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LIQUID PHASE METHANOL PROCESS DEVELOPMENT UNIT:
INSTALLATION, OPERATION, AND SUPPORT STUDIES

Topical Report

January 1984

Work Performed Under Contract No. AC22-81PC30019

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

and

Chem Systems Inc.
Tarrytown, New York

Technical Information Center
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United States Department of Energy

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**LIQUID PHASE METHANOL PROCESS DEVELOPMENT UNIT:
INSTALLATION, OPERATION, AND SUPPORT STUDIES**

Topical Report

EXPERIMENTAL CATALYST PREPARATION PROGRAM

Contractor

AIR PRODUCTS AND CHEMICALS, INC.

Allentown, Pennsylvania 18105

and

Subcontractor to APCI

**CHEM SYSTEMS INC.
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January 1984

MASTER

ABSTRACT

This report details the preparation of 29 catalyst samples under DOE contract No. DE-AC22-81PC30019. These were selected for gas phase activity testing from a total of 70 prepared. Based on activity results, three compositions were selected for further slurry phase testing in the Chem Systems, Inc. (CSI) laboratories.

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SECTION I

INTRODUCTION AND SUMMARY

I. INTRODUCTION AND SUMMARY

A. Introduction and Background

The objective of this work was to define and prepare exploratory methanol synthesis catalysts for testing in the slurry phase. The initial evaluation of all samples was carried out in our gas phase screening system. Between March 1982 and September 1983 over forty different catalyst compositions were considered and 70 samples prepared. Some of these were rejected outright and twenty-nine exploratory catalyst samples were submitted for gas phase screening in the APCI laboratories in Emmaus. Samples were rejected because of high (1-2%) sodium oxide levels, poor filtering characteristics and poor yields. Although a "standard" test program was adopted, some of the more novel preparations required gas phase testing program modifications to accommodate anticipated variations in activation procedure. This process resulted in three promising compositions that were submitted to CSI for further testing.

B. Objectives

The APCI portion of Task 7, Laboratory Support Program, of DOE Contract No. DE-AC22-81PC30019 included catalyst preparation and screening programs. Our responsibility in these two areas was to prepare and activity test at least 23 non-commercial catalysts for methanol synthesis. The specific goals were:

- a) Conduct literature surveys, develop a bibliography of pertinent references, and maintain liaison with others working on related liquid-entrained (slurry) systems.
- b) Synthesize new liquid-entrained catalysts.
- c) Screen new liquid-entrained catalysts in a fixed bed Gas Phase Screening Reactor. Recommend candidates for further liquid phase testing at CSI.

C. Summary

Tables I and II in the appendix provide summaries of the catalyst preparations and gas phase testing activities. The catalyst types prepared for gas phase screening were:

- o Metal oxides - unsupported
- o Metal oxides - supported on alumina or silica
- o Raney type catalysts
- o Borides
- o Aerogel

Over 70 different catalysts representing 40 compositions were prepared. From these 29 were submitted for gas phase screening in the APCI laboratories at Emmaus. The results of early tests were used to help define the later catalyst compositions. This process resulted in 3 promising catalysts that were submitted to CSI for further testing. These compositions were:

- o $\text{CuO/ZnO/Al}_2\text{O}_3$
- o CuO/ZnO/Boron
- o Cu/Zn/Al - Raney Type

D. Future Work

No further catalyst preparation work is planned under DOE contract No. DE-AC22-81PC30019.

Areas which warrant future study are many and are summarized below:

1. Reduction of dissolved metals to form supported alloys, i.e., reduction with hydrazine.
2. Variations in support and/or active elements such as zeolite or titania supports.

3. Variation in concentration of solutions used to supply active elements. This will produce precipitates of differing compositions.
4. Heat treatment at different temperatures.
5. Heat treatment in different atmospheres.
6. Development of Raney type preparations.
 - ° active elements
 - ° active element proportions
 - ° extraction procedure
 - ° particle size
7. Noble metal catalysts.
8. Precipitation using feedback pH control (i.e., homogeneous precipitation)
9. Development of a viable Aerogel procedure.
 - ° active elements
 - ° active element proportions
 - ° solvent used
 - ° heat treatment/activation procedure
 - ° Noble metal activation of aerogel base

SECTION II

DISCUSSION

II. DISCUSSION

A. Discussion of Catalyst Preparation Methods

Unsupported Catalysts

The method of preparation for all nonsupported catalysts submitted for testing to date is summarized below.

Aqueous metal nitrate solutions were used in all cases. These were mixed together in a well-stirred vessel and heated to between 80 and 90°C in a well ventilated area with total capture of all mist.

Precipitation of the carbonates and hydroxides was accomplished by adding sodium carbonate and/or sodium hydroxide until the required pH level was reached. The suspension was then cooled, diluted to improve ease of handling, and solids separated from the liquid by filtration. The solids were washed several times to remove residual caustic, dried and calcined. Only a minimum of manual size reduction was needed to achieve the desired particle size. In several cases, the resulting particle size was smaller than the targeted 45-75 micron range. The first three samples delivered had average particle sizes between 3.4 and 4.8 microns.

Supported Catalysts

The materials supported on alumina from beta trihydrate were prepared in a similar fashion except that the required hydrated alumina was placed in the vessel with the metal nitrates. The resulting suspension was agitated during pH adjustment and precipitation.

The gamma alumina support was prepared by first calcining CATAPAL® (Boehmite) alumina to convert it to the gamma phase. From this point, the preparations followed those with the beta trihydrate alumina support.

The silica-supported material was prepared differently. Initial scoping experiments indicated that after addition of sodium hydroxide to precipitate the metal hydroxides, it was very difficult to effectively remove residual sodium from the catalyst. As a result, acetates were used. The acetates provide weak acids that require less sodium hydroxide to neutralize and, in fact, when mixed with the colloidal silica (initial pH 13), almost allow precipitation without caustic addition.

The procedure used is as follows: The acetates and colloidal silica were mixed together at ambient temperature and allowed to stir overnight. The resulting pH was not sufficient for complete precipitation, so a small amount of sodium hydroxide was added.

The filtration, washing and drying steps were similar to those employed in the unsupported and alumina-supported catalysts. It was found that the cake formed from the acetates hardened during calcination. The calcined cake was crushed to 1/16 inch particles for gas phase testing.

Raney Type Catalysts

This method involved extraction of aluminum and zinc from a copper, aluminum, zinc alloy powder. The alloys were purchased as a -20 mesh powder in a variety of compositions. The aluminum and zinc are extracted by treating a slurry of the powder with a concentrated sodium hydroxide solution. After the initial vigorous evolution of hydrogen ceased, the slurry was washed sodium hydroxide free with deionized water.

Filtration and washing were carried out in a glove box under a nitrogen atmosphere. After partial drying on the filter the solids were transferred to a gas test reactor or oil for use in the slurry reactor while still in the glove box. As a result, deactivation due to oxygen exposure was minimized.

Borides

The borides were produced by treating a metal acetate solution with sodium borohydride. After the vigorous reaction subsided the solids were washed with water and separated by centrifugation. The product was stored under nitrogen until use.

Supported borides were produced by first suspending the support in the metal acetate solution. Upon treatment with the borohydride solution the resulting solids were dispersed throughout the support.

Aerogel

Organic salts of copper, zinc and aluminum were mixed in methanol as solvent to form a slurry. The slurry was placed in an autoclave and heated to above the critical temperature of methanol. At this combination of temperature and pressure (242°C and 1185 psi) all the methanol is in the vapor phase. The plan was to vent the methanol from the autoclave while holding the temperature above 242°C, cool to ambient, flush with nitrogen to remove any trace of methanol remaining and remove the product.

What happened, was that somewhere over 800 psi the rupture disk failed and released the system pressure to vent. After cooling, the product was removed and saved. Attempts were made to duplicate the experiment with proper venting control. However, due to a series of mechanical problems it was not repeated. Thus, the sample produced by this abbreviated procedure was submitted as our only aerogel candidate.

Properties

The properties of some catalysts are summarized in Table III. The data presented are incomplete because the decision was made to limit comprehensive analytical testing to those compositions that showed promise.

