

1. Contract Objectives

Alcohols have been used as transport fuels ever since the invention of the automobile, although inexpensive gasoline held a near-total domination of this market for many years following World War II. The development of synthetic transportation fuels based on domestic fossil fuel reserves, particularly coal, remains a mid-term goal of the U.S. government; the objective is to reduce our dependence on imported petroleum. More recently, however, it has been environmental concerns that have stimulated the interest of industry in developing oxygenated fuels. In particular, the restrictions on gasoline Reid vapor pressures (i.e., butane reductions) and lead phase-out have created an octane number shortage in most domestic refinery gasoline pools, while clean air regulations have heightened the need for cleaner burning fuels. Oxygenates afford a solution to meet both the octane and clean air demands. Most alcohols and ethers have very high octane numbers (>95) and burn to produce largely carbon dioxide and water. At the present, a substantial portion of the unleaded gasoline sold in the United States contains oxygenates, mainly ethanol and MTBE. These oxygenates could be used directly as transport fuels, but their direct use as fuels requires extensive modification of engines, fuel delivery systems, and storage and distribution facilities. It is probable that in the near to medium term the most important contribution of oxygenates to the fuels area will continue to be their use as gasoline octane enhancers and as emission reducing additives.

Overall, two approaches have been followed in developing the use of oxygenated fuel additives — the use of alcohol mixtures blended with gasoline, and the addition of ethers to gasoline. In both cases, the oxygenated additive replaces up to 10 to 20% of the gasoline, and no modification of engines or delivery systems is required.

Ethers, in particular methyl tertiary-butyl ether (MTBE), have become a very significant player in the U.S. fuel market. An analogue of MTBE, ethyl tertiary-butyl ether (ETBE) has also received recent attention. Much of the unleaded gasoline today contains MTBE as an octane enhancer. An advantage of MTBE is that it has good solubility characteristics in gasoline, requiring no co-solvents. The methyl portion of this molecule is obtained from methanol, and the t-butyl fragment is derived from isobutylene, a petroleum-derived fraction. As a result, MTBE production is feedstock limited.

The primary objective of this project has been the pursuit of a catalyst system which would allow the selective production from syngas of methanol and isobutanol. It is desirable to develop a process in which the methanol to isobutanol weight ratio could be varied from 70/30 to 30/70. The 70/30 mixture could be used directly as a fuel additive, while, with the appropriate downstream processing, the 30/70 mixture could be utilized for MTBE synthesis. The indirect manufacture of MTBE from a coal derived syngas to methanol and isobutanol process would appear to be a viable solution to MTBE feedstock limitations.

To become economically attractive, a process for producing oxygenates from coal-derived syngas must form these products with high selectivity and good rates, and must be capable of operating with a low-hydrogen-content syngas. This was to be accomplished through extensions of known catalyst systems and by the rational design of novel catalyst systems.

2. Project Organization

This contract for the study of alcohol production for fuels from syngas was conducted at Union Carbide's South Charleston Technical Center, South Charleston, West Virginia 25303.

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3. Project Summary

3.1 Approaches Pursued

Synthesis gas can be converted into mixtures of methanol and higher alcohols by use of alkali-modified methanol synthesis catalysts known for many years. Interest in higher alcohol synthesis from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Refining modifications and the use of oxygenated petrochemicals such as methyl tert-butyl ether (MTBE) have been implemented as alternatives. The production of a mixture of methanol and isobutanol is of interest due to its possible use as a feedstock in the production of other oxygenates such as MTBE and related ethers.

Previously known catalysts for Higher Alcohol Synthesis (HAS) can be divided into the following classes based on the alcohol product distribution.

Modified Fischer-Tropsch (FT) and Group VIII Metal-Based Catalysts. Traditional Fischer-Tropsch catalysts can be made to produce appreciable amounts of oxygenates (alcohols, aldehydes, acids, ketones and esters) by addition of alkali. Typical FT metals include Fe, Co, Ni, and Ru. The products observed follow an Anderson-Schulz-Flory (ASF) distribution, characteristic of the linear condensation polymerization mechanism. Molybdenum sulfide catalysts promoted with alkali also produce the ASF product distribution. Rh-based catalysts are similar, but produce more C₂₊ oxygenates.

Modified Methanol or Iso-Alcohol Catalysts. These consist of Methanol Synthesis catalysts modified with alkali promoters, forming significant quantities of branched primary alcohols. These can be divided into two classes:

(a) The "high-temperature" (~ 400°C operating temperature) catalysts, which are essentially alkali-modified ZnCrO and ZnMnCrO systems. The major products are methanol and iso-butanol, but small amounts of ketones, secondary alcohols, ethers and hydrocarbons are also observed. The formation of higher alcohols is maximized by operating under hydrogen lean conditions (syngas ratio of H₂/CO = 1). The operating catalyst is thought to consist of a microcrystalline ZnCr₂O₄ spinel oxide phase. Manganese can be substituted for chromium to reduce the acidity of the spinel, thus decreasing the amounts of ethers and hydrocarbons formed. The presence of alkali is thought to be essential to promote HAS.

