HETEROGENEOUS CATALYTIC PROCESS
FOR ALCOHOL FUELS FROM SYNGAS

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1. Executive Summary

The principal objectives of this project are to discover and evaluate novel heterogeneous catalysts for conversion of syngas to oxygenates having use as fuel enhancers, to explore novel reactor and process concepts applicable in this process, and to develop the best total process for converting syngas to liquid fuels.

The project is being pursued as two concurrent tasks. Task 1 involves catalyst research and development and is being largely conducted by catalyst chemists and analytical specialists. Task 2 is largely an engineering activity, and includes process conceptualization and economics and bench-scale process evaluation of systems developed in Task 1.

Our current targets for isobutanol-producing catalysts are to produce an equimolar mixture of methanol and isobutanol with a productivity for isobutanol of > 50 g/Kg-hr.

Reactor system modifications, undertaken to improve data quality, have been completed. The changes should help eliminate differences between the two reactors and allow for more accurate determination of higher molecular weight products.

To calibrate our new reactor system, we have retested our "best" isobutanol catalyst, 10-DAN-54 (a promoted Zn/Cr/Mn spinel oxide). Under standard test conditions (400°C, 1000 psi, 12000 GHSV and syngas ratio = 1:1), this catalyst produces 200-252 g/kg-hr of total alcohols (total alcohol selectivities of 57-68%) with an isobutanol rate of 94-130 g/kg-hr and a MeOH/i-BuOH product mole ratio of 3. These results compare with a productivity of 112 g/kg-hr of total alcohols (total alcohol selectivity of 86%) with an isobutanol rate of 38 g/kg-hr and a MeOH/i-BuOH product mole ratio of 3 observed in the original microreactor system configuration. It should be remembered that the test apparatus is designed for screening only. Detailed, more reliable data for kinetic modeling must be generated using larger catalyst charges (> 10g) and in larger scale test equipment.

The effects of space velocity and temperature have also been examined for 10-DAN-54. At lower space velocities, productivities fall, but higher alcohols are favored, resulting in a higher proportion of higher alcohols vs. methanol. At temperatures of 380°C and 400°C, the MeOH/i-BuOH product mole ratio stays constant at 3.6-3.8; in contrast, at 420°C, this ratio becomes 1.0 showing that HAS is favored at the higher temperature. However, selectivity to total alcohols falls from 48-57% down to 34%; hydrocarbon formation is also favored by higher temperatures and this effect appears to outweigh the benefit of increased isobutanol formation vs. methanol.

The catalyst appears to keep a constant alcohol productivity with time, but hydrocarbon production increases. Surface science analyses will determine if this loss in selectivity is due to promoter redistribution with time.
2. Project Objectives

- To discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. In particular, novel heterogeneous catalysts will be studied and optimized for the production of: (a) C₁-C₅ alcohols using conventional methanol synthesis conditions, and (b) methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates.

- To explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products.

- To develop on the bench scale the best combination of chemistry, catalyst, reactor, and total process configuration to achieve the minimum product cost for the conversion of syngas to liquid products.
3. Project Organization

This project has been divided into two tasks.

Task 1 is concerned with catalyst identification, preparation, performance evaluation, and characterization. This work is being largely conducted by catalyst chemists and analytical specialists. Chemical studies to support the engineering effort in Task 2 are included in this task, but fundamental aspects of the catalytic chemistry are emphasized in this effort.

Task 2 includes process conceptualization and economics, and bench-scale process evaluation of systems developed in Task 1. This is largely an engineering activity.

These tasks are being carried out concurrently throughout the project.
4. Technical Progress

4.1. Task 1 – Catalyst Studies

4.1.1. Introduction

It is well known that the addition of alkali promoters to ZnCrO, MnCrO, and ZnMnCrO systems will modify the selectivity of high temperature methanol catalysts towards C2+ alcohols. Interest in higher alcohol synthesis (HAS) from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Currently refining modifications and the use of oxygenated petrochemicals such as methyl-tert-butyl-ether (MTBE) have become favored 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 ethers related to MTBE. One could also envision dehydrating the isobutanol to isobutene, followed by reaction with methanol to form MTBE. Our working goals in the catalyst development program are isobutanol activity of greater than 50 g/kg-hr, with a 50% alcohol selectivity to isobutanol. During the past year we have identified a series of promoted Zn/Cr/Mn spinel oxide materials as promising catalysts for this process.