B. Experimental Catalyst Screening

Twenty-two experimental catalysts of the twenty-nine submitted from PSG Research were tested. The catalysts were:

- 1) R12/OE72-50 - Cu/Zn
- 2) R12/1E72-51 - Cu/Zn/Al
- 3) R15/OE72-52 - Cu/Ce
- 4) R12/1E72-53 - Cu/Ce/Al
- 5) R10/OE32-56 - Cu/Zn/Cr
- 6) R15/4E31-57 - Cu/Ce/Cr/Al
- 7) R12/1E32-59 - Cu/Zn/Al
- 8) R12/OE32-60 - Cu/Zn/B
- 9) R18/1E31-61 - Cu/Mo/Al
- 10) R18/OF31-62 - Cu/Mo/Si
- 11) R19/OF55-63 - Cu/Zn/Al Raney type
- 12) R19/OF55-64 - Cu/Mg/Al Raney type
- 13) R12/1F32-66 - Cu/Zn/Al
- 14) R19/OE55-67 - Cu/Zn/Al Raney type
- 15) R19/OE55-68 - Cu/Mg/Al Raney type
- 16) R19/OE55-69 - Cu/Zn/Al Raney type
- 17) R10/OE55-70 - Ni/B
- 18) R10/OE55-71 - Cu/B
- 19) R12/1E32-72 - Cu/Zn/Al
- 20) E12/1E32-73 - Cu/Zn/Al
- 21) R12/1E32-74 - Cu/B/Al and
- 22) R19/OE55-75 - Cu/Zn/Al Raney type

Reduction Procedures

The reduction procedure for the different types of catalysts varied. In general, these techniques embrace three general procedures:

- 1) Standard 2% H_2/N_2 gas phase reduction,
- 2) Pure H_2 gas phase reduction, and
- 3) No reduction.

The standard 2% H_2/N_2 gas phase reduction was originally adopted by CSI for reduction of commercial methanol catalysts for use in their slurry phase reactors. The procedure utilizes an initial 16 hour reduction of the catalyst at 180°C with 2% H_2/N_2 at a gas rate of 600 $\ell/hr\text{-kg}$. After this 16 hour period, the temperature is increased at 20°C/hr to 240°C. The latter condition is held for 2 hours. After reduction, the reactor is purged with N_2 and the temperature and pressure are adjusted to the initial run conditions.

The pure H_2 reduction procedure is used for the Cu/Mo type catalysts. This procedure utilizes a pure H_2 stream at a space velocity of 600 $\ell/hr\text{-kg}$ at 300°C and 90 psig. This condition is held for 16 hours after which, the reactor is heated to 400°C during 8 hours. This temperature is held for an additional 24 hours. The reactor is purged with N_2 and the temperature and pressure are adjusted to the initial run conditions.

The reduction procedures utilized varied with composition; see Discussion section for examples of each type. A summary of results is presented in Table II.

Discussion

Cu/Zn/Cr : R10/OE32-56

This catalyst was reduced utilizing the standard APCI/CSI gas phase reduction procedure and tested at 225°C, 515 psia, and 5000 $\ell/hr\text{-kg}$ with a balanced gas feed. The "balanced gas" feed has the following composition, 55% H_2 , 19% CO, 5% CO_2 and 21% N_2 . No methanol was produced and no CO was converted at this condition or at 250°C.

Cu/Ce/Cr/Al₂O₃ : R15/4E31-57

This catalyst was reduced as above and tested at 225°C, 515 psia, and 5000 l/hr-kg with a balanced gas feed. No methanol was produced and no CO was converted at this condition or when the temperature was raised to 250°C. No other conditions were tested.

Cu/ZnO/Al₂O₃ : R12/1E32-59

This catalyst was previously prepared by A. F. Nordquist of APCI. His final preparation showed good activity/stability compared to available commercial gas phase catalysts. The current preparation, though not as good as the commercial catalysts, shows a decided improvement over the previous noncommercial Cu/ZnO candidates. The reduction procedure was that used by CSI/APCI; 2% H₂ in N₂ 600 l/hr-kg and 90 psig. The reactors were slowly heated to 180°C and allowed to reduce for 16 hours. The temperature was then increased in 20°C steps (20°C/hr) to 240°C, where it remained for 2 hours. The reactors were then pressurized to 500 psig under N₂ and synthesis gas was introduced. The exit gas analysis shows a consistent, broad peak coincident to methyl formate. This peak is so broad and small that the integrator does not recognize it; however, commercial catalysts with roughly twice the CO conversion activity do not display any noticeable peak at this position. No dimethyl ether was seen during the tests. Based on this, it is predicted that this catalyst would display a lower selectivity toward MeOH formation than the normal commercial catalysts, even if the activity could be doubled.

Cu/Mo/Al₂O₃ Catalyst : R18/1E31-61

This candidate showed virtually no CO conversion between 225 and 250°C at 500 psig. The reduction technique utilized for this test was the CSI/APCI gas phase procedure.

A second screening of this catalyst utilizing a modified reduction procedure showed no improvement. In this test, the catalyst was heated to 300°C at 100 psig under 600 l/hr-kg of pure H₂ flow and allowed to reduce for 16 hours. The temperature was slowly increased to 400°C over 8 hours. The catalyst was then allowed to cool under H₂ flow and was pressurized to 500 psig for testing. Upon switching to a balanced synthesis gas blend, the activity was checked at between 210°C and 290°C at 500 psig and 5000 l/hr-kg. Little or no CO conversion was seen at all temperatures.

Cu/Mo/SiO₂ : R18/OF31-62

A sample of this catalyst was reduced utilizing the pure H₂ treatment as above and gave identical results as the alumina based analog described above.

Cu/Zn/Al : R19/OF55-63 (and) Cu/Mg/Al : R19/OF55-64, Raney Copper Catalysts

Samples of these catalysts were reduced utilizing the standard CSI/APCI gas phase reduction procedure with 2% H₂/N₂ at temperatures between 180°C and 240°C. Both catalysts produced a trace of methanol when tested at 500 psig, 5000 l/hr-kg and temperatures between 210°C and 290°C. These Raney catalysts were stored under water. A retest of subsequent batches of these catalysts was performed when the catalysts were prepared and tested within 1-2 days. It is suspected that these catalysts deactivate if allowed to set under water for an extended period.

Cu/ZnO/Al₂O₃ : R12/1F32-66

This catalyst is the third preparation of the Stiles-type and incorporates improved control of temperatures in the heat treatment. The catalyst was reduced with 2% H₂/N₂ at 600 l/hr-kg and 180°C for 16 hours. The temperature was then raised

in 20°C steps lasting 1 hour each to 240°C. This last condition was held for 2 hours. The catalyst was then placed under N₂ and the reactor was adjusted to the reaction conditions. At 225°C, 500 psia, and 5000 l/hr-kg, the methanol yield was 14.61 mmol/gm-hr with a CO conversion of 37% using a balanced feed gas. This yield of methanol approaches that of the commercial catalysts tested under similar conditions and represents a significant advancement over the previous preparation's performance (7.0 mmol/gm-hr).

Cu/ZnO/Al₂O₃ : 5801-42

This catalyst was prepared in a catalyst development program conducted at Air Products prior to the contract. The preparation procedure is the same as R12/1F32-66 and was re-tested to serve as a reference. The reduction procedure was the same as described above. The methanol yield at 225°C, 515 psia and 5000 l/hr-kg was 8.36 mmol/gm-hr with a CO conversion of 25.22% using a balanced gas feed. This yield is lower than was demonstrated with this same catalyst at the time of preparation, however; that test utilized a stoichiometric gas feed with no inerts.

Cu/Zn/Al Raney : R19/OE55-67

This Raney type catalyst was produced from a starting alloy having a weight ratio of Cu:Zn:Al = 38:12:50. This catalyst was prepared at the Linwood Labs and allowed to set under water for several days before testing. During this period, the catalyst was observed to be outgassing. No reduction procedure was used before testing. At testing conditions of 225°C, 500 psia, and 5000 l/hr-kg with a balanced gas feed, the methanol yield was 5.34 mmol/gm-hr with a CO conversion of 15%. The temperature was raised to 250°C and the methanol yield increased to 7.35 mmol/gm-hr. Because Raney type catalysts have characteristically been tested at higher temperatures, a 270°C test was also conducted. The catalyst deactivated at this temperature; therefore the test was discontinued.

Cu/Mg/Al Raney : R19/O55-68

This Raney type catalyst was produced from a starting alloy of Cu:Mg:Al = 38:12:50 (wt%). No reduction was used before testing at 225°C, 515 psia, and 5000 l/hr-kg with a balanced gas feed. No methanol was produced and no CO was converted at this condition and or 250°C.