(b) "Low-temperature" catalysts, which are generally alkali-modified copper-containing catalysts, based on low-temperature methanol catalysts.

The reaction over these iso-alcohol catalysts is believed to proceed by a combination of hydrogenation and carbon-carbon bond formation via aldol condensation. The result of this

is the formation of branched alcohols with a non-ASF product distribution. This should be contrasted with the modified FT catalysts which proceed by a classical polymerization mechanism.

We chose to investigate catalysts of the iso-alcohol type because of the greater possibility of forming a product mix in the range of most interest. Catalysts from both the high-temperature and low-temperature class were studied, but our efforts soon became focused largely on the high-temperature class of catalysts, where significant progress has been made in catalyst formulation and overall performance.

3.2 Summary of Progress

Work at Union Carbide under a previous contract (DE-AC22-86PC90013) on a methanol-isobutanol catalyst used consecutive Hyper-Greco-Latin Squares to identify and bracket levels of important variables in catalyst formulation and preparation. Catalysts with good isobutanol selectivities were developed, but the overall alcohol rate was low. Work under the present contract was focused on improving catalyst performance through studies of both catalyst formulation and catalyst preparation techniques. Process variables such as reaction conditions and product/feed recycle were also investigated.

The work completed under this contract has shown that catalysts based on ZnCrMn oxides are effective HAS catalysts, particularly when promoted with alkali metals such as potassium or cesium. Cesium is generally a more effective promoter than potassium for higher alcohol synthesis. Catalysts were prepared under various conditions, and it was found that a high precipitation pH and low calcination temperature gave catalysts with the highest surface areas.

Substitution of manganese for chromium in the spinel lowers the overall activity of the catalysts, although it improves the alcohol selectivity. The difference is not due to changes in relative surface areas of the two spinels. The Mn-containing catalysts also require less cesium promoter, consistent with manganese substitution lowering the overall spinel acidity.

The Zn/Cr/O catalysts prepared by our procedures are actually Zn/Cr spinel oxides containing excess zinc oxide. The performance of potassium-promoted Zn/Cr/O spinel oxide catalysts and potassium promoted ZnO catalysts is inferior to potassium promoted Zn/Cr/O spinel oxide catalysts containing excess ZnO. The combination of the two components performs better than each of the individual parts. The presence of excess zinc oxide has a beneficial effect on the performance of Zn/Cr spinel oxide catalysts (a) promoted with cesium and (b) promoted with both cesium and palladium. The presence of the excess zinc oxide results in a more active and selective catalyst to total alcohols and increased isobutanol rates.

Palladium addition to the cesium-promoted Zn/Cr spinel oxide containing excess zinc oxide catalyst allows operation at only 1000 psi with good selectivities to total alcohols (> 80%), good isobutanol productivities (> 150 g/kg-hr) and with a methanol/isobutanol mole ratio of 0.58: this is our best overall performance to date.

Surface science studies have shown that the surface of these catalysts is predominately ZnO and alkali. With use, the ZnO is reduced to Zn metal, and Cr migrates to the surface giving increased surface acidity. Mn addition tends to lower the overall acidity.

Operation at temperatures above 440°C results in a further increase in the isobutanol rate, a further decrease in the methanol rate, but a marked increase in the hydrocarbon rate. Promoter optimization may be necessary for successful operation in this higher temperature regime. The combination of high temperature and high pressure optimizes the yields of

higher alcohols. Lower space velocities and low H_2/CO ratios (<1) increase the relative proportion of higher alcohols, but at the expense of catalyst productivity.

Potassium addition promotes higher alcohol synthesis on a commercial Zn/Cr spinel oxide methanol synthesis catalyst. Incremental potassium levels (1, 3 and 5 wt%) result in an increase in total alcohol selectivity, while isobutanol rates are maximized at 1 wt% potassium. Rates greater than 100 g/kg-hr are achievable with this formulation. The commercially prepared catalyst promoted with potassium is slightly less active for isobutanol synthesis and less selective to total alcohols when compared with our spinel formulation promoted with potassium and containing excess ZnO.

Product/feed recycle studies show that the recycle of methanol is ineffective with this catalyst system. The recycle of ethanol and isopropanol was marginally effective, and addition of n-propanol gave significantly enhanced yields of isobutanol. Recycle of water and carbon dioxide increases the effective CO_2 concentration over the catalyst via the water gas shift reaction, and results in inhibition of higher alcohol synthesis. Presumably, the CO_2 occupies basic catalyst sites involved in the base-catalyzed aldol condensation steps responsible for higher alcohol synthesis.

