to a liquid condenser.

Results using this quartz lined reactor at 3:1 methane:air without water cofeed through the bed are listed in Tables 5-11 and 5.12, Figure 5-31. In contrast to measurements in the metal reactor, our methanol selectivities in the quartz reactor with the by-pass valve open improved to about 70% selectivity at ca. 7% methane conversion over silicate-bound iron sodalite after an aging period. Closing of the needle valve such that the entire vapor stream passed through the bed resulted in much lower methanol selectivity and correspondingly lower conversion (Table 5.12). Comparison of the performance of silicate-bound iron sodalite with glass beads and with silicate-bound hydroxysodalite with the by-pass valve open is shown in Table 5.12. In all cases, the use of [Fe]SOD resulted in enhanced methanol yield and selectivities relative to control runs. By applying

TABLE 5.11. Vapor Phase Air Oxidations Of Methane To Methanol

Catalyst	GHSV h ⁻¹	Bed T °C	CH ₃ OH Sel., %	CH ₄ Conv., %	O ₂ Conv., %
[Fe]SOD	530	407	64	4.6	76
		461	70	5.7	90
		418	68	5.4	91
		422	65	5.4	92
		432	63	5.5	90
		442	64	6.1	90
Hydroxysodalite	530	404	—	0.0	0
		430	9	0.3	4
		445	24	5.1	84
Fe _x O _y /SiO ₂ (10-15%)	530	431	26	5.1	85
		700	10	0.5	11
		409	18	1.2	16
		420	20	2.7	74
		428	23	3.9	83
[Fe] ZEOL	700	400	33	2.4	52
		430	34	3.8	74

^a P=800 psig. 3:1 methane:air. Quartz lined reactor with by-pass open.

TABLE 5.12 Effect of By-Pass In Methane Oxidation Over Fe[SOD] in Quartz Lined Tubular Reactor

By-Pass Status	Production CH ₃ OH	Rate CO	mmol/h CO ₂	O ₂ Consum mmoles	CH ₃ OH Selc. %	CH ₄ Conv. %
Closed	1.6	1.6	0.4	3.8	44	4.8
Open, no trap	3.5	0.6	0.7	4.0	72	6.5
Open, probe 15 cm ^b	2.04 bed	1.0	0.5	4.3	71	6.0
	<u>1.60 trap</u>					
	3.64 total					
Open, probe 5 cm ^b	1.27 bed	1.1	0.7	5.0	68	7.0
	<u>2.51 trap</u>					
	3.71 total					

^a GHSV=550±30 h⁻¹, P=800 psig, T bed=427±2°C, 3:1 methane:air feed.

^b Distance above bed of by-pass probe tip.

TEMPERATURE AND SPACE VELOCITY DEPENDENCE OF METHANOL SELECTIVITY IN QUARTZ BYPASS REACTOR

resulted in enhanced methanol yield and selectivities relative to control runs. By applying our model and assuming only an increase in $\text{CH}_3\bullet$ and no methanol decomposition, we estimate a methyl radical production rate enhancement of at least an order of magnitude from [Fe]SOD relative to glass beads in these experiments.

Any scheme which depicts a possible reaction pathway over silicoferrate catalysts must account for the following observations: a) a high iron concentration is required; b) supported and bulk iron oxides are poor catalysts; c) the activities of amorphous, high-iron catalysts are inferior to that of crystalline Fe[SOD]; d) the performance of Fe[SOD] improves with Fe(II) exchanged; e) an induction period during which some deferration is likely to occur is observed, and f) acidity is detrimental, but basicity is beneficial. A suggested catalytic reaction pathway which would account for these observations implicates a binuclear iron site to activate and split the oxygen molecule, Figure 5.32. Although several variants of this cycle can be drawn, a key feature is the proximity of an extra framework hydroxyiron cationic species to a framework iron site at which ion exchange capacity develops in the structure. The two irons might act in concert to activate oxygen at elevated temperatures. Formation of binuclear oxo-bridged Fe(III), could represent a deactivation path in this scheme, and this could account for the poor performance of iron oxide phases in our reactors.

FIGURE 5.32
HYPOTHETICAL CATALYTIC CYCLE FOR SILICOFERRATE ACTIVITY

5.4.2 Effects of Reactor Design on Methane Oxidation

In past Quarterly Reports we have discussed the question of reactor design and how it influences reaction rate and product selectivity. We have seen that a fully loaded packed bed reactor did not give the high selectivities that were seen in a reactor which contained a large empty void volume ahead of the heated packed bed of catalyst to which was attached a by-pass line leading to the reactor exit stream (4). This reactor had features which combined: 1) a lower temperature reaction zone in which a radical flux generated by the hot catalyst could selectively produce partial oxidation products, 2) a reactive distillation to remove methanol as formed, and 3) a component of the reaction mixture which passed through the catalyst bed in a conventional way. Using this reactor, we found that selectivities for the iron sodalite-catalyzed oxidation of methane to methanol which did not reach 50% in a conventional packed bed reactor, exceeded 70%.

We have compared three different reactor designs for the catalytic oxidation of methane to methanol. A complex design having a combination of a low-temperature back-mixed zone over a hot catalyst coupled with reactive distillation is shown in Fig. 5.32. Results of methane oxidations in this reactor are given in Table 5.12, and Fig. 5.31. Though relatively high selectivity (70%) to methanol can be achieved in this reactor system, it is too complex to use to generate unambiguous catalyst screening data.

QUARTZ LINED BYPASS REACTOR SYSTEM

We have constructed two simpler systems which separate the catalytic activity from the reactive distillation aspects. One system operates as simple downflow reactor in the plug flow mode, Fig. 5-34. In this system under conditions of temperature and pressure similar to those used in the complex reactor, but at considerably faster flow rate, iron sodalite catalyzes the oxidation of methane to methanol in 50% selectivity.

Another system which operates in the back-mixed mode, Fig. 5-35, gives methanol in about 30% selectivity at similar temperature, pressure and flow rate. Clearly, reactor design is critical in conducting these oxidations and is being closely examined. We are currently screening reactions in the simple plug-flow and back-mixed reactors but will consider beneficial effects of more complex design when appropriate to achieve more optimal results.

In the by-pass reactor we were at least partially optimizing several very important features of this reaction. The complexity of the system, however, obscured the origins or the extent of contribution of the several effects that were simultaneously at work. We realized that we needed to disentangle these effects and examine them systematically. There are at least four desirable goals that our reactor should help us to meet: 1) it should allow us to achieve high rates and selectivity, 2) it should be straightforward enough to have ultimate utility in scaling up a catalytic process, 3) it should allow us to screen catalysts in the most effective way possible, and 4) it should allow us to understand and control the factors leading to high selectivity. It was clear that while the by-pass

PLUG FLOW OPERATION

FIGURE 34

PRE-HEATED: 3/1 CH /AIR

CATALYST = $\text{Fe}_V[\text{Fe}] \text{ SOD}$

<u>T_e</u>	<u>T_i</u>	<u>GHSV</u>	<u>SEL, %</u>	<u>O_2 CONV., %</u>	<u>CH_4 CON</u>
405	404	2,800	45	99	6
410	406	5,800	50	90	6
416	409	12,000	48	48	3

CSTR WITH ROBINSON-MAHONEY INTERNALS AND EXTERNAL BYPASS

FIGURE 35

CATALYST

$\text{Fe}_x[\text{Fe}]\text{SOD}$

<u>T, °C</u>	<u>GHSV</u>	<u>CH₃OH SEL. %</u>	<u>CH₄ CONV., %</u>	<u>O₂ CONV. %</u>
400	1900	32	6-7	95

reactor was doing very well regarding the first feature, it was unsatisfactory with regard to the other three.

For these reasons we constructed and operated two additional reactor types over the past several months. One reactor was a gold-plated 50cc Autoclave Engineers CSTR with Robinson-Mahoney Internals. This is a back-mix reactor which enables us to control and understand temperature effects and to independently vary residence time and degree of back-mixing. We have screened both a silica surface and our iron sodalite catalyst at 400°C under conditions in which catalytic reactions and non-catalytic gas phase oxidation compete. We were able to show far higher rates and selectivities in the presence of the iron catalyst. This enables us to assess the contribution of catalytic generation of methanol to the process at these temperatures. We have used this reactor to generate the data which enables us to gauge the differences in catalysts apart from the other effects present in the by-pass reactor.

Simultaneously we are interested in studying the effect of a cool quench zone for radicals which exit a hot catalytic surface during oxidation of methane. This may be one of the phenomena that elevated the methanol yields in the by-pass reactor. While we search for the best design to study this phenomenon, we are using the expedient of partial packing of a tubular reactor to allow a short, hot catalyst zone to contact the reacting gases followed by a longer void space whose temperature can be controlled. We have completed the study of several catalysts. Even when no attempt is made to cool the void zone, methanol selectivity in this reactor configuration is much higher than in

a fully packed catalyst bed indicating that perhaps product formation continues in the void zone without methanol decomposition. Studies continue and further results will be reported in future Quarterly Reports.