Cu/Zn/Al Raney : R19/OE55-69

Because of the activity displayed by the previous Raney catalyst, it was decided that the preparation would be repeated at the Emmaus test site so that the time interval between preparation and testing would be minimized. To that end, the R19/OE55-67 catalyst preparation was reproduced and re-tested. Under the same testing conditions, 225°C, 515 psia, 5000 l/hr-kg, this second batch produced a 5.83 mmol/gm-hr methanol yield. This compares with the 5.34 mmol/gm-hr yield previously stated.

Ni/B : R10/OE55-70

This catalyst was produced at the Emmaus test site by Linwood PSG personnel to minimize the time lag between preparation and testing. The catalyst was tested as prepared with no reduction phase. The catalyst produced only 0.5 mmol/gm-hr of methanol, but did produce 25.80 mmol/gm-hr of methane with a CO conversion of 69.79%. The conditions of the test were 225°C, 515 psia, and 5000 l/hr-kg. The test was discontinued because of possible accumulation of heavier Fischer-Tropsch products within the reactor system.

Cu/B : R10/OE55-71

As shown above, a preparation of Ni/B had high CO conversion to methane. This catalyst was an attempt to capitalize on this high activity and by replacing the nickel with copper, increase the

methanol yield. No reduction was used for this catalyst. The test conducted at 225°C, 515 psia, and 5000 l/hr-kg showed no methanol produced with only a low CO conversion (0.3%). The test temperature was increased to 250°C and 0.2 mmol/gm-hr of methanol was produced. The test was discontinued.

Cu/Zn/Al₂O₃ Modified Prep : R12/1E32-72

This catalyst was prepared using a low temperature precipitation method and was calcined with a closed muffle furnace in stagnant air. The reduction procedure was the same as reported above for R12/1E32-66. The methanol yield at 225°C, 515 psia, and 5000 l/hr-kg was 8.06 mmol/gm-hr with a CO conversion of 19.14% using a balanced feed gas.

Cu/Zn/Al₂O₃ Modified Prep : R12/1E32-73

This catalyst was prepared from the same batch as described above, R12/1E32-72. However, in the present case the catalyst was calcined under flowing air. The reduction procedure and test conditions were the same as above. The methanol yield was 2.34 mmol/gm-hr at the 225°C condition. The temperature was increased to 250°C and the yield of methanol increased to 2.74 mmol/gm-hr, however, dimethyl ether was also formed at a rate of 4.2 mmol/gm-hr. At this point the test was discontinued.

Cu/B/ZnO : R12/1E32-74

Previous testing of the Cu/B catalyst showed negligible activity. This preparation uses a ZnO substrate for the Cu/B catalyst in an attempt to increase its activity. No reduction procedure was utilized before testing. At the normal testing conditions of 225°C, 515 psia, and 5000 l/hr-kg, the methanol yield was 0.15 mmol/gm-hr with a balanced gas feed. No other conditions were tested for this catalyst.

Cu/Zn Raney : R19/OE55-75

This Raney catalyst was prepared from a starting alloy of Cu:Zn:Al = 33:17:50 (wt%). No reduction was used prior to testing. The yield of methanol was 5.76 mmol/gm-hr with a balanced feed at 225°C, 515 psia, and 5000 μ /hr-kg. The yield of methanol at 250°C was 6.18 mmol/gm-hr. All of the alloys were purchased as powders of size less than 20 mesh. No particle size distributions were obtained; however, the alloy used for this preparation appeared to have more larger particles than prior samples. It is suspected that this larger size may have resulted in an incomplete aluminum leach since these catalysts are soaked for a specific time interval based on literature optimums.

SECTION III

EXPERIMENTAL

III. EXPERIMENTAL

A. Catalyst Preparations

1. Apparatus

Most of the experimental work was carried out in standard laboratory glassware with a magnetic stirrer for the smaller preparations and a paddle stirrer for the larger scale preparations. For the single aerogel preparation, a one-liter autoclave (Autoclave Engineers) installed in a high pressure room. This was fitted with an inert gas purge, temperature recorder, temperature controller and pressure indicator.

2. Experimental Procedure

a. R12/072-50 Copper-Zinc Catalyst

This preparation started with a hot (80-90°C) well-stirred solution of zinc and copper nitrates and required addition of sodium carbonate to adjust the pH to 7.51. During the addition period the pH was monitored. The precipitated was filtered, washed by reslurring, dried overnight at 100°C and muffle treated at 350°C. The dried material was placed in the hot muffle at 350°C and the temperature held for three hours. The most effective wash procedure was found to be reslurring of the solids in deionized water. This was the method used in this preparation and in subsequent preparations involving precipitation from the nitrate solutions.

b. R12/1E72-51 Copper-Zinc-Alumina Catalyst

A solution of the copper and zinc nitrates with suspended Alcoa C-37 alumina was heated to 80-90°C with vigorous stirring. The pH was adjusted to 7.52 with the addition of 1 molar sodium carbonate solution. The precipitate was filtered, washed and dried overnight at 100°C. The dry material was placed in a muffle at 350°C and held at temperature for 3 hours.

c. R15/0E72-52 Copper-Cerium Catalyst

A hot solution (80-90°C) of copper and cerium nitrate was neutralized with a 1 molar solution of sodium carbonate to pH 6.56. The neutralization was completed with the addition of a 10% sodium hydroxide solution. The final pH was 7.47. The precipitate was separated by filtration, washed and dried at 100°C overnight. The dry cake was placed in a 350°C muffle and held at temperature for three hours.

d. R12/1E72-53 Copper-Cerium-Alumina Catalyst

This was first prepared as 1812JX1-1 by heating a well stirred mixture of copper and cerium nitrate solutions and Alcoa C-37 alumina and neutralizing with 6.9 liters of 1 molar sodium carbonate solution to a pH of 6.73. The blue color of the liquid was lost at the end of the neutralization. The solids were separated by filtration and dried overnight at 100°C. The dry solids were placed in a muffle at 350°C and held at temperature for 3 hours. This was to have been the finished product, however, the sodium content of this material was judged to be too high for activity testing. The muffle treated produce was water washed 3 additional times, dried and muffle treated once again at 350°C for three additional hours. This was renumbered 1812JX2-2X1. The sodium content reduction was from 0.34% to 0.08% of sodium oxide by weight.

e. R12/2E22-54 Copper-Zinc-Silica Catalyst

This was an attempt to follow up on the idea used in a previous small-scale sample where we mixed the metal salts and the silica and accepted the product with no further neutralization. This procedure did work, but the initial filtrate had far too much unreacted metal indicated by its color. In order to reduce the metal loss in the filtrate, the mixture of silica and metal salts was neutralized to a

pH of 7.1/7.3 with 10% sodium hydroxide. There was still metal present in the filtrate so the solids were reslurried once again and more sodium hydroxide was added to a pH of 8.2/8.5. Between the time required for the extra sodium hydroxide addition and reslurry time it was a matter of several days before the precipitate was properly filtered and washed. The solids were dried overnight at 100°C and muffle treated for 6 hours at 350°C.

f. R13/1E22-55 Copper-Magnesium-Alumina Catalyst

A solution of the copper and magnesium nitrates was mixed with the alumina and heated to 80-90°C. The mixture was then neutralized with a 1 molar solution of sodium carbonate. In order to completely precipitate the magnesium it was necessary to finally neutralize with much 10% sodium hydroxide. The solids were very slow filtering. These solids were finally dried overnight at 100°C and muffle treated at 350°C for three hours.

g. R10/0E32-56 Chromium-Copper-Zinc Catalyst

Chromium nitrate was added to a hot, well stirred solution of copper and zinc nitrates. The resulting solution was held at 80-90°C while being neutralized with a sodium carbonate solution to pH 7.3. The resulting precipitate sat overnight and the pH was 7.7 at room temperature the next morning. The solids were filtered, water washed five times and dried overnight at 100°C. The pH of the five washes were 8.3, 7.9, 7.3, 7.0 and 6.8. The dried cake was muffle treated for 3 hours at 360°C.

h. R15/4E31-57 Copper-Cerium-Chromia-Alumina Catalyst

This was an impregnation of an alumina support which has been dipped in a chromic acid solution. The base material was a commercially produced alumina support which was pulverized and screened on 45 mesh to remove the fines.