3.3 Conclusions and Prospects for Future Work

After several years of work on spinel oxide-based catalysts for the synthesis of higher alcohols from syngas, we now have a significantly better understanding of the catalyst system and conditions of operation. Our progress on catalyst preparation, catalyst composition, catalyst operation and product recycle, taken together with detailed surface science and other analytical measurements suggest the following directions for future work:

1. Use high temperature catalysts to control selectivity among the alcohols

Higher alcohol formation increases with increasing temperature, due to two complementary kinetic and thermodynamic processes.

- Higher alcohol synthesis proceeds in a stepwise fashion from lower molecular weight building blocks; thus a higher proportion and absolute amount of higher alcohols are made as the rates of these consecutive reactions increase with increasing temperature.

- The thermodynamics of the methanol equilibrium disfavor methanol formation at higher temperatures. In this case, high temperature operation is actually an advantage, as methanol is best made separately (with high selectivities and yields) by conventional methanol catalysts; in higher alcohol synthesis, methanol formation should be minimized.

The overall result of high temperature operation is that less of the undesired methanol is made and the amount that is made is more rapidly converted to higher alcohols.

However, a temperature ceiling, where hydrocarbon formation becomes the thermodynamically favored product, is reached much above 450°C. This defines the operating window in the range 400-450°C.

2. Use higher pressures to increase reaction rate

The largest handle on overall reaction rate is pressure, not temperature. Increasing pressure results in an increased selectivity to total alcohols vs. hydrocarbons and in methanol production over higher alcohols.

3. Use a combination of higher temperatures and higher pressures to maximize higher alcohol yield

Based on the above discussion, the *combination* of higher temperatures and higher pressures will maximize higher alcohol yield.

4. Use inert high surface area conventional supports for higher activity catalysts

Higher alcohol production rates (and CO conversion) still fall below commercial targets. Surface science results show that the surface of the catalysts consists of alkali/zinc oxide

supported on the spinel. Zinc oxide/alkali catalysts do show activity for higher alcohol synthesis, but are relatively inactive due to their correspondingly low surface area versus the spinels.

It is not unreasonable to suggest that supporting alkali/zinc oxide or palladium/alkali/zinc oxide on an inert, high surface area conventional support such as silica, alumina or titania would be equally as effective as supporting these materials on a spinel. Care should be taken to choose the support to be as non-acidic as possible to mitigate hydrocarbon formation.

5. Use basic supports

The proposed mechanism for branched higher alcohol synthesis over the high temperature catalyst is via base-catalyzed aldol condensation. The use of basic supports, such as magnesium oxide, or a lanthanide oxide, might provide additional help for this chemistry. The use of a basic support should also lower overall catalyst acidity, thus increasing alcohol selectivity over hydrocarbon formation. This will, in turn, allow higher catalyst operating temperatures.

6. Palladium is beneficial; other metals also may be useful

Palladium has been found to be a beneficial promoter, increasing higher alcohol production and allowing lower pressure operation. The use of other metals similar to palladium (near neighbors in the periodic table) might provide equivalent or better performance, e.g., ruthenium, rhodium, iridium or even platinum.

7. Recycle of alcohols for isobutanol synthesis is unlikely to be practical

Based on the alcohol feed/recycle experiments, n-propanol can be used as a feedstock or could be recycled to boost higher alcohol synthesis, but ethanol recycle is less successful. Note that *methanol* feed/recycle is NOT effective over our catalysts at high temperatures (>400°C).

4. Experimental Data

4.1 Copper-Containing Catalysts

We have investigated a family of copper-based low-temperature higher alcohol catalysts, which could be suitable for use in slurry reactors. We prepared the spinel oxide, $\text{Co}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4$, where x ranges from 0 to 1, using a coprecipitation method. It was hypothesized that the introduction of a Fischer-Tropsch metal such as Co to the Cu induces a classical ASF chain growth mechanism with primary alcohols as the main products. Unfortunately, this also gives rise to the parallel production of hydrocarbons. The active site for alcohol formation is thought to be highly divided Cu-Co clusters that are formed under reaction conditions.

A designed set of these copper/cobalt/chromium catalysts was tested at 275°C, 1000 psi, syngas ratio = 1:1, GHSV = 12,000. The materials consisted of a basic spinel structure AB_2O_4 where $A = \text{Cu/Co}$ and $B = \text{Cr}$ and are promoted with potassium. The Cu/Co ratio and the addition of palladium, platinum and silver were examined in a statistical design outlined in Tables 4.1-1 and 4.1-2. These formulations contain a good methanol synthesis metal (Cu) and a Fischer-Tropsch metal (Co) to promote carbon-carbon bond formation and chain growth. The expectation was that Cu/Co metal clusters are generated upon reduction that should catalyze the synthesis of higher alcohols.