5.4.2.1 Catalytic testing in a Downflow Reactor

We discussed early observations on the effect of reactor design on methanol productivity in the vapor phase air-oxidation of methane. We have found that reactions conducted under similar conditions of temperature and pressure at methane conversions between 4 and 8%, a) gave up to 30% methanol selectivity in a well-controlled back-mixed reactor, b) gave up to 50% selectivity in plug flow operation depending on the reactor/catalyst bed configuration, and c) gave greater than 70% selectivity in partially plug flow operation wherein methane was activated hot and reacted at a cooler temperature in a zone from which reactive distillation could occur. Figure 5-36 indicates results of methane oxidation in a fully or partially packed reactor operating near plug flow conditions.

It can be seen that practically no methanol is produced in a tube fully packed with glass beads at 390°C, whereas methane can be produced in over 30% selectivity when a catalyst, $\text{Fe}_x[\text{Fe}]\text{SOD}$, was used. An even more effective mode of operation was established when only the top third of the reactor was packed with catalyst and the bottom 2/3 was left empty. Even though the conversion was less, the selectivity to methanol was 50%. The interpretation of this result is that radicals were

FIGURE 5.36

METHANE OXIDATIONS

PACKING CONFIG.	CATALYST	OXYGEN CONV., %	METHANE CONV., %	METHANOL SEL., %	METHANOL YIELD, %
A	Fe _x [Fe]SOD	99	5.9	32	1.9
A	Glass Beads	10	0.2	10	0.02
B	Fe _x [Fe]SOD	67	4.0	50	2.0
B	Glass Beads	10	0.9	34	0.3
C	Fe _x [Fe]SOD (1/3) Glass Beads (2/3)	8	0.2	45	0.1
D	Fe _x [Fe]SOD	10	0.5	20	0.1

T = 390°C, P = 800 psig, 3/1 CH₄/AIR, GHSV = 2800 hr.⁻¹

that radicals were generated on the hot catalyst surface which migrated to the vapor space to react. If one filled this vapor space with a relatively inert material (glass beads), reaction of these radicals was quenched and little product was generated. Similarly, if the methyl radicals generated on the catalyst were sent rapidly through a capillary they did not propagate chains and low product yields resulted.

These results are consistent with a reaction pathway in which methyl radicals are generated at the top of a catalyst bed. Methanol and other oxidation products are formed in the vapor space. If the entire reactor space is filled with catalyst, a significant amount of methanol decomposition occurs. Methanol decomposition over $\text{Fe}_x[\text{Fe}]\text{SOD}$ has been demonstrated with and without air present. If the majority of the reactor space is empty, a gas phase methane oxidation ensues in the presence of a high methyl radical flux. We have shown by a kinetic model of gas phase methane oxidation at this temperature that increased methyl radical flux increases both reaction rate and methanol selectivity. If the methyl radicals are quenched after exiting the radical generating zone, low product yields result. These results therefore are consistent with a catalyst which operates by producing methyl radicals which generate methane in subsequent gas phase radical pathways.

Because of the critical role that reactor design plays in the oxidation of methane to methanol, and because there is no provision for significant amounts of reactor design, construction, and evaluation in the Cooperative Agreement Sun initiated a companion project for examining the effects

of reactor design on the methane oxidation reaction. This also resulted in the design and construction of an optimal reactor design for a catalyst which operates in the "heterogeneous-homogeneous" mode, i.e. the catalytic generation of intermediates on a surface followed by the gas phase reaction of these intermediates to form stable reaction products.

Finally, as discussed in past Quarterly Reports, our work on kinetic modelling of the gas phase oxidation of methane via the "heterogeneous-homogeneous" mechanism suggests that it will be difficult to achieve greater than 80% methanol selectivity at greater than 20% conversion by this mechanism. Our analysis indicates that greater than 80% methanol selectivity at greater than 20% methane conversion will be needed for such a process to be economic. This has encouraged us to begin a new catalyst synthesis initiative to produce catalytic materials which encourage "rebound" of methyl radicals to OH groups on the catalyst as a **surface mechanism for methanol formation**. These sites should exist in a very hydrophobic environment so that methanol is rapidly expelled as formed - otherwise oxidative decomposition will lower selectivity and yield. This new synthesis initiative is now underway and we will report on this topic in future quarterly reports.

5.4.2.1.1 Oxidation of Ethane Over Fex[Fe]SOD

We have also oxidized ethane over the iron exchanged and framework substituted sodalite that we have used for the catalytic oxidation of methane. Table 5-13 gives the product analysis for

TABLE 5-13

OXIDATIONS OF ETHANE OVER $\text{Fe}_x[\text{Fe}]\text{SOD}^a$

Gas Flow Mls/Min	T°C	Carbon Selectivity				Ethane Conv. %	Alcohol Sel., %	Liq Oxyg. Sel., %
		CH_3OH	$\text{C}_2\text{H}_5\text{OH}$	CH_2O	CH_3CHO			
30	284	28.1	21.8	9.1	5.1	4.6	49.9	65.1
45	305	26.9	17.8	6.8	4.5	5.3	44.7	56.0
188	310	25.7	12.3	7.3	2.6	3.6	38.0	47.9
286	313	26.1	7.8	7.4	3.9	4.0	33.9	45.2

^a P = 800 psig 3/1 $\text{C}_2\text{H}_5/\text{Air}$

Table 5-13 gives the product analysis for several oxidation reactions. We have obtained good material balances for these reactions and are confident of the reliability of the data. The vapor phase non-catalytic oxidation of ethane has been reported recently by H. Gesser, et al., Energy and Fuels, 5, 1991, 423-427. These authors did not report the presence of a number of important products including hydrogen, formaldehyde, ethylene, acetone, propane and butane, among others. They also reported slightly higher alcohol selectivities than we observed. Of particular importance is the formation of formaldehyde which is difficult to analyze by glpc. We have begun to use differential pulse polarography with excellent success to get quantitative analysis of formaldehyde in the aqueous reactor effluent (see below).

It is important to detect significant quantities of formaldehyde in the vapor phase oxidation of ethane since it seems likely that it is a key product in the essential step for forming methanol and perhaps other C_1 products, eq. 1., below:

As Gesser points out, the ratio of the rate constants for reactions 1 and 2 may play a key role in the ratio of methanol to ethanol or in the C_1/C_2 ratios in the oxidations of ethane.

5.4.2.1.1.1 Formaldehyde Analysis

Formaldehyde analysis in the presence of methanol was conducted on diluted aliquots of the aqueous reaction products from ethane oxidations by the differential pulse polarography technique. Direct analysis at a DME using 1 sec. drop time, 2 mv/sec scan rate, 50 mv pulse height, in deaerated 0.1M lithium hydroxide/0.1 M lithium chloride electrolyte resulted in a diagnostic wave for formaldehyde at -1.65 V vs. SCE reference. Analysis of standards prepared by serial dilution of a prestandardized stock solution of formaldehyde resulted in linear calibration plots showing negligible residual current in the absence of analyte and exhibiting a typical response of 50nA peak height per each ppm concentration. Stock solutions were standardized by oxidation of formaldehyde to formic acid with hydrogen peroxide followed by repetitive titrations with standard base to a bromthymol blue end point. The technique is capable of high precision down to ppb concentrations.

The aqueous reactor effluent from four ethane oxidations was analyzed by this technique and the results are shown in Figures 5.37-5.40.

5.4.2.1.2 Oxidation of Methane Over MnAPO-X

We have been able for the first time to prepare an active and selective methane oxidation catalyst having manganese in the framework of a zeolitic material. In past reports we have disclosed that framework-substituted iron sodalite can be an active and relatively selective catalyst for

FIGURE 5.37

FORMALDEHYDE ANALYSIS OF REACTION 5.1, TABLE 8

PN Model 270 Electrochemical Analysis Software

EXT DPV EXPERT DIFF. PULSE VOLTAMMETRY

PT 200 CP PASS vs. R

FP -1.800 vs. R SI 0.002

NP 402 RU 0.000E+00

PH 0.050 PW 5.000E-02

DR 10 31 91

C⁺ PASS

SH 2.000E-03

IR NONE

REF 0.22220 AgCl

FV 3.00

TR 14:09:31

DT PASS

ST 1.000E+00

FL LOW PASS

WAK DME

FIS NORMAL

IP -1.400 vs. R

ET 5

CH AUTO

RT HIGH STABILITY

31_9595

6853 26 ppm

9.110 uA

FIGURE 5.38

FORMALDEHYDE ANALYSIS OF REACTION 62, TABLE 6

PII Model: 270 Electrochemical Analysis Software
 EXT OPV EXPERT DIFF. PULSE VOLTAMMETRY
 PT 200 CP PASS vs. R DH 10-31 91
 FP -1.800 vs. R SI 0.002 CT PASS
 NP 402 RU 0.000E+00 SR 2.000E-03
 PH 0.050 PW 5.000E-02 IR NONE
 REF 0.22220 AgCl
 FLS NORMAL
 IP -1.400 vs. R
 CR AUTO
 RT HIGH STABILITY
 FV 3.00
 TR 14:46:31
 DT PASS
 ST 1.000L+00
 FL LOW PASS
 MARK DHE