The resulting particles were dipped in a 50% chromic oxide solution for 30 minutes, drained, dried at 250°F for 2 hours and heat treated at 600°C for 4 hours in flowing air. This procedure approximates that used for a commercially produced catalyst. A solution of the nitrates of copper and cerium were prepared targeting a Cr:Cu:Ce ratio of 50:15:35 as oxides in the final material. The solids were impregnated with the nitrate solution, dried overnight at 100°C and muffle treated for three hours at 350°C.

i. R12/4E32-58 Chromia-Alumina-Copper-Zinc Catalyst

This preparation is a duplicate of the previous one except that the impregnating solution contained zinc nitrate instead of cerium nitrate. However, the one difference observed when the nitrate solution was added to the support was that not all of the solution was absorbed. Thus it was necessary to dry the partially impregnated particles and reimpregnate with the balance of the solution. The final heat treatment was the same as in the previous sample.

j. R12/1F32-59 Copper-Zinc-Aluminum Catalyst

The initial preparation was done using ammonium carbonate as the neutralizing agent. However, the material submitted for activity testing was made using ammonium bicarbonate. The patent example used bicarbonate.

A solution containing the nitrates of copper, zinc and aluminum was heated to 30°C and neutralized with 20% w/v solution of ammonium-bicarbonate to pH 6.8. The resulting solids were digested at 30°C for 30 minutes with agitation. The precipitate was filtered, washed and dried overnight at 100°C. The cake was then muffle treated in air starting at 150°C and increasing 50°C each half hour to 400°C.

We have since determined that the heat treatment given the -59 catalyst was not as closely controlled as we would have wished. The oven used does not control well at temperatures as low as 150°C and so the initial treatment temperature was probably higher.

The subject of close precipitation control suggests an additional preparation using the copper and zinc nitrates and ammonium bicarbonate for neutralization. This would involve placing the pH on feedback control and separating the solids from the liquid as soon as they are formed.

k. R12/OE32-60 Copper-Zinc-Boron Catalyst

The copper and zinc were from nitrates and the boron from a boric acid. A solution of the copper, zinc and boron was prepared, heated to 80°C, and neutralized by mixing with a hot 20% solution of sodium carbonate. The resulting mixture was cooled with stirring for two hours. The solids were then separated by filtration and dried overnight at 80°C. They were then heat treated in a glass tube with flowing air at 375°C for 2 hours.

l. R18/1E31-61 Copper-Molybdenum-Alumina Catalyst

A solution containing ammonium heptamolybdate (AHM) in deionized water and 25% of 30% hydrogen peroxide was prepared. The resulting bright yellow solution was acidified with nitric acid to approximately pH 5. A solution of cupric nitrate in deionized water was added quickly to the vigorously stirring AHM solution. The resulting copper-molybdenum solution was then contacted with the Catapal alumina and mixed so that the powder was thoroughly and uniformly wetted. The solution volume was controlled so that no excess liquid was present during the impregnation step. The resulting powder was dried at 250°F overnight. The catalyst was then treated in a muffle furnace at 350°C for 2 hours.

m. R18/2E31-62 Copper-Molybdenum-Silica Catalyst

A solution containing AHM in deionized water and 25% of 30% hydrogen peroxide was prepared. This solution was then acidified to pH 5 with nitric acid to prevent precipitation of the molybdate species upon addition of copper nitrate. A second solution was prepared containing copper(II) nitrate in deionized water. The two solutions are then rapidly mixed and the meta-stable solution contacted with silica support. The solution was completely soaked up by the silica and the resulting damp powder was blended thoroughly. The catalyst was then dried at 250°F and calcined at 350°C in a muffle furnace.

n. R19/0E55-63 Copper-Zinc-Aluminum Catalyst

The starting alloy was purchased as a finely divided (-20 mesh) powder of composition ratio Cu:Zn:Al of 40:20:40 (wt%). This particle size was specified for all Raney-type catalysts and although some variation did exist, the particle size range was never measured. the alloy composition was also accepted without analytical confirmations. The alloy was placed in a reaction flask with deionized water and heated to 45/50°C. Measured volumes of 50% solution of sodium hydroxide were added over an hour. The addition was made in small increments to control the temperature at a maximum of 55°C. The resulting solids were washed to remove the caustic and stored under water with a nitrogen blanket. After about 10 days the solids were tested and found not pyrophoric. In order to facilitate temperature control of smaller volumes, three batches were made using 100 grams of the starting alloy each time. The resulting solids were mixed for activity testing.

o. R19/0E55-64 Copper-Zinc-Magnesium Catalyst

This alloy was purchased with the same specifications as that for catalyst -63 except that the starting composition was ratio Cu:Mg:Al of 40:20:40 (wt%). The preparation was carried out in the same manner as that for catalyst -63.

p. R18/2E32-65 Copper-Molybdenum-Silica Catalyst

A solution containing sodium 12-molybdosilicate was dissolved in deionized water and contacted with DOWEX 50X8 resin in the acid form to prepare a solution of 12-molybdosilic acid (12-MSA). The 12-MSA was then reduced by dropwise addition of hydrazine hydrate. The resulting solution turned from yellow to blue-green indicating the presence of Mo(IV) and Mo(V). A cupric nitrate solution was then added dropwise to this solution. The dark/black precipitate that formed was filtered, washed 3X with deionized water and air dried. The entire preparation was repeated and the product from both blended before submission for activity testing.

q. R12/1E32-66 Copper-Zinc-Aluminum Catalyst

The preparation was an attempt to follow the preparation of R12/1E32-59 exactly, up to the solids separation. It is, prepare solutions of the metal nitrates, heat this solution to 30°C and adjust the pH to 6.8 with ammonium bicarbonate. The resulting solids were digested at 30°C for 30 minutes with agitation. A centrifuge was used to separate the solids instead of the usual filter. The wet cake was dried overnight at 110°C and the resulting dry cake carefully heat treated at from 150°C to 400°C in 50°C intervals.

The difference between this and the prior preparation was the close control of the heat treatment temperatures and the use of a centrifuge to separate the solids.

r. R19/OE55-67 Copper-Zinc-Aluminum Catalyst

This catalyst was prepared from an alloy with composition ratio Cu:Zn:Al of 38:12:50 (wt%). The preparation followed that of -63 closely except that greater care was exercised to exclude air (oxygen) from contacting the product. The previous sample (R19/OE55-63) had been permitted to stand for about two weeks before it was activity tested. Even though that sample was protected from contact with air, the possibility exists that it reacted with the water present releasing hydrogen and coating its surface with a less active oxide layer. In order to reduce this exposure the test reactors were sent from Emmaus to Linwood for filling. The reactors were filled with fresh catalyst in a nitrogen atmosphere, transferred to Emmaus the following day and placed in the test system with a flowing nitrogen atmosphere. These precautions reduced the possibility for surface degradation.

s. R19/OE55-68 Copper-Magnesium-Aluminum Catalyst

This catalyst was prepared from an alloy with the composition ratio Cu:Mg:Al of 38:12:50 (wt%). It was prepared in the same fashion as -67. That is, all care was taken to exclude air and the reaction sample holders were filled in Catalyst Preparation Laboratory immediately after catalyst preparation.

t. R19/OE55-69 Copper-Zinc-Aluminum Catalyst

It was prepared from an alloy with the composition ratio Cu:Zn:Al of 38:12:50 (wt%). This sample was prepared following the procedure of -67 except that it was prepared in the Emmaus laboratory to further reduce the potential for oxygen contact. Directly after preparation in the nitrogen atmosphere the sample was placed in a sample holder. The sample holder was then installed in the test unit to purge the sample with nitrogen and completely dry the surface.

u. R10/OE55-70 Nickel-Boron Catalyst

Nickel acetate was dissolved in a deionized water, cooled with ice and blanketed with nitrogen. To this solution a cold suspension of sodium borohydride was carefully added. After the rapid evolution of gas ceased, the suspension was removed from the ice bath and allowed to warm to room temperature. The black solid product was constantly protected from exposure to air and was washed by decantation and centrifuging. After the final wash, the solids were transferred directly to a test reactor without any exposure to air.

v. R10/OE55-71 Copper-Boron Catalyst

This preparation followed the same general plan as R10/OE55-70, except that copper acetate replaced nickel acetate. The solids were protected from contact with air and loaded directly into reactors as soon as washing was complete. The problem with this synthesis was not the exotherm but the foaming. As the gas evolved it caused a great deal of froth to be formed and required a reaction vessel several times larger than the reacting volume.

w. R12/1E32-72 Copper-Zinc-Aluminum Catalyst

The metal salt solution was prepared as in the case of the R12/1E32-59 and -66 preparations. It was cooled with dry ice to 9-10°C and held there during the pH adjustment. This adjustment was made with ammonium bicarbonate and the resulting solids were separated using the centrifuge. The wet cake was dried overnight and heat treated in a muffle furnace using the same care the same care exercised on R12/1E32-66.