Catalyst test results showed that these catalysts were very selective for methanol at 350°C and below (96-99%) and produced hydrocarbons and small amounts of higher alcohols at 400°C and above. These observations are consistent with a supported copper metal-based methanol catalyst operating at the lower temperatures and a spinel oxide support acting as the catalyst at the higher temperatures.

The hydrocarbon production follows a regular Anderson-Schulz-Flory distribution, indicating that Fischer-Tropsch chemistry is responsible for hydrocarbon formation. The catalysts deactivate rapidly, even at 275°C, probably due to sintering of the copper metal. A typical product profile is shown in Figure 4.1-1.

These materials were designed to produce higher alcohols at temperatures at or below 300°C. Detailed examination of the data (see Table 4.1-2) shows that the catalysts display a range of activities at 275°C, from completely inactive to up to 139 g/kg-hr of methanol. No higher alcohols were observed at this temperature.

Table 4.1-1. Designed Set to Examine Effect of Promoters on Cu/Co/Cr Catalysts.

Reference	Formula	KNO ₃ wt% K	Pd(NH ₃) ₄ (NO ₃) ₂ wt% Pd
10DAN103	Co ₁ Cr ₂ O ₄	3	2.5
10DAN104	Co _{0.25} Cu _{0.74} Cr ₂ O ₄	3	2.5
10DAN105	Cu ₁ Cr ₂ O ₄	3	2.5

Reference	Formula	KNO ₃ wt% K	Pt(NH ₃) ₄ (NO ₃) ₂ wt% Pt
10DAN109	Co ₁ Cr ₂ O ₄	3	2.5
10DAN107	Co _{0.25} Cu _{0.74} Cr ₂ O ₄	3	2.5
10DAN108	Cu ₁ Cr ₂ O ₄	3	2.5

Reference	Formula	KNO ₃ wt% K	AgNO ₃ wt% Ag
10DAN113	Co ₁ Cr ₂ O ₄	3	2.5
10DAN111	Co _{0.25} Cu _{0.74} Cr ₂ O ₄	3	2.5
10DAN112	Cu ₁ Cr ₂ O ₄	3	2.5

Raising the temperature to 400°C results in an overall drop in total alcohol activity (70 – 80 g/kg-hr) and the production of small quantities of higher alcohols. Hydrocarbon production now becomes a serious inefficiency, with selectivities to alcohols only in the 16-69% range. Isobutanol comprises only a maximum of 19% of the alcohol product at a rate of around 12 g/kg-hr (Run 19, Table 4.1-2). Lowering the temperature back down to 275°C results in resumption of methanol production, but at rates reduced by as much as an order of magnitude, indicative of massive sintering of the copper.

One silver-promoted material (10DAN113) is an outstanding methanation catalyst at 400°C, producing 3597 g/kg cat-hr of total hydrocarbons with an ASF distribution at 90% syngas conversion (see Table 4.1-3). The formulation consists of a cobalt/chromium spinel promoted with 2.5 wt% silver and 3.0 wt% potassium. Industrial methanation to produce synthetic natural gas (SNG) is usually conducted with a nickel on alumina catalyst at 300-400°C and 200-400 psi.

Because these results were not as promising as our results with other families of catalysts, the study of copper-containing catalysts was not pursued further under this contract.

Table 4.1-2. Catalyst Results for Cu/Co Catalysts

Run #	Catalyst	Temp (°C)	ROH Sel (mol%)	ROH Act (g/kg-hr)	i-BuOH Act (g/kg-hr)	C3-C4 / Tot ROH*	i-BuOH / Tot ROH*
1	10DAN103	275	73	3	0	0	0
2		275	100	2.56	0	0	0
3		275	100	2.57	0	0	0
4	10DAN104	275	100	25.3	0	0	0
5		275	100	15.23	0	0	0
6		300	98.1	33.7	0	0	0
7		350	94.9	70.6	0.9	0.032	0.012
8		400	54.7	27.6	1.4	0.192	0.051
9		450	24.6	37.3	11.4	0.829	0.098
10	10DAN105	275	98.6	136.9	0	0	0
11		275	98.4	94.4	0	0	0
12		300	98.3	205.8	0	0	0
13		350	89.8	259.1	2.2	0.026	0.008
14		400	52.9	84.1	1.9	0.23	0.089
15		450	15.5	29.9	3.31	0.407	0.111
16	10DAN107	275	95.5	139.1	0	0	0
17		275	94.7	81.7	0	0	0
18		350	59.3	106	4.58	0.068	0.021
19		400	16.8	61	11.7	0.399	0.192
20		275	86.9	21.5	0	0	0
21	10DAN108	275	98.4	112.3	0	0	0
22		275	98.2	86.1	0	0	0
23		350	90.1	228.7	2.49	0.029	0.01
24		400	48.4	68.3	5.67	0.1935	0.09
25		275	100	10.6	0	0	0
26	10DAN109	275	0	0	0	0	0
27		350	13.7	20.6	0.7	0.23	0.035
28		400	50.6	73.9	6.15	0.237	0.083
29		275	92.5	20.6	2.33	0.455	0.113
30	10DAN 111	275	0	0	0	0	0
31		350	18.4	20.1	0	0.219	0
32		400	12.1	73.3	0	0.515	0
33		275	0	0	0	0	0
34	10DAN112	275	100	99.5	0	0	0
35		275	100	77.3	0	0	0
36		350	90.4	148.7	2.91	0.046	0.02
37		400	53	46.4	5.26	0.236	0.113
38		275	100	2.9	0	0	0
39	10DAN113	275	0	0	0	0	0
40		275	0	0	0	0	0
41		350	9.7	151.5	10	0.551	0.066
42		400	5	244.6	33.3	0.842	0.136
43		275	0	0	0	0	0