— 31.9654

11209 PPM

FIGURE 5.39

FORMALDEHYDE ANALYSIS OF REACTION 67, TABLE 6

PN Model 270 Electrochemical Analysis Software

EXT DPV EXPERT DIFF. PULSE VOLTAMMETRY

PT 200 CP PASS vs. R

FP -1.800 vs. R SI 0.002

NP 402 RU 0.000E+00

PH 0.050 PW 5.000E-02

OR 10-31-91

CT PASS

SH 2.000E-03

IR NONE

REF 0.22220 AgCl

FV 3.00

TR 14:37:40

DT PASS

ST 1.000E+00

FL LOW PASS

MARK DHE

FLS NORMAL

IP -1.400 vs. R

CR AUTO

RT HIGH STABILITY

ET 5

31_9677

910.3 ppm

FIGURE 5.40

FORMALDEHYDE ANALYSIS OF REACTION 71, TABLE 6

PN Model 270 Electrochemical Analysis Software

EXT DPV EXPERT DIFF. PULSE VOLTAMMETRY

PT 200 CP PASS vs. R

FP -1.800 vs. R SI 0.002

NP 402 RU 0.000E+00

PH 0.050 PW 5.000E-02

DR 10-31-91

CT PASS

SR 2.000E-03

IR NOISE

REF 0.22220 AgCl

FV 3.00

TR 14:28:49

DT PASS

ST 1.000E+00

FL LOW PASS

NRK DME

FLS NORMAL

IP -1.400 vs. R

CR AUTO

RT HIGH STABILITY

ET 5

31_9713

1150.9 ppm

1.530 uA

converting methane to methanol. All attempts to incorporate large amounts of manganese into the sodalite framework failed. Supported manganese catalysts such as manganese oxides on silica or alumina largely gave combustion to carbon oxides with little or no methanol formed. We have now found a new and as yet uncharacterized crystalline aluminophosphate phase containing over 8% manganese which catalyzes selective oxidation of methane and produces significant amounts of methanol below 400°C. Table 5-14 compares the activity of alumina (iron and trace metals not removed), silica, $\text{Fe}_x[\text{Fe}]\text{Sod}$, and MnAPO-X under comparable conditions.

5.4.2.1.3 Oxidation of Ethane and Methane Over Framework Substituted Zeolites

Table 5-15 and 5-16 show the results of the catalytic oxidation of ethane and methane over a series of three framework substituted zeolites: Fe_xFeSOD , MnAPO-5/47 , and CoAPSO-5/47 . It can be seen that the two metal substituted aluminophosphates have greater low temperature activity than does our iron sodalite catalyst. Reactions were run in a top-loaded downflow reactor of a design not intended to maximize methanol selectivity. Nonetheless, the important feature of this work is that the C-H bond of methane is more readily broken using metal substituted aluminophosphate catalysts than with iron sodalite - the most active catalyst previously found in our laboratories. Methane can be activated at temperature 30°C or more lower using the aluminophosphate catalysts than with iron sodalite. Low temperature activation of methane is crucial to the development of new catalysts capable of surface activation of methane.

TABLE 5-14

METHANE OXIDATIONS

	PRODUCTS, mmole/hr.			O ₂ CONV.	CH ₄ CONV.	CH ₃ OH	
	<u>CO</u>	<u>CO₂</u>	<u>CH₃OH</u>		<u>%</u>	<u>%</u>	<u>%</u>
Al ₂ O ₃	2.6	0.6	1.5		18	1.2	32
SiO ₂	3.6	0.8	3.0		37	1.9	41
Fe _x [Fe]SOD	6.8	1.2	7.8		65	4.0	50
MnAPO-X	6.7	1.2	8.2		65	4.2	51

A 3/1 mixture of methane and air (5% O₂) (800 psig) was passed over the catalyst (GHSV = 2800 hr⁻¹) at 392°C and product quantities determined by a combination of gas chromatography and mass spectral analysis.

TABLE 5-15

ETHANE OXIDATIONS
PRODUCTS, mmole/hr.

Catalyst	Temp.	Flow	EtOH	Et&Ald.	C ₂ =	Me	MeOH	Form	CO	CO ₂	O ₂ Conv.	MeOH Conv.
Fe _x FeSOD	290	165	0.1	0.1			0.4	0.7	0.2	0.2	10	0.2
MnAPO 5/47	290	92	1.4	0.3	0.1	1.1	4.0	1.0	3.6	0.6	94	2.9
CoAPSO 5/47	290	102	0.05	0.05	0.03	tr	0.10	tr	0.1	0.22	15	0.2
Fe _x FeSOD	300	161	2.6	0.8	0	2.9	8.9	3.0	8.4	1.4	99	3.7
MnAPO 5/47	300	190	3.3	0.8	0.3	2.7	11.1	3.4	2.1	1.1	97	3.5
CoAPSO 5/47	300	176	0.15	0.12	0.04	tr	0.42	0.19	0.47	0.42	12	0.3

a Continuous oxidation of a 3/1 CH₄/air stream at 800 psig over a 1.5 ml. bed of catalyst top loaded into a heated 5 ml. reactor.

b Temperature applied to the reactor skin.

c Less than 0.5 mmole/hr.

TABLE S-16

METHANE OXIDATIONS

Catalyst	Temp	Flow mlg/min	MeOH mmoles/hr	Form mmoles/hr	CO mmoles/hr	CO ₂ mmoles/hr	O ₂ Conv %	CH ₄ Conv	MeOH Sel %
MnAPO 5/47	365	55	1.59	0.08	1.47	41	58	31	45
CoAPO 5/47	365	50	1.21	1.2	1.3	1.5	75	38	30
MnAPO 5/47	375	55	2.20	0.4	2.24	99	86	4.7	40
CoAPO 5/47	375	50	1.89	0.8	1.9	1.1	82	4.6	34
MnAPO 5	375	49	.73	0.5	.75	.85	65	2.3	31
Fe _x FeSOD	390	50	70		1.33	.32	49	2.3	<33
FeSOD (Unhd)	385	49	1.06		1.5	8	75	3.3	32
MnAPO 5	385	47	1.36	0.5	1.1	1.5	86	4.1	3.4

a A 3/1 methane/air mixture was continuously passed over a 1.5 cc bed of catalyst top loaded into a 5 ml. fully heated quartz lined reactor operated at a pressure of 800 psig

b Applied external temperature (to reactor skin)

5.4.2.1.4 Methane and Ethane Oxidations Over MnAPO-5

We have prepared the known manganese substituted aluminophosphate MnAPO-5 and used it as a catalyst for the vapor phase oxidation of methane, Table 5-17a, and ethane, Table 5-17b. Reactions were conducted in a reactor in which the top third was packed with catalyst and the bottom two thirds was void space. We hoped to generate methyl radicals over the catalyst and allow them to be converted in the void space under conditions in which catalytic decomposition of methanol would be reduced. Methane can be converted to methanol in roughly 50% selectivity at elevated temperatures over an iron exchanged, iron framework substituted sodalite catalyst, $\text{Fe}_x[\text{Fe}]\text{SOD}$, in this reactor configuration. We have found that methane activation occurs at temperatures about 35°C lower with the MnAPO-5 than over $\text{Fe}_x[\text{Fe}]\text{SOD}$. Although selectivity is not improved, the finding that the manganese catalyst activates the difficult C-H bond of methane more easily than our iron sodalite system is an exciting and potentially important one. We have not yet done the appropriate comparisons between the two catalysts to determine whether the same C-H bond activation relationship holds for ethane as well. Data available to date, however, has shown that ethanol yields are higher and CO make lower over the manganese catalyst. We are continuing to work on the manganese and other aluminophosphate derived catalysts.

We have compared results of methane and ethane oxidations over MnAPO-5, MnAPO-5/47 and CoAPSO-5/47 with those using iron sodalite catalysts. While methanol selectivities were not

TABLE 5-17a

METHANE OXIDATIONS OVER MnAPO-5 AND Fe_x[Fe]SOD^a

<u>CATALYST</u>	<u>T_b</u> <u>°C</u>	<u>FLOW</u> <u>MS/MIN</u>	<u>PRODUCTS, MMOLE/HR.</u>				<u>O₂</u> <u>CONV.,%</u>	<u>CH₄</u> <u>CONV.,%</u>	<u>CH₃OH</u> <u>SEL.,%</u>
			<u>CH₃OH</u>	<u>CH₂O</u>	<u>CO</u>	<u>CO₂</u>			
MnAPO-5	375	55	2.20	0.04	2.24	0.99	86	4.7	40
		98	4.60	0.13	4.94	1.36	93	5.2	42
		377	15.20	1.14	22.00	5.05	99	5.4	35
Fe _x [Fe]SOD	410	50	2.22	NA	2.84	0.66	91	5.4	<39
		92	4.02	NA	5.32	0.96	93	5.3	<39
		378	20.96	NA	19.74	3.14	90	5.5	<48
MnAPO-5	365	55	1.59	0.08	1.47	0.41	58	3.1	45
Fe _x [Fe]SOD	390	50	0.70	NA	1.33	0.32	49	2.3	<33

^a A 3/1 methane/air mixture was continuously passed over a 1.5 cc bed of catalyst top-loaded into a 5 mL fully heated quartz-lined reactor operated at a pressure of 800 psig.