x. R12/1E32-73

A portion of the dried cake from R12/1E32-72 was heat treated in flowing air.

y. R12/1E32-74 Copper-Zinc-Boron Catalyst

This preparation closely followed the prior boride system (R10/OE55-70). Copper acetate was dissolved in water, zinc oxide was added, the mixture was cooled, stirred vigorously and treated with a water-sodium borohydride suspension. The entire operation took place under a nitrogen atmosphere to protect the catalyst surface from oxidation. The zinc oxide acted to break the froth and the preparation proceeded without incident. The resulting solids were washed by decantation, separated by centrifugation and transferred to the test reactor under nitrogen atmosphere.

z. R19/OE55-75 Copper-Zinc-Aluminum Catalyst

The starting alloy of copper, zinc and aluminum was composition ratio Cu:Zn:Al of 33:17:50 (wt%). This sample was prepared using the same procedure as R19/OE55-63. The effect of surface deactivation through contact with air or water was felt to be of significant importance. To protect against deactivation this material was prepared in the Emmaus laboratory under strictly controlled conditions and immediately transferred to a sample holder for activity testing. The sample holder was then placed in the test unit and purged with nitrogen to dry the surface and protect it from deactivation.

aa. R12/1E32-76 Copper-Zinc-Aluminum Catalyst

This preparation was a duplication of R12/1E32-66 in order to obtain wet cake for heat treatment experiments. The activity test results on catalysts -72 and -73 indicated the oxidizing nature of the heat treatment atmosphere had an effect on the activity of the product. This preparation was split into two portions to further test for this effect with an assumed starting activity. This sample was heat treated in a flowing air atmosphere.

bb. R12/1E32-77

The same starting material as used to prepare -76 was heat treated in a flowing nitrogen atmosphere.

cc. R12/1E32-78 Copper-Zinc-Aluminum Catalyst

The organic metal salts were dissolved in methanol. After all the components were added the resulting clumps were broken up with the aid of a high shear mixer. The resulting mixture was placed in an autoclave for Aerogel generation. The plan was to raise the temperature of the mixture above the critical temperature of the solvent, methanol, release the methanol to vent while maintaining temperature, cool and remove the product. At the critical temperature methanol will generate about 1200 psi pressure. The slow release of the methanol was to be controlled so that the cooling effect would not reduce the autoclave temperature below the methanol critical temperature. However, the safety disk ruptured during the heating period and allowed the methanol to vent rapidly. The internal temperature was somewhat above 215°C but below the 242°C critical temperature. The pressure was over 800 psi at the time of the discharge.

After cooling and venting the autoclave was opened and 37 grams of dull red product was recovered. While setting up the system with a new safety disk to repeat the experiment, it was found that a hold down ring in the safety disk holder was damaged. It was not possible to replace this piece of equipment in time to make a second attempt at this preparation and have a product ready to be tested in the gas phase test unit in time to be included in the program.

As a result the dull red powder was tested for surface area ($320 \text{ m}^2/\text{g}$), heat treated with the "standard" staged 400°C muffle treat and submitted for activity testing. The final catalyst surface area was $168 \text{ m}^2/\text{g}$. Even though the surface area is not as high as would be expected for a proper Aerogel preparation, it is still much higher after heat treatment than many of the other mixed oxides. This product was then submitted for gas phase activity testing.

dd. R12/1E32-79 and R12/1E32-82

These samples were duplications of the R12/1E32-66 and were prepared for testing in the CSI autoclave. They were not tested in the gas phase system.

ee. R12/OE32-80 and R12/OE32-83

These catalysts were duplications of R12/OE32-60 prepared for testing in the CSI autoclave.

ff. R19/OE55-81

This is a duplication of R19/OE55-75 made in the CSI laboratories and submitted directly for autoclave testing.

B. APCI Gas Phase Catalyst Screening Reactor

The gas phase screening reactor is a CDS 800 series CF-HP continuous flow catalytic reaction system (CDS = Chemical Data Systems, Inc.). Specifications for this unit are presented in Table 4 and typical operating parameters in Table 5. The reaction system provides two reactant inlets for each of two reactors which can be operated independently. The system provides heat control of all internal surfaces as well as flow control and pressure control/relief devices. Figure 1 shows a detailed schematic of the system. Valves 1, 2, 3 and 4 (high pressure sampling valves) are not used under its current configuration. Sampling and analysis of the product is done at atmospheric pressure with the gas flow from the reactor "A" vent #1 and reactor "B" vent #2 lines at the exit of each reactor's back

pressure regulator. This modification allows the same analytical system to service both of the gas phase reactors and a bench-scale slurry phase reactor. Figure 2 is a detailed schematic of the auxiliary equipment which was constructed to service the CDS reactor system. Synthesis gas (premixed) is supplied in 2500 psi cylinders to the gas delivery system. Pressure reduction regulators PR1 and 2 establish the delivery pressure at 50 psig above the reactor pressure. Excess flow valves (EFV1 and 2) have been provided to guard against excessive reactant leakage in the event of a tube or valve failure. The synthesis gas, at reactor pressure, is conducted to a carbonyl scrubbing unit (CS1). This scrubbing unit consists of a bed of activated carbon. The gas delivery system is guarded from excessive pressure surges by pressure relief valves (RV1 and 2) which are set at 1100 psig. The scrubbed synthesis gas is conducted to one reactant inlet port for each of the two reactors. The second reactant inlet for each reactor is supplied with high pressure inert gas for purging. Each of the two reactant inlet flows for each reactor is metered through 0-2000 sccm thermal mass flow controllers. The outlet of each mass flow controller is conducted to a mixing area. The mixing area supplies the reactant flow for each reactor. The inlet pressure for each reactor is monitored and contains a safety relief blow-out disc. A low pressure limit switch was installed to shut-down the system in the event of a large leak or disc rupture. This safety switch is typically set at 100 psi below the operating pressure. The inlet gas is conducted to the external reactor module via a heated transfer line (150°C) and enters at the top of the reactor body. After traversing the catalyst bed, it exits into a gas/liquid separator (200°C) located below the reactor tube. The exit gas is conducted from the external module to a heated gauge assembly via another heated transfer line (150°C). This gauge assembly (150°C) allows monitoring of the reactor exit pressure and provides another safety blow-out disc. The combination of inlet and outlet gauge assemblies allows monitoring of the reactor and catalyst bed pressure drop. The exit gas is then conducted through the valve oven (170°C) to a heated

back pressure regulator (110°C). The exit gas, at near atmospheric pressure, is conducted to valving network to allow exit gas flow velocity measurement and component analysis. The initial transfer line is heated to 110-120°C; the valving network is heated to 80-90°C to prevent product condensation. Flow measurements are made with a 1-liter per revolution wet test meter filled with instrument oil and heated to 76°C.

Analysis of the product (and inlet stream) is accomplished with a Carle #1156 (special) series-SX analytical gas chromatograph. As is shown in Figure 1, solenoid valves (V7 and 8) are used to automatically select reactor A or reactor B for sampling. A third solenoid valve allows sampling of the bench scale slurry phase reactor. Manual valve V6 is used to select either reactor exit gas or gas standards. Each component analyzed is standardized periodically with either primary gravimetric standards (methanol, ethanol and dimethyl ether) or by primary grade premixed standards provided by APCI specialty gas division (CO, CO₂, H₂, ethane, ethylene). Standardization of the water response is done utilizing literature values in conjunction with the standardized responses for the remaining components. Figure 3 shows a typical chromatogram for this analysis scheme. All components except hydrogen, are detected utilizing a thermal conductivity detector with a helium carrier gas. Hydrogen is transferred to a nitrogen carrier gas, through a heated palladium H₂ transfer system, and then detected by a thermal conductivity detector. This transfer into a nitrogen carrier allows accurate quantitation of the hydrogen content.

Table 6 shows typical operating parameters for the gas phase screening reactor during the shakedown runs.