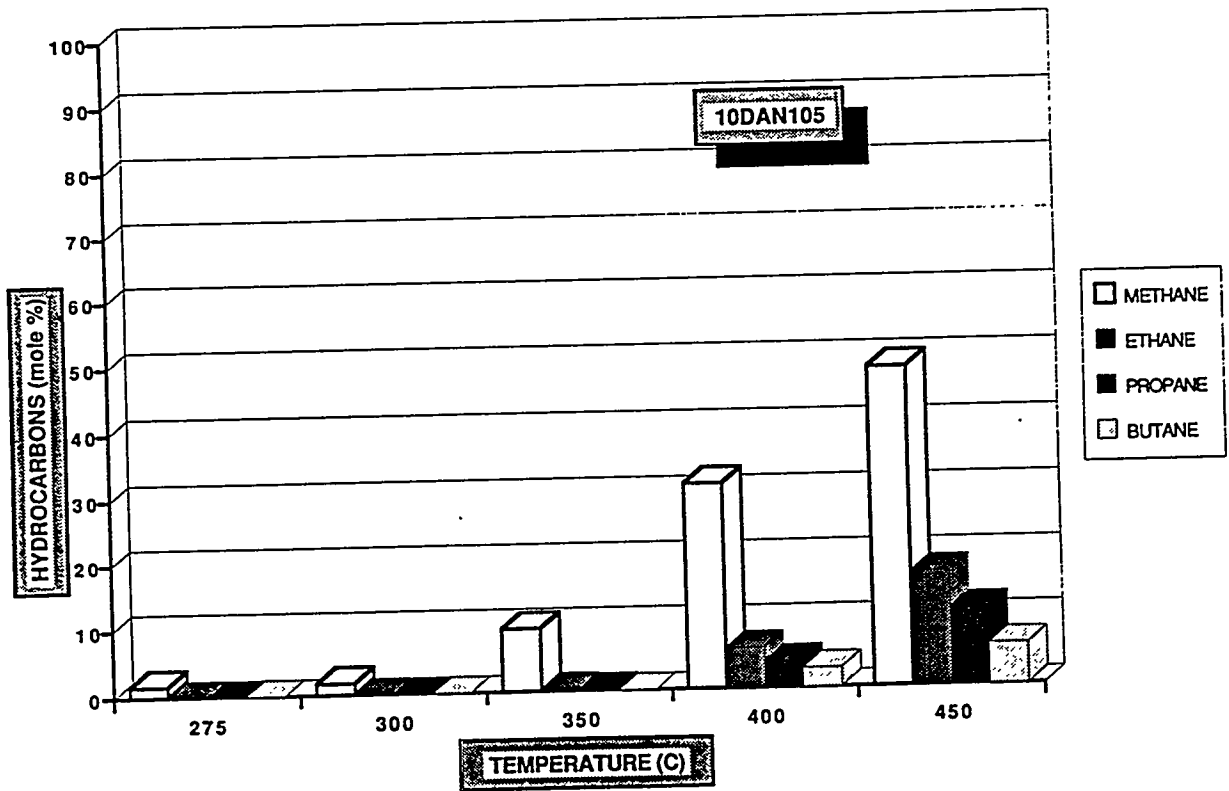
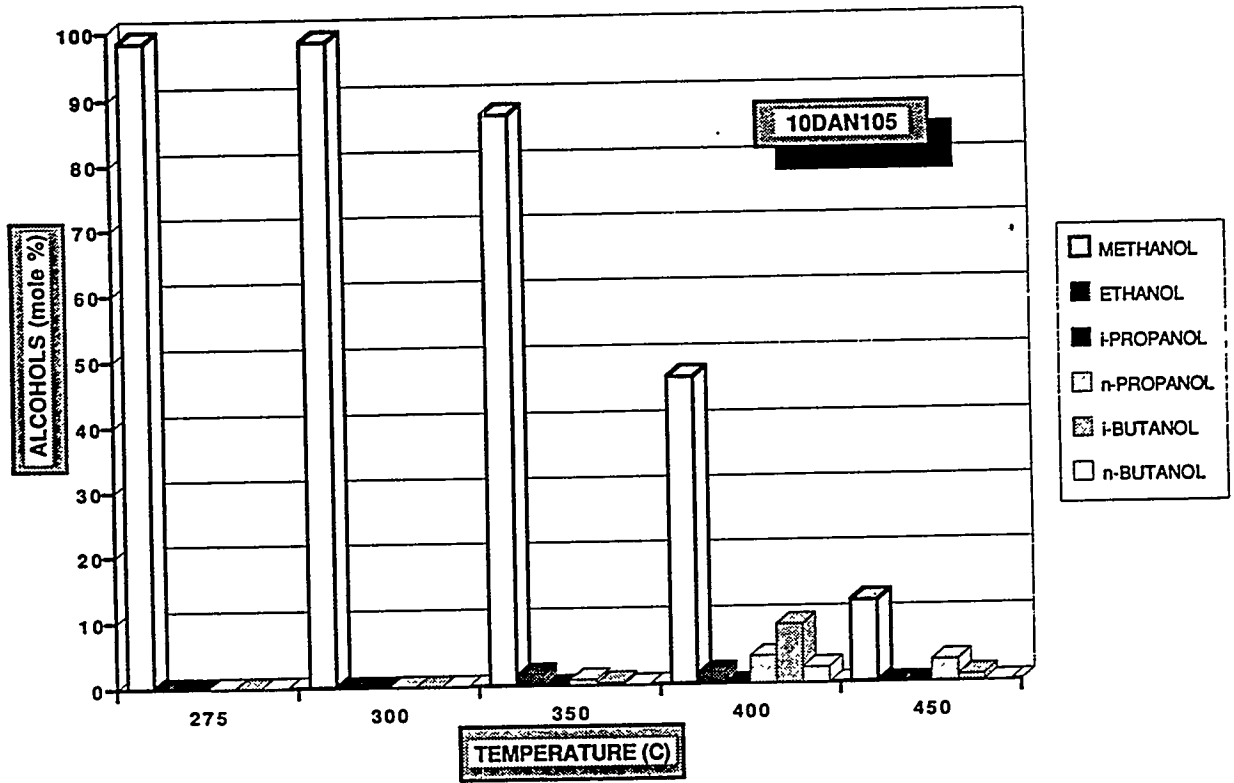
* By weight. Conditions: 1000 psig, H₂/CO = 1, GHSV 12000