^b Applied external temperature (to reactor skin)

TABLE 5-17b

ETHANE OXIDATIONS CATALYZED BY Fe_x[Fe]SOD OR MnAPO-5

Catalyst	T. _b C	Flow Ms/Min	C2's. mmoles/hr.			C1's mmoles/hr.					Others mmoles/ hr.	O ₂ Used %	C ₂ H ₅ Conv., %
			CH ₃ CH ₂ OH	CH ₃ CHO	CH ₂ =CH ₂	CH ₄	CH ₃ OH	CH ₂ O	CO	CO ₂			
Fe _x [Fe]SOD	290	165	0.1	0.1	c	c	0.4	tr	0.2	0.2	c	10	0.2
MnAPO-5	290	92	1.4	0.3	0.1	1.3	4.0	1.0	3.6	0.6	0.3	94	2.9
Fe _x [Fe]SOD	300	161	2.6	0.8	0	2.9	8.9	3.0	8.4	1.4	0.2	99	3.7
MnAPO-5	300	190	3.3	0.8	0.3	2.7	11.1	3.4	2.1	1.1	0.4	97	3.5
Fe _x [Fe]SOD	315	386	3.0	1.9	4.1	10.0	18.1	14.0	25.1	3.3	0.5	93	3.7
MnAPO-5	300	406	6.2	1.7	1.0	9.1	24.9	8.3	10.5	3.3	0.8	98	4.2

a) Continuous Oxidation of a 3/1 CH₄/air stream at 800 psig over a 1.5 mL bed of catalyst top loaded into a heated 5 mL reactor.

b) Temperature applied to the reactor skin.

c) Less than 0.5 mmoles/hr

quite as high as in the case of iron sodalite catalysts the reactions could be run at considerably lower temperatures with the Mn and Co catalysts. The zeolitic matrix into which the iron is substituted can control the oxidation state(s) of the metal which are critical to oxidation catalysis. For this reason, we are interested in making catalysis which can accommodate first-row oxidation-active metals in both the (III) and (II) states as a minimum. We are also interested in zeolitic environments which have very high metal loadings for possible proximate effects in dioxygen binding.

Thus, we felt it imperative to find a zeolitic framework into which we could substitute large amounts of either iron, manganese or cobalt so that a proper comparison could be made. We synthesized MeAPO-11 (Me=Fe, Co, Mn) in an attempt to accomplish this. Unfortunately the metal loadings were not as high as those in the sodalite samples which were first investigated but we decided to test them anyway. To date we have completed test runs on FAPO-11 and MnAPO-11 and will begin testing CoAPO-11 shortly. BOTH the iron AND the manganese substituted materials were catalytically active at lower temperatures than was iron sodalite. Both catalysts changed rather quickly while on stream. At 375°C, 800 psig of 3/1 methane/air, ~1000 gshv, the selectivity of FAPO-11 decreased from an initial value of 44% (3-7hr avg.) to 33% at 2.4% methane conversion after less than 20 hours on stream. Under the same conditions using MnAPO-11, selectivity dropped from 46% (3-7 hr. avg.) to 37% at 3.7% methane conversion after about 40 hours on stream.

5.4.2.1.5 Methane Oxidation Over [Fe]ZSM-5

Table 5-18 presents some of the results of the testing of the sodium exchanged pentasil zeolite, [Fe]ZSM-5, the synthesis and characterization of which was described in an earlier progress report. It should be noticed that the framework iron content of this catalyst was far lower than that of Fe[SOD] and the methanol production was less than half of that produced using [Fe]SOD.

5.4.2.1.6 Reactions catalyzed by 0.5% CrO₃/SiO₂

We have found that low levels of chromia on silica prepared according to the method of McDaniels, et al., (21) which contains surface chromium(VI) oxo groups having the structure, I, below, is active for the oxidation of methane to methanol.

Initial results of the testing of this catalyst were obtained in a downflow reactor under conditions which were not optimized for high methanol selectivity.

TABLE 5-18
OXIDATION OF METHANE^a OVER Fe[ZSM-5]^b IN THE VAPOR PHASE

BED. T. ^{°C}	GHSV. HR ⁻¹	<u>PRODUCTS, mmoles/Hr.</u>			CH ₃ OH	CH ₄ %	O ₂
		<u>CH₃OH</u>	<u>CO</u>	<u>CO₂</u>	<u>SEL.,%</u>	<u>CONV.,%</u>	<u>CONV.,%</u>
410	12,000	0.1	0.9	9.3	1.0	0.6	15
418	12,000	0.2	0.9	9.1	2.0	0.6	15
428	12,000	17.4	60.8	17.6	17.4	6.2	97
430	12,000	15.4	67.2	13.4	15.0	6.3	97

^a P=800 psig, 3.1 methane: are Quartz lined reactor described in earlier reports.

^b 7.58% iron, 0.07% Al

^c Measured at mid-bed.

Table 5-19 presents some preliminary results of tests over this "surface-oxo" catalyst which were compared to tests of both [Fe]SOD and 3% $\text{CrO}_3/\text{SiO}_2$ under the same conditions. The chromium oxo catalyst compared favorably to iron sodalite in methanol selectivity and was quite superior to heavy loadings of CrO_3 which have been shown to be less active coatings of CrO_3 and di- and poly-chromates. It is of interest that defined chromium oxo species anchored to the oxidic surface structure have methane-to-methanol activity and catalysts of this type will be explored in more detail in the future.

5.4.2.2 Catalyst Testing in a CSTR

We have performed work on the synthesis of catalyst candidates based on binuclear metal-ion sites isolated in silicometalate matrices, and we have begun preliminary catalyst testing of these candidate solids in our gold plated CSTR reactor with Robinson-Mahoney internals for their ability to catalyze methanol synthesis under oxygen limited conditions.

Previous work in packed bed reactors along with modelling studies lead us to conclude that we could not appropriately measure the exact reaction temperature (as opposed to the catalyst bed temperature) and that we could not disentangle the degree of backmixing from the residence time in the reactor. Use of the CSTR reactor (Figure 5.41) has enabled us to precisely determine the reaction temperature and to separate residence time (GHSV) effects from those which are related to the

FIGURE 5.19

OXIDATION OF METHANE OVER CHROMIA ON SILICA^a

	Applied T °C	Gas Flow. m/s/Hr.	O ₂ Converted. %	CH ₄ Converted. %	CH ₃ OH Produced. mmoles/Hr.	Methanol Selectivity. %
Iron Sodalite	400	300	15	0.9	3.6	24
3% CrO ₃ /SiO ₂	400	300	16	0.6	5.6	b
"	420	300	20	0.7	5.1	b
"	430	300	22	0.7	4.6	b
"	400	400	18	0.7	2.5	b
"	400	200	22	0.7	0.9	b
"	375	200	22	0.9	1.3	b
"	350	100	22	0.9	0.3	b
"	300	50	18	0.4	0.02	b
Iron Sodalite	300	50	0	0	0	-
0.5% CrO ₃ /SiO ₂	390	300	15	0.6	3.9	41
"	400	300	29	1.8	10.9	38
"	410	300	38	2.0	11.8	38
"	420 ^c	800	90	5.4	18.5	22
"	350	100	15	0.4	0.3	34
"	300	b	b	b	b	b

^a Continuous oxidation of methane (800 psig, 3l. methane air) over one cc of catalyst. Results reported are average of four hourly samples taken after a two-hour line-out period.

^b Data will become available on completion of gas analysis.

^c Exotherm caused internal temperature of 442° during reaction.

degree of backmixing. In parallel to the experimental effort, we have modified a version of our computer simulation of the homogeneous kinetics to take into account backmixing effects. This model has been employed to identify those factors which might be altered in a CSTR reactor relative to a packed bed.

We chose to experimentally examine a "low" temperature region with hopes of better discriminating a catalyzed process in parallel to the homogeneous vapor phase non-catalyzed processes leading to methanol, since the non-catalyzed processes are relatively slow at low temperature. We fixed $T=400^{\circ}\text{C}$, $P=900$ psig, feed=3:1 CH_4 :AIR. Using silica gel packing which should account for peroxide quenching effects but not show further catalysis, we studied the effect of varying flow rate, reactor bypass side arm utilization, and side arm-reactor outlet mixing temperature. A statistically significant number of runs were conducted for each process variable measurement; only data of acceptable carbon balances utilized; and error limits representing a 95% confidence interval were computed for each data set.