C. Baseline Gas Phase Tests of Commercial Methanol Catalyst F51/4E75-81
(Reactor Shakedown)

Activity tests of this catalyst were conducted at both 515 psia (3500 Kpa), 895 psia (6500 Kpa), and 225°C and 250°C, with space velocities from 4000 to 17000 l/hr-kg. The catalyst activation procedure used was the preferred gas phase reduction technique used by Chemical Systems, Inc., in their evaluation of catalyst R71/OF12-Z in the CSI Liquid-Fluidized PDU (July 1982). Figure 4 shows the CO conversion plotted vs space velocity for a balanced gas feed consisting of 55% H₂/19% CO/5% CO₂/21% N₂. The nitrogen content represents inerts in the actual pilot plant feed and serves as an internal standard in analysis of the exit gas. Figure 4 shows that the 225°C runs at both 515 psia and 895 psia are essentially free from equilibrium limitations within the space velocities studied. The zero velocity value represents a value calculated for equilibrium under reaction conditions of temperature and pressure. The 250°C plots at both pressures show severe equilibrium limitations at low space velocities. These low space velocities, of course, are not realistic operating regimes for commercial units. The reactor system used for these determinations utilizes a small tubular reactor (1/2 inch ID) situated in a massive inconel heat sink which allows this type of operation. The data shown in Figure 4 will be used as a basis of catalyst activity comparison for test runs utilizing experimental catalyst and also serves as a criterion for selecting conditions for these tests that would not exhibit equilibrium limitations.

Figure 5 shows a comparison of methanol production rates for both balanced and unbalanced feed gases at 515 psia (3550 Kpa) and at both 225°C and 250°C. The formation rates for the balanced feed gas are higher than that determined for the unbalanced feed gas; however, the difference between the two feed gases is not as

striking as was expected. No attempt was made to determine the effect of unbalanced feed on catalyst lifetime in these gas phase tests.

Table 7 shows a comparison of performance of this catalyst with both balanced and unbalanced feed gases at 895 psia (6170 Kpa) and at both 225°C and 250°C. This table shows that slightly higher DME (dimethyl ether) and EtOH (ethanol) by-product formation occurs in the unbalanced feed gas cases even though the methanol formation rates are comparable.

SECTION IV

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IV. REFERENCES

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SECTION V

APPENDIX

Table 1

PREPARATION SUMMARY

Twenty-nine experimental samples were prepared and delivered for gas phase activity testing. A brief description of these catalysts in chronological order is as follows:

Code

-50	CuO/ZnO	Baseline
-51	CuO/ZnO/Al ₂ O ₃	Eta-Al ₂ O ₃ supported (Al ₂ O ₃ from Beta Trihydrate)
-52	CuO/Ce ₂ O ₃	
-53	CuO/Ce ₂ O ₃ /Al ₂ O ₃	Eta-Al ₂ O ₃ supported (Al ₂ O ₃ from Beta Trihydrate)
-54	CuO/ZnO/SiO ₂	SiO ₂ supported
-55	CuO/MgO/Al ₂ O ₃	Gamma-Al ₂ O ₃ supported (Al ₂ O ₃ from Boehmite)
-56	CuO/ZnO/Cr ₂ O ₃	Precipitation from Nitrate Solution
-57	CuO/Ce ₂ O ₃ /Cr ₂ O ₃ -Al ₂ O ₃	Metal Oxides deposited on chromia alumina base
-58	CuO/ZnO/Cr ₂ O ₃ -Al ₂ O ₃	" " " "
-59	CuO/ZnO/Al ₂ O ₃	Precipitation from Nitrate Solution - AB Stiles patent
-60	CuO/ZnO/Boron	Mitsubishi patent derivative
-61	Cu/Mo/Al ₂ O ₃	Soak powdered alumina with solution of metals
-62	Cu ₂ MoO ₅ /SiO ₂	Soak powdered silica with acidified solution of metal salts
-63	Cu/Zn/Al	Raney-type from starting alloy of composition 40:20:40
-64	Cu/Mg/Al	Raney-type from starting alloy of composition 40:20:40
-65	Cu/Mo Heteropoly	Hydrazine reduction of molybdosilic acid
-66	CuO/ZnO/Al ₂ O ₃	Precipitation from nitrate solution - Stiles derivative
-67	Cu/Zn/Al	Raney type from starting alloy of composition 38:12:50
-68	Cu/Mg/Al	Raney type from starting alloy of composition 38:12:50

Table 1 (continued)

<u>Code</u>		
-69	Cu/Zn/Al	Raney type from starting alloy of composition 38:12:50
-70	Ni/B	Coprecipitation from solutions of metal acetate and sodium borohydride
-71	Cu/B	Solutions of metal acetate and sodium borohydride
-72,73	CuO/ZnO/Al ₂ O ₃	Precipitation from nitrate solution - Stiles derivative heat treatment comparison
-74	Cu/B/ZnO	Sodium borohydride added to solution of metal acetate containing suspended zinc oxide powder
-75	Cu/Zn/Al	Raney type from starting alloy of composition 33:17:50
-76,77	CuO/ZnO/Al ₂ O ₃	Precipitation from nitrate solution - Stiles derivative - heat treatment atmosphere comparison
-78	CuO/ZnO/Al ₂ O ₃	Aerogel
-79,82	CuO/ZnO/Al ₂ O ₃	Stiles derivative for CSI autoclave testing
-80,83	CuO/ZnO/Boron	For SCI autoclave testing
-81	Cu/Zn/Al	Raney type from starting alloy of composition 33:17:50 for CSI autoclave testing

Table 2

APCI EXPLORATORY CATALYSTSSCREENING SUMMARY

<u>Catalyst Code</u>	<u>Type</u>	<u>MeOH Yield</u> <u>mmol/gm-hr*</u>
F50/4E75-81	ICI Ref/ (Cu/Zn/Al ₂ O ₃)	18.6
R12/0E72-50	Cu/Zn	0.66
R12/1E72-51	Cu/Zn/Al ₂ O ₃	0.53
R15/0E72-52	Cu/Ce	0.13
R15/1E72-53	Cu/Ce/Al ₂ O ₃	0.06
R12/2E22-54	Cu/Zn/SiO ₂	0.21
R13/1E22-55	Cu/Mg/Al ₂ O ₃	Untested
R10/0E32-56	Cu/Zn/Cr ₂ O ₃	Nil
R15/4E31-57	Cu/Ce/Cr ₂ O ₃ -Al ₂ O ₃	Nil
R12/4E31-58	Cu/Zn/Cr ₂ O ₃ -Al ₂ O ₃	Untested
R12/1E32-59	Cu/Zn/Al ₂ O ₃	9.5 (17.5)
R12/0E32-60	Cu/ZnO/Boron	7.8
R18/1E31-61	Cu ₂ MoO ₅ /Al ₂ O ₃	Trace
R18/0E55-62	Cu ₂ MoO ₅ /SiO ₂	Trace
R19/0E55-63	Raney Cu/Zn/Al 40/20/40: Alloy Ratio	1.0
R19/0E55-64	Raney Cu/Mg/Al 40/20/40: Alloy Ratio	1.0
R18/2E32-65	Cu/Mo Heteropoly	Untested
R12/1E32-66	Cu/Zn/Al ₂ O ₃ Stiles Derivative	14.6
5801-42	Cu/Zn/Al ₂ O ₃ Stiles Reference	8.4
R19/0E55-67	Raney Cu/Zn/Al 38/12/50: Under Water	5.3
R19/0E55-68	Raney Cu/Mg/Al 38/12/50: Under Water	0.2
R19/0E55-69	Raney Cu/Zn/Al 38/12/50: Fresh	5.8
R10/0E55-70	Ni/Boride	0.05 (CH ₄)
R10/0E55-71	Cu/Boride	Nil (H ₂ O)
R12/1E32-72	Cu/Zn/Al ₂ O ₃ Low Temp/Stagnant Air	8.1
R12/1E32-73	Cu/Zn/Al ₂ O ₃ Low Temp/Flowing Air	2.3
R12/1E32-74	Cu/Boride/ZnO	0.15
R10/0E55-75	Raney Cu/Zn/Al 33/17/50: Fresh	5.8

Table 2 (continued)

APCI EXPLORATORY CATALYSTS

<u>Catalyst Code</u>	<u>Type</u>	<u>MeOH Yield</u> <u>mmol/gm-hr*</u>
R12/1E32-76	Cu/Zn/Al ₂ O ₃ Stiles Derivative/Air	0.8
R12/1E32-77	Cu/Zn/Al ₂ O ₃ Stiles Derivative/N ₂	4.9
R12/1E32-78	Cu/Zn/Al ₂ O ₃ Aerogel	1.8
R12/1E32-79 ^o	Cu/Zn/Al ₂ O ₃ Stiles Derivative	
R12/0E32-80 ^o	Cu/Zn/Boron	
R19/0E55-81 ^o	Raney Cu/Zn/Al 33/17/50: Alloy Ratio	
R12/1E32-82 ^o	Remake of -79	
R12/0E32-83 ^o	Remake of -80	