Table 4.1-3. Catalyst Results for Cu/Co Catalyst 10DAN113

Run #	Catalyst	Temp (°C)	HC Sel (mol%)	HC Act (g/kg-hr)	CH4 Sel (wt%)	C2H6 Sel (wt%)	C3+ Sel (wt%)
39	10DAN113	275	100	30	62	15.4	22.6
40		275	100	26.4	64.1	14.9	21
41		350	90.3	1026.6	61.2	10.8	28
42		400	95	3596.6	69.3	12.4	18.3
43		275	100	5.6	67.9	19.2	12.9

Conditions: 1000 psi, H₂/CO = 1, GHSV 12000

Figure 4.1-1. Product Selectivities for a Cu/Co/Cr Catalyst (10DAN105).



4.2 Isobutanol Catalyst Synthesis - Design #1

An area of research that we identified as having potential for further progress was that of modified "high-temperature" (~ 400°C operating temperature) methanol catalysts, which are essentially alkali-modified ZnCrO and ZnMnCrO systems. The major products are methanol and iso-butanol, but small amounts of ketones, secondary alcohols, ethers and hydrocarbons are also observed.

Our initial investigations on these catalysts focused on the catalyst preparation, and particularly on the influence of precipitation pH on surface area, porosity, and thermal characteristics of the resulting precipitate. Potentiometric titrations during coprecipitation were conducted to aid in improving this catalyst preparation technique. Potentiometric titrations were carried out during coprecipitation from aqueous solutions containing zinc, chromium, and manganese nitrates. Titration curves of pH versus $\text{CO}_3^{2-}/\text{total Mn}^{n+}$ have shown, for example, that if a coprecipitation is to be carried out at a constant pH of 9, the rate of addition for the respective solutions should be such that the $\text{CO}_3^{2-}/\text{total metal}$ ratio is 1.7.