Figures 5.42-46 summarize the effects of flow rate and the degree of backmixing (stirring rate) on methanol and CO_x selectivities and on conversions over silica gel. We found that a high flow rate and high stirring rate, i.e. a fully backmixed reaction, were the most favorable operating conditions. This finding corresponds to our qualitative conclusion from modelling studies that oxygen consumption (the limiting reagent) should decrease as backmixing increases when approaching 100% oxygen conversion.

FIGURE 5.41

CSTR BASKET REACTOR

FIGURE 5.42

CH₃OH SELECTIVITY - 95% CONFIDENCE

FIGURE 5.43

CO SELECTIVITY

FIGURE 5.44

CO₂ SELECTIVITY

FIGURE 5.45

C CONVERSION - 95% CONFIDENCE

FIGURE 5.46

O₂ CONVERSION - 96% CONFIDENCE

We had previously noted that utilization of a particular reactor design feature appended to a packed bed reactor led to enhanced methanol selectivity under low flow conditions. This design feature consisted of a side-arm on the packed bed reactor connecting an unoccupied fore-chamber ahead of the catalyst bed to the effluent stream exiting from the catalyst. We believe that the conditions under which this "bypass reactor" operated resulted in backmixing of intermediates desorbed from the catalyst surface into the unoccupied void space ahead of the catalyst where a further reaction could ensue without either quenching or decomposition by the solid packing. The bypass served to draw off reaction products from the region not occupied by catalyst. Unfortunately, we could not independently control the degree of backmixing without altering the flow rate.

We have confirmed the beneficial effect of the bypass on the CSTR reactor in fully backmixed operation using only silica gel packing. Here flow rate and the degree of backmixing (stirring rate) are independent process variables. Figure 5.47 shows methanol selectivity as the micrometering valve of the side arm is opened. With a high degree of confidence, we can conclude that opening the side arm results in significant enhancement of the observed methanol selectivity and that there is an optimum opening. A U.S. patent claiming this reactor design benefit for catalyzed reactions has been filed.

We have now also discovered (Figure 5.48, Table 5-20) that deliberate cooling of the connection between the side-arm bypass and the main reactor effluent line (see Figure 5.41) results

TABLE 5.20

METHANE OXIDATION IN A CSTR

<u>Silica Gel</u>		<u>Gold/CSTR</u>			<u>Methane:Air</u>		3:1				
<u>Feed</u>	<u>Stir Rate</u>	<u>Temp</u>	<u>Pres</u>	<u>Sidearm</u>	<u>T. Sidearm</u>	<u>Conversion, %</u>			<u>Selectivity, %</u>		
						<u>C</u>	<u>O₂</u>		<u>CH₃OH</u>	<u>CO</u>	<u>CO₂</u>
High	2000 RPM	400	900	Closed	100-120	5.11 [±] .17	95.36 [±] 1.71		9.77 [±] 1.89	50.77 [±] 2.33	39.46 [±] 2.38
High	2000 RPM	400	900	.5 Rev.	100-120	5.11 [±] .11	96.74 [±] 1.13		14.44 [±] .76	50.15 [±] 1.91	35.61 [±] 2.06
High	2000 RPM	400	900	.5 Rev.	56-64	5.78 [±] .18	95.26 [±] 1.77		22.71 [±] 1.18	43.99 [±] 1.88	33.29 [±] 2.28
Low	2000 RPM	400	900	.5 Rev.	6-9	6.26 [±] .09	96.46 [±] 3.71		18.74 [±] .25	43.58 [±] 1.04	37.68 [±] .88
Low	NONE	400	900	.5 Rev.	7-15	6.45 [±] .07	96.36 [±] 1.14		19.47 [±] 1.59	47.03 [±] 3.26	33.62 [±] 2.52
High	2000 RPM	400	900	1 Rev.	100-120	5.17 [±] .15	96.08 [±] 2.38		13.23 [±] 1.85	48.39 [±] 2.01	38.38 [±] 1.51
High	2000 RPM	400	900	2 Rev.	100-120	5.18 [±] .09	94.98 [±] 1.47		12.34 [±] .43	50.85 [±] 1.08	36.81 [±] 1.33

FIGURE 5.47a

CH₃OH SELECTIVITY - 95% CONFIDENCE

FIGURE 5.47b

CH3OH selectivity - 95% Confidence Limit

FIGURE 5.47c

CO₂ SELECTIVITY - 96% CONFIDENCE

FIGURE 5.48a

CH₃OH SELECTIVITY - 96% CONFIDENCE

FIGURE 4.48b

CO SELECTIVITY - 95% CONFIDENCE

in still further improvement in methanol selectivity when the side arm is at the optimal opening. Although the detailed mechanistic chemistry which is responsible for these observations is not clear, it is interesting to speculate that the activation energy for decomposition of intermediates potentially leading to methanol (or for decomposition of methanol itself) to CO_x must have a higher activation energy than do the pathways leading to methanol synthesis from the common intermediate. We do not yet know if the cooling effect improves selectivity in the absence of the side arm. If it does, a "quick quench" reactor may be desired to optimize yield of methanol.

We have begun to test a series of catalyst candidates based on ion exchanged silicoferrates. The first of the series is [Fe]SOD with no additional exchange but of a different synthetic batch than found to be active in packed bed reactors previously. Although the present results do not represent optimum conditions for yield maximization, the data has been measured under rigorously controlled conditions so that observed differences from control runs can be ascribed to reactor packing. The bypass line was utilized at an opening that had previously been found to be optimal for silica gel; cooling of the bypass intersection was effected to the same degree in both the control runs and in the actual catalyst runs.

Initial use of a calcined [Fe]SOD at 400°C resulted in methanol yields indistinguishable from those measured over silica gel. An attempt to activate the material by simply heating to 450°C followed by a 400 degree extended run (10 hours) failed to boost methanol selectivity or conversion.

hours) failed to boost methanol selectivity or conversion. However, subsequent injection of several ml of water into the system at 450°C to steam-treat the [Fe]SOD followed by operation at 400 degree did result in activation of the catalyst. Over a period of about 4-5 hours, the methanol selectivity improved then lined out and remained steady over the next 8 hours on-stream. About 40 gas or liquid aliquots were gathered over this time period and subsequently analyzed. Mean data and error limits representing 95% confidence are listed in Table 5-20 for the activated and lined out [Fe]SOD compared to silica gel. Comparable experiments over silica gel indicated line out time to be certainly within 1 hour and possibly within an even shorter time. These observations are consistent with the hypothesis that some framework iron must move to exchange sites for the catalyst to become active. Once established, the iron-iron pair sites catalyze methanol formation, even at the relatively low temperature of 400°C.

TABLE 5-20b

**COMPARISON OF AN ACTIVATED [Fe]SOD AND SILICA GEL IN A CSTR REACTOR
AT 400°C UNDER FULLY BACKMIXED CONDITIONS WITH THE BYPASS OPEN**

<u>PACKING</u>	<u>SIDEARM</u>	<u>PRODUCT SELECTIVITY, %</u>			<u>CONVERSION, %</u>	
		<u>CH₃OH</u>	<u>CO</u>	<u>CO₂</u>	<u>ARBON</u>	<u>O₂</u>
Silica Gel	82°C	21.19	43.7	35.1	5.34	96.6
[Fe]SOD	80.9°C	31.81±1.21	40.2±1.1	28.0±.6	6.32±1.1	92.4±1.5

5.4.2.3 Methane Oxidations Under Different Conditions

In past reports we have stressed the critical nature of the methane oxidation conditions on methanol selectivity. We have shown how under the same conditions of temperature, pressure and flow rate, selectivities of the iron sodalite catalyzed oxidation of methane could vary from under 20% in a back mixed spinning basket reactor to under 30% in a fully packed down-flow reactor to around 50% in a top-loaded down-flow reactor to 70% in a flow reactor aided by product removal by reactive distillation. Table 5-21 shows how changes in feed mixture, catalyst loading and flow rate in yet another reactor design described below can also affect product selectivity. A combination of higher flow rate, higher oxygen partial pressure, different configuration and the presence of a glass frit all may contribute to poorer methanol selectivity. Table 5.22 shows how selectivity varies dramatically with pressure under one set of conditions and Figure 5.49 shows the same phenomenon under somewhat different conditions.