*At 500 psig, 225°C, 5000 Space Velocity (l/hr-kg)

Feed Gas, 5% CO₂/19% CO, 21% N₂/55% H₂

^oFor testing in CSI stirred autoclave

Table 3

CATALYST PROPERTIES

Catalyst Code	Bulk Density Kg/L	Surface Area m ² /g	LOI wt %	CuO, wt %	ZnO, wt%	Al ₂ O ₃ wt %	Na ₂ O ₃ wt %	Other, wt %	Cr ₂ O ₃ wt %	XRD
-50	0.473	10 (350°C)	1.6	29.8	68.9		0.035			ZnO, CuO Cu(OH) ₃ NO ₃ -
-51	0.651	103 (350°C)	14.8	20.5	30.1		0.2			ZnO, CuO, Al ₂ O ₃
-52	0.649	65 (350°C)	3.5	45.2	--	--	0.3	Ce ₂ O ₃ 52.5		CeO ₂ , CuO
-53	1.004	182 (350°C)	7.2	26.9	--	50.1	0.05	Ce ₂ O ₃ 22.8		CeO ₂ , CuO, Al ₂ O ₃
-54	0.529	106	12.5	16.6	33.4	SiO ₂ -48.5	0.14			CuO, ZnO
-55	1.017	157 (1400°C)	27.9	14.0		52.9	0.03	MgO 32.4		MgO, CuO
-56	--	109	5.4	15.2	34.2	--	0.02		48.7	ZnCr ₂ O ₄
-57	1.225	118	3.8	6.0	--	65.7	0.15	Ce ₂ O ₃ 6.9	22.1	CuO, CeO ₂
-58	--	121	4.9	4.8	10.9	65.9	0.25		19.1	Weak Al ₂ O ₃
-59	--		7.3	59.3/60.4	14.5/16.1	22.9/23.8	0.008/0.003			CuO Major - ZnO Possible
-60	0.635									
-61-65	--									
-66	--		--	50.7	15.9	24.7	0.014			
-67	--		17.9	78.7	7.2	13.6	--			
-68	--		--							
-69	--		13.3	78.1	8.5	12.4	--			
-70	--		62.1	--	--	--	--	Ni 68.6%, B 4.2%		
-71	--		72.2	124.5			0.12	B <0.03		
-72	0.501		9.9	45.4	18.6	33.8	0.004			
-73	0.574		--	45.4	18.6	33.8	0.004			
-74	--		74.9	73.8	21.1	--	0.009			

Table 3 (continued)

Catalyst Code	Bulk Density Kg/L	Surface Area %	LOI wt %	CuO, wt %	ZnO, wt%	Al ₂ O ₃ wt %	Na ₂ O ₃ wt %	Other, wt %	Cr ₂ O ₃ wt %	XRD
-75	---		10.0	72.3	11.4	21.6	0.028			
-76	---		14.8	32.8	24.3	41.8	Trace			
-77	---		---	32.8	24.3	41.8				
-78	---	168	10.1	51.2	14.3	33.1	0.031			
-79	0.663		5.2	56.5	17.2	26.3	<0.0008			
-80	---		4.3	37.7	61.6		0.080	8 0.034		
-81	---		21.2	80.0	5.0	14.2	0.121			
-82	---	136	5.51	54.5	14.4	20.5	0.039			
-83	---	92	5.62	37.3	60.5	---	0.057			

TABLE 4

Series 800 CF-HP

CDS Gas Phase Screening Reactor

SPECIFICATIONS

Dimensions: 30" wide x 22.5" deep x 26" high

Shipping Weight: 250 pounds (approx.)

Power Requirements: 115V, 50-60 cycle, 20 amps

Flow Controllers for Internal GC Carrier Gas: (2) 0-180
cc/min; CDS 2090-0001

Flow Diverter Valves: (6) stainless steel, three way;
CDS 2460-0035

(3) brass, three way; CDS 2460-0032

Metering Valves for Reactants and Reactor Purges: (6)
stainless steel precision; CDS 2460-0122

Metering Valve for Oven Purge: (1) brass; CDS 2460-0039

Check Valves for Reactants: (4) stainless steel; CDS
2460-0064

Filters for Reactants: (4) stainless steel, 7 micron
frits; CDS 2090-0012

Reactant Mixing Chamber: stainless steel; 4 input - 2
output

Valves: (2) Reactor Bypass - 8 port, 300°C, 2000 psig
1/16" fittings

(2) Inlet Sampling - 8 port, 300°C, 2000 psig, 1/16"
fittings

(2) Outlet Sampling - 8 port, 300°C, 2000 psig, 1/16"
fittings

TABLE 4

All valves are polyimide faced (maximum temp. 300°C); CDS 2460-0011.

All valves are manually operated.

All tubing in valve oven (except sample loops) is 1/16" O.D. stainless steel.

Sample Loops: (4 pairs) 1/16" O.D. stainless steel loops

on Inlet and Outlet Sample valves, volume 100 ul.

(3 pairs) 1/8" O.D. stainless steel loops, volumes 1 ml, 2 ml, and 4 ml.

Valve Oven: 12" x 12" x 5 3/4" stainless steel; Dual RTD

Sensor/Type K Thermocouple (CDS 2330-0008); Coil heater

(CDS 1740-0001-1); Thermostat (CDS 2305-0001)

Air Operators: (2) CDS 2460-0082; each operator controls

two two-way diverters (CDS 2460-0063) for automatic Reactant shutdown

Solenoid Valve: (1) For air operator control; CDS 2465-0003

Temperature Controllers (CDS 800): (2) Fully propor-

tioning, zero-crossing type with digital setting, ambient to 700°C (Reactor A and B) - CDS 2120-0035.

Dual RTD sensor/Type K thermocouple (CDS 2330-0008).

(2) Fully proportioning, zero-crossing type with digital setting, ambient - 150°C (Gauges A and B)

CDS 2120-0035. Dual RTD Sensor/Type K thermocouples (CDS 2330-0008)

(1) Fully proportioning, zero-crossing type with Standard click-stop setting, ambient - 150°C (BPR) - CDS

2120-0039. Dual RTD sensor/Type K thermocouple (CDS 2330-0008)..

TABLE 4

(4) Fully proportioning, zero-crossing type with Standard click-stop setting, ambient to 300°C (CDS 2120-0039).

Dual RTD Sensor/Type K thermocouple (CDS 2330-0008).

Auxiliary Temperature Controller: (1) CDS 200. Includes

(2) controllers with Standard click-stop settings, ambient to 300°C (Gas/Liquid Separators A and B), plus pyrometer with selector switch.

Temperature Readout: (1) Digital Pyrometer with 10-position monitoring switch.

Vents: (6) from diverter valves on flow module

(4) in valve oven module front panel (Reactor A and B, Purge A and B)

(1) in right side of cabinet (Oven Purge)

(4) in pressure gauge modules

Injection Ports: (2) GC A and B Inlets. Dual RTD Sensor/ Type K thermocouple (CDS 2330-0008); one cartridge heater (CDS 1740-0003).

Back Pressure Regulators: (2) 10 - 2500 psig, all stainless steel (CDS 2090-0040). Dual RTD Sensor/Type K thermocouple (CDS 2330-0008); one cartridge heater (CDS 1740-0003).

Reactor Module Assemblies: (2) Catalytic - each contains:

Reactor Tube - (1) unpacked stainless steel tube - length 9", O.D. 1/2", I.D. 3/8".

Reactor Cap - (1) 1/2" stainless steel vacuum lock tube cap with 1/16" thermocouple fitting.

TABLE 4

Heating Element - (2) Hemicylindrical heaters - 1200°
(CDS 1740-0015).

Reactor Core - (1) 1/2" I.D. - 6" length - Inconel 600

Temperature Sensor - (1) Platinum Resistance Element
(CDS 2330-0012)

Thermocouples - (1) Type K 1/16" O.D., in core (CDS
2370-0054)

(1) Type K in thermowell (CDS 2370-0056)

Temperature Range - to 700°C

Insulation - Johns-Manville Min-K

Cabinetry - Anodized finished aluminum

Preheat Coil - 5 ft., 1/8" O.D., .015 wall

Reactor Pressure Gauges: (4) at inlet and outlet of
reactors - to 1500 psig ($\pm$ 1%) and 150°C, welded
stainless steel isolator diaphragm, Type SW seal; CDS
1950-0006.