Variables in catalyst preparation were examined by a fractional factorial designed experiment. The effect of precipitating pH, calcination temperature and time on surface area, porosity, and powder x-ray diffraction pattern were examined in a preliminary 3x3 designed set (#1). The immediate goal was to map the response surface of the crucial variables using fractional factorial experimental designs.

The 3x3 design was carried out to determine best values for the precipitating pH and the range for calcination temperature and time to obtain high surface area and porosity. The designed set as well as the analytical results are shown in Table 4.2-1.

The analytical data clearly showed that the BET surface area is dependent on the calcination temperature as expected. The pH has a very strong effect on the surface area. These two parameters are the main factors influencing the resulting surface area within this design. This is graphically shown in Figure 4.2-1.

Statistical analysis of the data yielded a model for the BET surface area, pore volume, and pore diameter in terms of pH and temperature. Importantly, calcination time was not a significant factor in any model. Numbers in parentheses below the equations are t-ratios, which indicate the relative significance of the corresponding term in the model.

$$\text{BET Surface Area} = 71.19 + 11.72(\text{pH}-9.33) - 0.198(\text{Temp} - 400) - 7.6(\text{pH}-9.33)**2$$

(4.6)
(4.5)
(3.0)

$R^{**2} = 0.922$
 $RSD = 10.7$

$$\text{Pore Volume} = 0.373 + 0.085(\text{pH}-9.33) - 0.000317(\text{Temp} - 400) - 0.0232(\text{pH}-9.33)**2$$

(15.4) (3.4) (4.3)

$R^{**2} = 0.922$ $RSD = 10.7$

$$\text{Pore Diameter} = 24.86 + 0.057(\text{Temp} - 400)$$

(4.3)

$R^{**2} = 0.722$ $RSD = 3.27$

Therefore from these models (see Figures 4.2-2 and 4.2-3) the optimal pH to achieve the maximum surface area would be around 10.0-10.3. Calcination time is not a factor in these models and therefore could be removed as a variable in the fractional factorial design.

Table 4.2-1. Designed set (#1) and analytical results for the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.

Sample Reference	pH	Temp (°C)	Time (hr)	BET S.A. (m²/g)	Pore Volume (cc/g)	Pore Diameter (nm)
3DAN79	7.5	300.0	4.0	36.6	0.19	20.9
3DAN79	7.5	400.0	11.0	16.1	0.10	25.1
3DAN79	7.5	500.0	18.0	20.2	0.13	26.1
3DAN69	9.5	300.0	18.0	98.2	0.41	16.6
3DAN69	9.5	400.0	4.0	74.7	0.39	20.9
3DAN69	9.5	500.0	11.0	46.0	0.36	31.1
3DAN75	11.0	300.0	11.0	97.9	0.49	20.0
3DAN75	11.0	400.0	18.0	63.0	0.45	28.5
3DAN75	11.0	500.0	4.0	47.8	0.41	34.5

Figure 4.2-1. Surface area of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst as a function of precipitation pH and calcination temperature.