5.4.2.3.1 Experimental Details of Methane Oxidations

Some recent experimentation in our laboratory was conducted under reactor test conditions including relatively high proportions of air in the feed. These runs were conducted in a quartz-lined downflow packed bed reactor in which 2-4 ml of an 18/35 mesh solid catalyst were packed over a quartz frit. About 4 ml of empty space preceded the catalyst in the heated zone and about 5 ml of empty space was present below the frit in the heated zone. A thermocouple was inserted into the middle of the packed bed in most runs, but this was removed in others to

TABLE 5-21

OXIDATIONS OF METHANE AT HIGH O₂ AND GHSV^a

CATALYST	MLS CAT	CH ₄ / AIR	GHSV (TOT. VOL.)	GHSV (CAT)	T°C	CH ₄ CONV.,%	O ₂ CONV.,%	CH ₃ OH SEL.,%
[Fe]SOD	1.3	2.23	2,724	14,668	414	5.7	93	16
	1.3	2.23	2,724	14,668	414	5.6	94	15
	2.7	2.23	2,724	7,063	405	4.8	79	22
	2.7	2.23	2,724	7,063	375	0.6	64	9
Fe ²⁺ [Fe]SOD	3.3	2.23	2,724	5,779	408	6.8	99	20
MnAPO-5	5.0	2.23	2,724	3,814	380	4.9	96	3
Fe-FPc/[Fe]SOD	2.1	2.23	2,724	9,080	407	5.8	94	15
	2.1	2.23	2,724	9,080	407	5.4	96	15
Fe-FPc/SiO ₂	3.1	2.23	2,724	6,151	406	3.4	72	22
	3.1	2.23	2,724	6,151	375	1.3	62	12
SiO ₂ gel	3.2	2.23	2,724	5,959	405	3.0	78	30
	3.2	2.23	2,724	5,959	380	2.1	22	0.4

^aSee experimental detail.

TABLE 5.22

EFFECT OF PRESSURE ON METHANE OXIDATIONS
CATALYZED BY Fe[SOD] IN A KUNG REACTOR^a

T°C	414	414
P,psig	803	205
O ₂ CONV.	96.0%	9.2%
CH ₄ CONV.	5.32	0.39
CH ₃ OH SEL.	23.8	9.0
CO SEL.	60.0	5.7
CO ₂ SEL.	16.2	85.3
C BALANCE	97.6%	100.6%

^aCatalyst, 1.39 ml, top-loaded into a quartz-lined reactor (ID=0.7cm).

Methane/air (3:1) fed at 190m NTP (GHSV (Total Vol.)=1815h⁻¹).

FIGURE 5.49

P DEPENDENCE OF CH₃OH YIELD

KUNG RXTR: 414 DEGREES

ensure no contribution by the thermocouple material to catalysis. Prior to the reactor, methane and air were mixed and preheated in a hastelloy C CSTR operated at an impeller speed of several thousand RPM and 300°C. All runs were conducted at 820+/-5 psig.

Control runs were conducted with silica gel packing in the reactor which was expected to provide surface for alkylperoxy radical quenching but not to contribute to catalysis beyond the homogeneous thermal reaction. Several batches of [Fe]SOD with and without further Fe²⁺ exchange were examined as well as MeAPO-type molecular sieves containing manganese, and a perfluorophthalocyanineiron(II) compound supported on either silica or [Fe]SOD. Data measured after 300-400 minutes on-stream are presented in Table 5-21. Each data point represents the mean of at least four gas analyses and three liquid analyses; additional data from these runs including 21 additional analyses for each run are archived at the Sun Laboratories. Since in all but one case, the catalysts had not been aged on-stream, these data represent minimum performance for the [Fe]SOD cases and perhaps also for the MnAPO catalysts.

Comparison of the present experimental results to lower oxygen content runs leads one to the general conclusion that methane conversion is not necessarily increased by a higher partial pressure of oxygen in the feed. Despite higher oxygen partial pressure, conversions of about 2-6% were observed in the present runs, on average, just as had been observed for 3:1 methane:air mixtures previously. Methanol selectivity was found to be generally lower than in earlier runs at higher

methane concentration, however. Considering the strong tie between conversion and selectivity, i.e., at constant oxygen conversion, the more methanol produced relative to CO_2 , the greater the conversion of methane, it is not surprising that methane conversion was not observed to be higher in our recent runs since modelling studies predict that CO_2 formation is increased at the expense of methanol by higher oxygen concentration.

Another area of continuing interest is formaldehyde production. Using a differential pulse polarographic analytical technique, we have examined the formaldehyde yield from a number of methane oxidation runs reported above and have found a correlation between yields of methanol and formaldehyde in most runs examined (Figure 5.50). This suggests that a common progenitor to methanol and formaldehyde might exist, in agreement with our homogeneous reaction kinetic model prediction. The formaldehyde yield was found to be roughly 10-15 times smaller than the methanol yield in our runs, also consistent with semiquantitative model predictions made earlier.

CH₃OH yield vs CH₂O yield

5.4.2.4 Methane Oxidation Over Mixed Metal Oxides

Our initial proposal called for the examination of the mixed metal oxides: ABO_3 perovskite, AB_2O_4 , spinel (inverse spinel), and $A_2B_2O_7$ pyrchlore, for activity in mild oxidation of methane. These catalysts tended to be combustion catalysts and produced largely carbon oxides and water. We were particularly interested in the cobalt and manganese ferrites: $CoFe_2O_4$ and $MnFe_2O_4$ because of their ability to decompose peroxides, Table 5-22 and their relatively low methane combustion rates, Tables 5-23, 5-24. Nonetheless, the cobalt and manganese ferrites were poor methanol makers. Under conditions in which $[Fe]SOD$ gave 17-27% methanol selectivity and silica gel gave 6-14% methanol selectivity, these catalysts gave less than 7% methane selectivity in the test case Table 5-25. For this reason, work in this area was abandoned early on.

5.5 NEW METHANE OXIDATION LABORATORY

In addition to carrying out the research program outlined above, we have constructed methane oxidation laboratory housing a new reactor for highly controlled and monitored methane oxidation for screening catalysts and performing kinetic analysis.

Using resources made available through a companion project funded by Sun, we have constructed an automated pre-pilot screening reactor for methane oxidation equipped with fail-safe

TABLE 5-22

"FERRO SPINELS" CATALYSIS OF $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$ ^a

<u>Catalyst</u>	<u>Specific rate constant normalized to unit B.E.T. specific surface area (k_p) $\text{min}^{-1} \text{m}^{-2} 10^{-3}$ (5%)</u>				<u>*H (kJ mol^{-1}) (2%)</u>	<u>*S (JK-1 mol^{-1}) (2%)</u>
	<u>303 K</u>	<u>308 K</u>	<u>313 K</u>	<u>318 K</u>		
ZnFe_2O_4	0.84	1.43	1.93	2.82	56.06	-125.96
CdFe_2O_4	3.09	4.62	6.31	9.44	61.27	-95.67
NiFe_2O_4	2.45	3.68	5.55	6.79	61.27	-93.28
CuFe_2O_4	3.47	5.35	10.70	16.72	83.48	-15.16
CoFe_2O_4	32.16	41.89	57.65	72.06	38.29	-145.93
MnFe_2O_4	223.80	383.30	501.10	696.00	54.70	-79.00

^aLAHIRI & SENGUPTA, CAN. J. CHEM., (1991) 69, 33 [22]

TABLE 5.23

**REACTION RATE OF OXIDATION OF METHANE AT A
STATIONARY CONCENTRATION OF 1 VOL. %^a**

Catalyst	w 10 ⁻¹¹	w 10 ⁻⁴	Temp. Range, °C
	at 400° C	at 300° C	
	<u>Molecule O₂</u> cm ² ·sec		
MgFe ₂ O ₄	6.7	6.4	450-500
MnFe ₂ O ₄	3.4	6.3	505-335
Fe ₂ O ₄	52.0	36.5	350-400
CoFe ₂ O ₄	18.2	29.3	375-425
NiFe ₂ O ₄	28.7	29.4	375-425
CuFe ₂ O ₄ (from hydroxides)	7.5	11.9	460-500
CuFe ₂ O ₄ from schoenites)	14.6	24.6	480-520
ZnFe ₂ O ₄	11.3	7.2	400-450
CdFe ₂ O ₄	17.6	17.9	400-450

^aG.K. Boreskov et.al... Kind Kat (1970)

TABLE 5.24

REACTION RATE OF METHANE OXIDATION AT 300°C AND C_{CH₄}=1 vol.%^a

Metal	Wsp molecule O ₂ /cm ² · sec.	
	ferrate	cobaltite
Co	3.0·10 ¹⁰	7.4·10 ¹²
Cu	2.5·10 ¹⁰ (from schoenites)	
	1.2·10 ¹⁰ (from hydroxides)	2.8·10 ¹²
Zn	7.2·10 ⁹	1.6·10 ¹²
Mg	6.4·10 ⁹	4.9·10 ¹¹
Mn	6.8·10 ⁹	1.0·10 ¹¹
Ni	2.9·10 ¹⁰	2.7·10 ¹²