Gauge Purge Metering Valves: (4) stainless steel, 2000
psig, CDS 2460-0040. In pressure gauge modules.

System Pressure Relief Discs: (4) 316 stainless steel
rupture discs, 1500 psig, in gauge modules; CDS
2095-0011

Reactor Purge Gauges: (2) to 2000 psig, located in valve
oven module front panel.

Failsafe: (1) CDS 450 Level II; automatic or manual shut
down modes. Monitors system for electrical failure.
Includes four auxiliary heater stations, ambient -
300°C, for control of transfer lines to and from
Reactors A and B.

TABLE 4

Transfer Lines: (6) 1/8" O.D. x 4' stainless steel microbore tubing, ambient - 300°C, controlled by CDS 800 and CDS 450; CDS 0101-5080-2

Gas/Liquid Separators: (2) stainless steel separator vessels, aluminum heater shells, ambient - 300°C (controlled by CDS 200), installed at the base of the reactors (1) Dual RTD sensor/Type K thermocouple (CDS 2330-0008), (2) cartridge heaters (CDS 1740-0003) per separator. Each separator includes a stainless steel diverter valve (CDS 2460-0035), metering valves (CDS 2460-0040), and outlet fitting for drain.

Digital Mass Flow Controllers: (2) calibrated for hydrogen, 0-2000 cc/minute
(2) calibrated for carbon monoxide, 0-2000 cc/minute
Mass flow controllers and digital flow rate displays installed in CDS 500 Mass Flow Controller Module

Digital Mass Flow Totalizers: (4) totalizer modules with digital readouts

TABLE 5

Typical Operating Parameters

CDS 800 Series CF-HP Reactor

1. Reactant feed: premixed synthesis gas (APCI - Specialty Gases Div.)
2. Catalyst charge: 2.5 -3.5 grams (8-9 cm³)
3. Catalyst bed length: 2.5-3.5 inches (centered in reactor heating block)
4. Reactor pressure: 500 psig-880 psig (1500 psig maximum)
5. Reactor temperature: 200-300°C (700°C maximum)
6. Reactant flow rate: 5000-20,000 GHSV (cm³ of gas per gram of catalyst per hour)
7. Gas/Liquid separator temperature: 150°C
8. Reactor transfer line temperature: 150°C
9. Gauge module temperature: 150°C
10. Valve oven temperature: 170°C
11. Back pressure regulator temperature: 110°C-140°C
12. GC feed transfer line temperature: 105°C
13. GC transfer line temperature: 90°C
14. Wet-test meter transfer line temperature: 80°C
15. Wet-test meter temperature: 76°C

TABLE 6

Sample Run Data*Gas Phase Screening ReactorsShake-down Test

	<u>Reactor A</u>	<u>Reactor B</u>
Catalyst Charge	3.37 grams	2.83 grams
Reaction temperature	225°C	225°C
Reaction pressure	515 PSIA	515 PSIA
Reactant inlet flow	552 SCCM	491 SCCM
Space Velocity	9828 l/hr-kg	10410 l/hr-kg
Inlet gas composition -- CO	23.8%	23.8%
CO ₂	5.93%	5.93%
H ₂	70.27%	70.27%
Exit flow rate	480 SCCM	435 SCCM
Exit Gas Composition -- CO	20.68%	19.23%
CO ₂	7.33%	7.27%
H ₂	69.14%	66.5%
Methanol	5.88%	6.29%
Ethanol	trace	trace
Methane	trace	trace
Ethane	trace	trace
Ethylene	trace	trace
Water	trace	trace
Carbon balance	99%	98%
Hydrogen balance	100%	100%

*Data presented here only to demonstrate reactor system performance. This does not contain a complete data set for catalyst evaluation purposes.

TABLE 7

COMPARISON OF GAS TYPES

<u>GAS TYPE</u>	<u>BAL</u>	<u>BAL</u>	<u>UNBAL</u>	<u>UNBAL</u>
Temp, °C	225	250	225	250
Pressure, PSIA	895	895	895	895
Space Vel., l/kg-hr	8060	9349	8500	8336
CO Conversion, %	49.7	54.0	18.87	18.79
CO ₂ Conversion, %	11.61	10.77	4.18	0.42
H ₂ Conversion, %	36.6	40.1	41.9	46.4
Rate MeOH ^{mmol} /gm-hr	28.9	34.4	28.5	31.2
Rate DME ^{mmol} /gm-hr	0.05	0.21	0.08	0.34
Rate EtOH ^{mmol} /gm-hr	-	0.06	0.03	0.24
Rate H ₂ O ^{mmol} /gm-hr	1.19	0.18	0.38	0.42
Rate CO ₂ ^{mmol} /gm-hr	(-2.08)	(-2.22)	(-2.06)	(-0.21)
Rate H ₂ ^{mmol} /gm-hr	(-72.5)	(-91.9)	(-56.9)	(-61.8)
Rate CO ^{mmol} /gm-hr	(-34.0)	(-42.8)	(-36.0)	(-35.0)
H Recovery, %	93.1	95.0	100.3	101.0
C Recovery, %	91.7	94.4	96.02	98.3
O Recovery, %	92.2	94.5	96.12	98.6

FIGURE 1

GAS PHASE SCREENING REACTOR SYSTEM SCHEMATIC

REV	DATE	REVISION	BY	CHK	APP

TOLERANCES UNLESS OTHERWISE SPECIFIED					
CHEMICAL DATA SYSTEMS, INC.					
OXFORD, MA. 01525					
DECIMAL					
FRACTIONAL					
ANGULAR					
DATE		DRAWING NUMBER		TITLE	
4-15-72		B-0404-801008-0		AIR PRODUCTS EXTERNAL REACTOR	

FIGURE 2

GAS PHASE SCREENING AUXILIARY EQUIPMENT SCHEMATIC

COS REACTOR 1500 PSIG, (MAXIMUM)
 V1,2,3,4 SS-1K34 WHITE SHUT-OFF VALVE 3000 PSIG
 V5 B-434F2 WHITE 4-INCH BALL VALVE 2500 PSIG
 V6 B-41X32 WHITE 3-INCH BALL VALVE 2500 PSIG
 V7,8 SS-92F2 WHITE SHUT-OFF AIR OPERATED 150 PSIG
 PV1,2 5159-2M CIRCLE SEAL RELIEF VALVE 100 PSIG
 RV3,4 559-2M CIRCLE SEAL RELIEF VALVE 10 PSIG
 EFV1,2 EFV-250-BNP-PSO CHEM-TEC 3500 PSIG

CV1,2	SS-4C-10	NUPRO CHECK VALVE	3000 PSIG
CV3,4	SS-2C-1	NUPRO CHECK VALVE	3000 PSIG
PV1,2	PC54B11K	CIRCLE SEAL REDUCING REGULATOR	6000/1500 PSIG
PS1,2	H300-610	UNITED ELECTRIC PRESSURE SWITCH	1000-PSIG/1000
P1,3		US GAUGE	0-5000 PSIG
P2,4		US GAUGE	0-3000 PSIG
DS1,2	MODEL 88	ANMETER	DIAPHRAGM SEAL 1500 PSIG
CS1	304-ND4-500	WHITE	SWAPALE CYLINDER 1800 PSIG

JML 24 JUNE 1982

CUSTOMER Ac Products
INSTRUMENT 456 SERIAL NO. 2109
APPLICATION 100°C COOL DOWN TEMP. 80
MIL TEMP. 100° METAL TEMP. 80
IN. 30 mil piece of 89 mils

4. 10 mils NR 80 4. 101
SAMPLE SIZE 75 ml
ATTENTION A 16
CHART SPEED 25 in/min
DATE 12/24/82 TECHNICIAN GP

FIGURE 4
CATALYST ACTIVITY IN
APCI GAS PHASE SCREENING REACTOR

FEED GAS = 55% H₂/19% CO/5% CO₂/N₂

CATALYST = F50/4E75-81

REACTOR LOAD = 3gm (AS OXIDE)

EFFECT OF GAS COMPOSITION

APCI GAS PHASE SCREENING REACTOR

--- FEED GAS = 55% H₂/19% CO/5% CO₂/N₂

- · - FEED GAS = 35% H₂/50% CO/13% CO₂/N₂

CATALYST = F50/4E75-81

PRESSURE = 515 PSIA (3500 KPA)