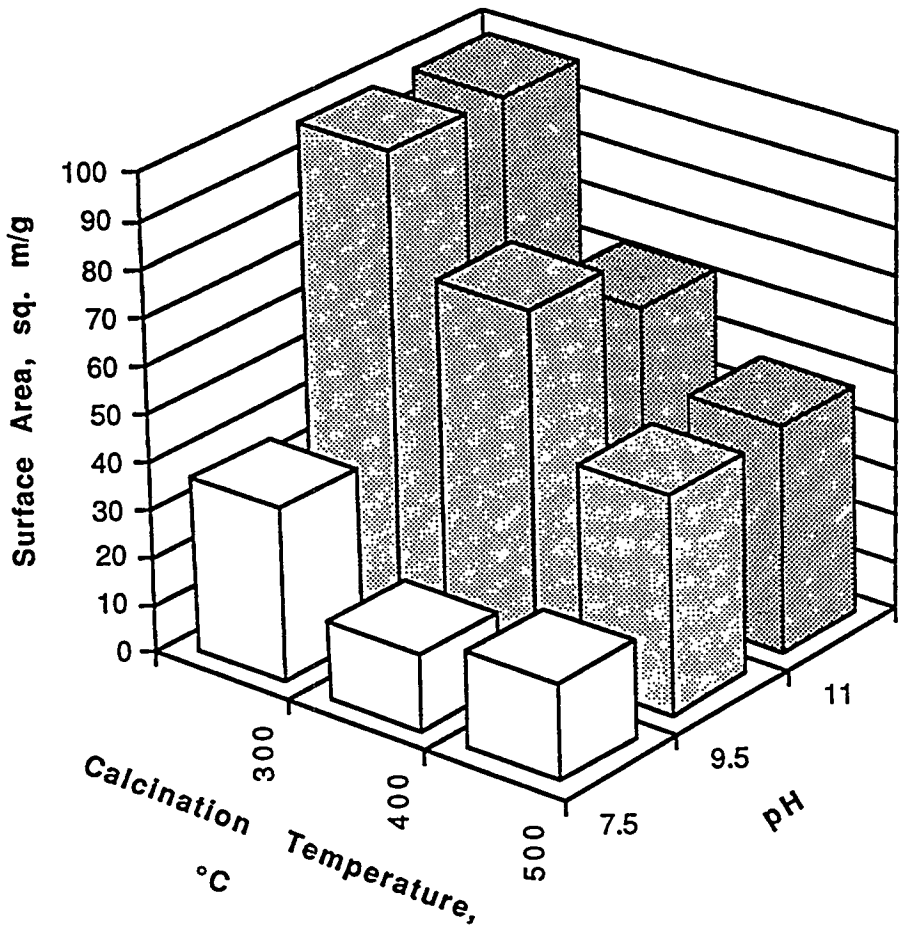


Figure 4.2-2. Effects of precipitation pH and calcination temperature on BET surface area of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.

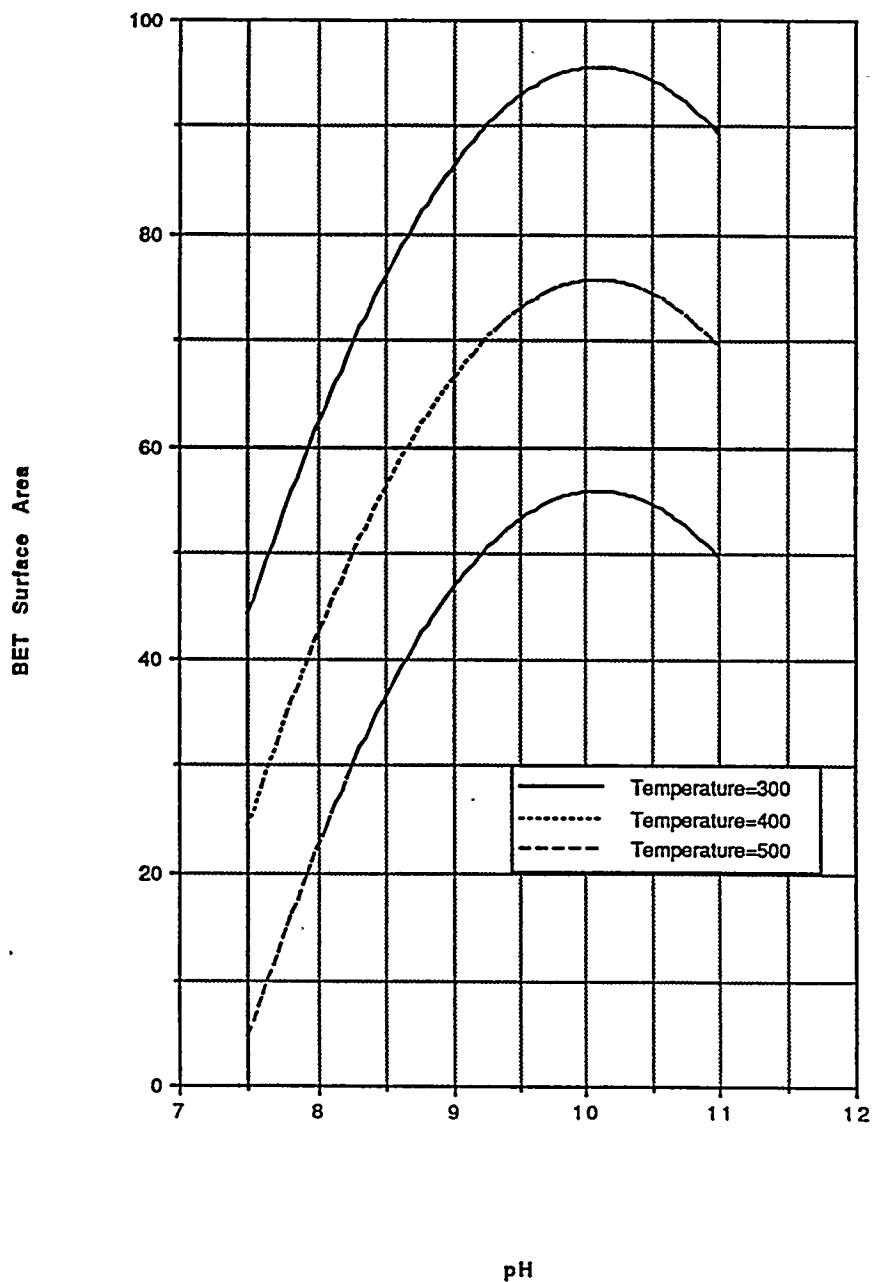


Figure 4.2-3. Effects of precipitation pH and calcination temperature on pore volume of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.