TABLE 5.25

SELECTED METHANE OXIDATION RUNS
(P. Bowden Screening RxTR)*

CATALYST	RUN	X _{CH₄}	X _{O₂}	S _{CH₃OH}	S _{CO}	S _{CO₂}	C _{BAL.}
[Fe]SOD	55	7.4	97	26.2	48	26	105
[Fe]SOD	56	6.4	96	27.3	56	17	105
SiO ₂	77	5.7	96	14.2	66	19	101
CoFe ₂ O ₄	85	4.8	92	0.1	34	66	105
CoFe ₂ O ₄	86	4.3	96	0.05	17	83	102
MnFe ₂ O ₄	87	4.9	96	5.0	15	80	100
MnFe ₂ O ₄ OH	89	4.3	95	4.6	10	85	101
MnFe ₂ O ₄	90	4.2	97	0.2	3.5	96	101
MnFe ₂ O ₄	93	4.6	97	1.3	13	88	101
MnFe ₂ O ₄ OH	94	5.3	95	6.9	12	81	102
CoFe ₂ O ₄	95	4.5	95	2.6	20	77	101
[Fe]SOD	96	5.8	97	17.2	63	20	100
SiO ₂ gel	97	4.3	96	7.5	61	32	106
SiO ₂ gel	98	5.0	94	6.3	69	26	103
SiO ₂ gel	99	5.4	94	6.4	64	29	99
CoFe ₂ O ₄ OH	03	4.9	94	6.7	28	65	100

*Reactor Temp 428°C (All others 412-418°C); sidearm probe open

Downflow packed Btd.; Quartz liner; 2 cm of Cat sits on sintered glass frit; open space above & below cat; CH₄/air = 3:1; GHSV 8700 h⁻¹; Cat Bed T 412-418°C; P = 825 2 psig; sidearm probe inserted, but valve closed (except selected runs)

devices including emergency shut-down, on-line product analyses, and data analyses which are fully automated via a dedicated IBM PC. Communication between the PC database and other process simulation packages or databases on R&D's VAX computers has been established. This will facilitate future process economics studies by making data for design bases readily available in a suitable format. This unit will be made available for studying catalysts generated on the Cooperative Agreement.

6.0 CONCLUSIONS

6.1 THE SUPRABIOTIC CONCEPT

At the conclusion of work on the initial stage of the Cooperative Agreement it is instructive to re-visit the Suprabiotic concept and evaluate catalyst performance relative to this idea. As we first envisioned a suprabiotic catalyst, it was one which could operate in the absence of costly stoichiometric co-reductants using only air to oxidize an alkane to an alcohol but in some respects mimic biology in that the active intermediates would be similar. It appears as though the active intermediate which oxidizes alkanes in both Cytochrome P-450 and methane monooxygenase is a ferryl species, $\text{Fe}=\text{O}$. We devised a possible conceptual route to active ferryl using only iron, air and substrate, Figure 5.56.

Prior to our work no success had been achieved in attempting to oxidize alkanes to alcohols with only air or oxygen in this manner. Many attempts had been made using porphyrinato complexes both with and without bulky groups which would prevent μ -oxo dimer formation, Figure

5.56f. The only successful alkane oxidations using porphyrinato complexes were achieved using costly single atom donor oxidants such as iodosylbenzene, hypochlorites, or hydroperoxides.

6.1.1 Molecular complexes for Homogeneous Liquid Phase Conversions

The problems associated with this system for air-oxidations of alkanes to alcohols were many. First, although formation of μ -oxo dimer from the iron(II) precursor is detrimental, μ -peroxo dimer formation is crucial. Secondly, access of the alkane to the active center must be good. Thirdly, the alkyl radical formed by C-H bond homolysis should remain in the coordination sphere until rebound to the alcohol occurs. Fourth, the alcohol should be expelled as quickly from the coordination sphere as possible to prevent over-oxidation. Next, μ -oxo dimer formation must be reversed or prevented. Finally, the iron(III)/(II) reduction potential must be high enough to continuously regenerate active Fe(II) from the pool of Fe(III) even in the presence of molecular oxygen. In addition, the ligand system must be robust to oxygenation, and must not have electrons readily available to reduce the high oxidation state ferryl before it can oxidize the alkane. The kind of porphyrin complexes available prior to our work did none of these things and consequently were inactive catalysts.

Using perhaloporphyrin complexes we: a) stabilized active iron-oxygen centers to both of the kinds of decay referred to above, b) provided a lipophilic environment to attract the alkane to the active site, c) provided a hydrophilic environment to expel alcohol from the coordination sphere, d) tuned the redox potential of the metal center so that μ -oxo dimer was no longer inactive and so that

iron(II) species could be continually regenerated in an oxidizing environment. Figure 5-54 suggests how our perhaloporphyrins may act as a suprabiotic catalyst for converting alkanes to alcohols.

We have discussed how the electronic and steric environment about the oxidation-active metal center affects the rate and selectivity of alkane oxidation in both homogeneous liquid phase oxidations as well as heterogeneous catalytic vapor phase reactions. Reaction rate seems to be highly dependent on proper tuning of redox potentials. In the liquid phase we have achieved unprecedented reaction rates and have electrochemical evidence that much higher rates can still be achieved. In the vapor phase we have shown the need for proper tuning of reduction potential but we must synthesize catalysts which have far greater reduction potentials than those which we currently have if we are to achieve the rates that will ultimately be necessary.

While steric effects influence rate as well, we are finding that their prime importance is in reaction selectivity. Ejecting formed alcohol from the coordination sphere is of great importance as we have seen in both homogeneous and heterogeneous alkane oxidation. Although our greatest gains to date are in tuning the redox potential for high activity, and although there is still room for significant improvement here, we will be concentrating in the future on those aspects of catalyst structure that will effect selectivity to alcohol. Of all of these structural factors, the most important is hydrophobicity of the ligand or surface environment. Our current designs address these points

FIGURE 5.54

PROPERTIES OF A SUPRABIOTIC CATALYST

- COOPERATIVE IRON (II) SITES

- LIPOPHILIC ENVIRONMENT *

- HIGH $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ REDUCTION POTENTIAL^I

* HYDROPHOBIC ENVIRONMENT

- SUPPRESSED L-OXO FORMATION

- STABILITY TO OXIDATION

and we are confident that we will continue to make significant gains in both reaction rate and selectivity until all of the light alkanes can be smoothly converted to alcohols by direct, practical, air-oxidations.

In the three Topical Reports on the Cooperative Agreement, we have mentioned the exciting new results which are enabling us to convert light alkanes to alcohol-rich oxygenates for use as fuels and chemicals. As we progress in this research, the national climate mandating oxygenates in fuels for clean air and the growing need for alternate fuels add further impetus in addition to the economic incentive for generating high octane oxygenates from inexpensive light alkanes found in natural gas and in light refinery streams being rejected from gasoline because of emission restrictions. We have also noted that we are getting close to new catalytic technology which will enable us to produce TBA from isobutane. The commercial impact such technology will have on the production of MTBE, the largest growing fuel oxygenate could be very great. In addition, it is being realized that alcohols such as TBA and IPA will become important additions to the gasoline pool not only as cosolvents for methanol and ethanol but in mixtures with ethers. Sun has participated with several other oil companies in helping to procure recent EPA approval of oxygenate compositions containing TBA or IPA together with MTBE and other ethers to meet oxygenate requirements in transportation fuels. The oxygenates which we are producing directly from alkanes and oxygen using our novel catalytic chemistry will have immediate utility in an emerging new energy scenario.

At the end of the first stage of work on the Cooperative Agreement it is well to step back and look not only at our catalytic accomplishments and their relevance to the national energy picture, but also to assess the strides made in understanding what is clearly a new class of oxidation catalysts. Only through understanding the mechanism of the action of this new class of catalysts will we be able to fully utilize them in producing valuable products.

As we have noted in past reports, we developed the concepts leading to the preparation of the catalysts used in this program from considerations of how enzymatic systems such as methane monooxygenase are able to convert light alkanes to alcohols, Figures 5.55. It became clear that high oxidation state metal oxo intermediates were the key intermediates which reacted with the alkane to produce the alcohol. One of the practical problems inherent in mimicking this approach is the need for expensive coreductants (sources of electrons) to take the role supplied by NADH in the biological systems. We asked the question whether it would be possible to adjust the redox potential of simple metal complexes modeled after the biological systems such that they could do something heretofore not accomplished - convert alkanes to alcohols through high oxidation state metal oxo intermediates using only air or oxygen without the need for stoichiometric consumption of expensive coreductants. The mechanism which we envisioned for accomplishing this is outlined schematically in Figure 5.56 and the technique used to adjust the redox potential was to make complexes in which there was a high degree of electron withdrawal from the active iron center. Additionally we wished to create

FIGURE 5.55

PROPOSED MECHANISM FOR MMO ACTIVITY

FIGURE 5.56

**HYPOTHETICAL REACTION PATHWAY FOR A SUPRABIOTIC
CATALYTIC ALKANE OXIDATION**

$\text{Fe} = \textcircled{\text{Fe}} = \text{PORPHYRINATO IRON}$

molecular environments in which two iron centers could cooperate in reductively splitting the O-O bond without forming inactive μ -oxo dimers.

The finding that by steadily increasing the degree of halogenation and therefore the amount of electron withdrawal from the iron center, one steadily increases both the catalytic air-oxidation activity and the reduction potential of the iron complex, shows that our catalytic chemistry responds to the same factors that biomimetic catalysts do - with one important exception - our catalysts use only air or oxygen as the oxidant. This is good circumstantial evidence that the reaction may be going through the originally postulated reaction mechanism.

Subsequent findings that proximate diiron centers are superior to single iron sites in both liquid phase reactions catalyzed by polyoxometallates as well as gas phase reactions catalyzed by framework substituted solid catalysts infer a special activity which may be related to the ability of these systems to bind and activate oxygen across both iron sites. These catalysts are generally used at relatively high temperatures so that intermediates within the catalytic cycles liberate alkyl radicals either to a small extent or, in some instances, as a major reaction pathway and this allows radical chain processes to compete with catalysis.

In summary, it is gratifying to have obtained a large amount of evidence which is consistent

with our original hypotheses. This shows that, although we are still learning much about the details of the reaction pathways involved, we are indeed on the right track in observing truly novel chemistry and that continued extrapolation of the principles which are being uncovered will continue to produce catalysts with increasingly superior properties for conversion of light alkanes to fuel oxygenates.

6.1.2 Framework Substituted Zeolites

Now that we have established structure-reactivity relationships which correlate both the Fe(III)/Fe(II) reduction potential and the steric environment about the metal center with catalytic activity we are beginning to design ligand systems which have electronic and steric properties that will produce superior catalysts. Paramount among the considerations now being employed in addition to chemical characteristics are economic characteristics as well. For instance, the cost of raw materials and the molecular weight of the macrocycle are two factors which will be critical in the design of inexpensive catalysts for commercial production of fuels. We are indeed fortunate that iron provides the most active catalyst rather than a costly noble metal.

We have now learned how to tune the redox potential of metalloprophyrin catalysts toward high oxidation activity. In addition we have learned how to prepare active, thermally stable polyoxometallates with proximate metal centers, but these catalysts do not have the good low-temperature activity of the perhaloporphyrin systems and produce a less alcohol-rich product. We

now feel that the redox potentials of the proximate metals must be further tuned [$M(III) + e^- \rightarrow M(II)$] to make superior catalysts of this type. Similarly we have learned how to prepare active iron sodalite and manganese aluminophosphate catalysts for vapor phase oxidation of methane to methanol which have proximate metal centers. The sodalite framework, however may impede the ability of substituted iron to achieve the full range of oxidation states desired for catalytic oxidation. This may be the reason that we need extra-framework iron ($Fe_x[Fe]SOD$) for high activity. What may be needed for a heterogeneous catalyst which exhibits good low-temperature alkane oxidation activity is proximate metal centers each of which have a high reduction potential. Much of the emphasis in research on the Cooperative Agreement focused on catalysts containing binuclear metal centers having high $M(III)/M(II)$ reduction potentials to enable them to reductively couple dioxygen.

An active suprabiotic Catalyst should therefore have: (a) high reduction potential (to create oxygen binding sites) and (b) proximate iron centers (for oxygen cleavage). Fig. 5.57.

We have made substantial progress in the area of increasing the activity of heterogeneous catalysts for methane and ethane oxidations. In our laboratories we have recently addressed the structural limitations that some zeolites impose on $M(III)/M(II)$ transformations by incorporating large metal concentrations in aluminophosphates. A manganese aluminophosphate in which both $Mn(III)$ and $Mn(II)$ may be incorporated allows us to activate methane for catalytic conversion to

FIGURE 5.57

SCHEMATIC BINUCLEAR SUPRABIOTIC CATALYTIC ALKANE ACTIVATION

methanol at temperatures fully 35°C lower than are required for Fex[Fe]SOD and over 50°C lower than is necessary for thermal oxidation. Other catalysts of this type have also been prepared during the initial stage of the Cooperative Agreement.

6.1.3 Catalyst Synthesis and Testing

We have completed all of the laboratory tasks set out in the SOW for the Cooperative Agreement. More importantly, we have found highly active catalyst systems which give unprecedented rates of activation of light alkanes to form oxygenates in liquid and vapor phase. Results of our research confirms many of our initial ideas and suggests that there is a high probability of success in achieving practical processes for alkane conversions based on the new science and technology which we have generated. Recent success in making potentially cheaper and more active catalysts is particularly important as we enter the proof-of-concept stage for a process to make tert-butyl alcohol from C_4 gas components. Continued research is likely to result in future process technology for C_1 - C_3 gas components as well.

During the first year of work on PHASE III of the Cooperative Agreement we made a number of heterogeneous catalysts and screened them for methane oxidation to methanol (Cf. TABLE 6-3 Unsolicited Proposal ARD-AT-88-0001). We synthesized, characterized and tested several [M]Pentasil compounds namely, [Fe]ZSM-5, [V]ZSM-5, and [Ru]ZSM-5 and determined that

metal contents above 3% were not obtained and catalytic activity and selectivity to methanol were not high. We were unable to make [Mn]ZSM-5 after several attempts. We synthesized, characterized and tested several [M]Sodalite catalysts as well. We were able to synthesize the iron substituted [Fe]Sod which had over 15% iron in the sodalite framework and this gave much higher activity and produced methanol in better selectivity. We believe that the high iron loading must place iron atoms in close proximity and these proximate iron sites might bind dioxygen in a cooperative manner. We found that incorporating more iron into the exchange sites of [Fe]Sod gave an even better catalyst (Fe)_x[Fe]Sod. Activity was further enhanced by treatment of this catalyst with sodium azide. We failed to make the manganese analog, [Mn]Sod after many attempts. We were able to make a manganese exchanged iron substituted sodalite, (Mn)_x[Fe]Sod, but it was inferior to (Fe)_x[Fe]Sod. The final series on our program was designated [M]Sieve. These materials were the framework metal substituted aluminophosphates (ALPO's). In this case we were able to incorporate **both** iron and manganese into aluminophosphate frameworks in high concentrations to give in one instance FAPO-11 - a known material, and in the other case, MnAPO-X - a crystalline manganese aluminophosphate of as yet unknown structure. We have completed both of these syntheses have characterized the materials and have tested the manganese ALPO for methane oxidation. MnAPO-X has incorporated 8% by weight of Mn and it's activity is comparable to that of (Fe)_x[Fe]Sod under mild conditions. This represents the first time we have been able to "tame" a manganese center to give a significant yield of methanol rather than to yield only combustion

products. The FAPO-11 will be tested during the next quarter.

The series of catalysts which were designated to be prepared during the second year of PHASE III activity were catalysts having the highest number of binuclear active metal sites possible. We have synthesized new mixed metal oxides of the perovskite, $MM'O_3$ stoichiometry which has much higher metal-oxygen ratios than those of the framework-substituted zeolites discussed above. Another reason for our interest in perovskite-like materials having a high metal-oxygen ratio was the mobility of lattice oxygen in such structures. We believe that low temperature oxygen mobility is characteristic of systems which are expected to demonstrate lattice oxygen involvement in alkane oxidations, perhaps through creation of metal-oxo intermediates at redox active metal sites in these structures. Another important feature which a low temperature oxidation catalyst should have is the ability to regenerate lower oxidation states capable of activating molecular oxygen. Of particular interest in this regard are the manganites in which the oxidation state of one of the metals in the binuclear site can be affected by the nature of the second metal. We have synthesized catalysts of all of these types and many were active catalysts but all gave predominant combustion and no methanol.

Throughout the second and third year of the Cooperative Agreement, we continued to screen FAPO, MnAPO and CoAPSO catalysts which demonstrate interesting low temperature heterogeneous catalytic activity for vapor phase oxidation of methane and ethane. We also assessed

the kinetic modelling study which we performed on hypothetical catalytic and non-catalytic oxidations which proceeded via generation of gas-phase methyl radical. These studies combined with supporting experiment convince us that it is unlikely that gas phase methyl radicals, whether generated thermally in small amounts or catalytically in greater quantity, will provide sufficiently selective high yield pathways to be commercially attractive in the future fuel scenarios that we envision.

We must add two important criteria to our heterogeneous catalyst design in order to achieve practical systems for converting methane or ethane to alcohols in high yield. Figure 5.54 shows the suprabiotic criteria for liquid phase oxidation of an alkane to an alcohol. The first criterion indicates that low oxidation state metal centers must cooperate to reductively bind dioxygen. In solution, mononuclear macrocyclic complexes can migrate to a single oxygen site. Surface migration might not be as easy a process and segregated sites will not suffice. We have made a large number of catalysts which have proximate metal sites, however the ease of reduction of these sites (or the number of reduced sites in proximity) might not be sufficient to reductively bind dioxygen. A criterion for future catalysts will be binuclear iron centers and a number of these have been designed and are being synthesized at the present time.

We have discussed the need for high reduction potential but another criterion which has been

missing in our catalysts is that of a hydrophobic environment. Future catalysts will be constructed so that the oxidation-active metal center is in a hydrophobic site which attracts alkane, encourages surface reaction and rapidly expels alcohol as product. The catalysts of the future will operate at lower temperature, will have a low contribution of vapor phase radical reaction and operate via surface reactions to a greater extent than those we have generated in the past.

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