Our recent attempts to run a designed set of experiments to determine the effect of process parameters (temperature, pressure, space velocity and syngas ratio) on catalyst performance were unsuccessful. The catalyst employed (11-DAN-115), a cousin of 10-DAN-54 (our "best" isobutanol catalyst) prepared via ammonium hydroxide precipitation, was not very selective to total alcohols and showed marked differences from sample to sample. Overall performance also decayed with time. These trends were not observed to the same extent with the same formulation prepared by potassium carbonate precipitation (e.g., 10-DAN-54), indicating that we will have to revisit the catalyst preparation procedure in order to obtain selective and stable materials.

We also observed differences between the performance of the two reactors and reactor system modifications were undertaken this quarter to improve data quality. The changes are designed to help eliminate the differences between the two reactors and allow for more accurate determination of higher molecular weight products.

These factors, taken together, obscured the effects of the process variables. Nonetheless, the design provided useful information: two design points showed that the catalyst can achieve the production of methanol and isobutanol in a 1:1 mole ratio, with an isobutanol activity of > 30 g/kg-hr. This demonstrates that the catalyst system is capable of meeting all of the individual goals set for the program. We now need to meet all of the goals simultaneously.

We report here (a) the modifications in the reactor design, (b) tests with a standard methanol catalyst to confirm the new reactor system's operability, (c) tests with catalyst 10-DAN-115, and (d) tests with 10-DAN-54.
4.1.2. Reactor System Modifications

Reactor system modifications, undertaken to improve data quality, have been completed. An aluminum box was fabricated to house the gas sampling system components. These included the back pressure regulators, gas sampling valves (GSV-1 & GSV-2), reactor downstream pressure gauges and the calib./gas sample 3-way valves. Independent block heaters were used on the gas sampling valves and provide some of the heat required by the box. However, the majority of heat is provided by a 4 ft section of heat tape attached to the inside of the box cover and regulated by a Payne Controller. The 4-way valves used to direct product collection under pressure have been eliminated. Pre-fabricated 0.5 ml sample loops (obtained from Supelco) replaced the home-made sample loops previously used. All gas sample lines were re-plumbed with new, cleaned tubing and fittings. The gas sample line connecting GSV-2 with GSV-4 was shortened from 5 ft. to 10 in., heat traced and insulated with fiberglass tape. The gas sample lines leading to the GC columns were reduced in length about 3 ft. All these lines were heat traced and insulated. The back-pressure regulators were cleaned and rebuilt.

These modifications resulted in changes to the GC data acquisition procedures. The methods used to acquire and process data had to be revised. Peak directives and relative retention time (RRT's) programs were re-configured to accommodate the sampling system modifications. The changes should help eliminate differences between the two reactors and allow for more accurate determination of higher molecular weight products.

Future modifications to the Syngas Reactor System will include the addition of a molecular sieve drying column on the feed gas lines to eliminate the presence of water in the feed gas stream. An activated carbon trap will also be added to the feed gas supply lines to remove any carbonyls present in the feed gases.

4.1.3. Tests With A Standard Methanol Catalyst

The microreactor system has two reactor tubes. The standard methanol catalyst (a copper-based catalyst, SN.2537-S, obtained from United Catalysts) was charged into both tubes and tested under the following conditions: 285°C, 1050 psi, 12000 GHSV and syngas ratio = 1:1. Results were as follows:

<table>
<thead>
<tr>
<th></th>
<th>Reactor 1</th>
<th>Reactor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol Activity (g/kg-hr)</td>
<td>791</td>
<td>781</td>
</tr>
<tr>
<td>Hydrocarbon Activity (g/kg-hr)</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>Total Alcohol Selectivity (%)</td>
<td>98.8</td>
<td>96.4</td>
</tr>
<tr>
<td>Methanol Selectivity (%)</td>
<td>97.4</td>
<td>95.3</td>
</tr>
<tr>
<td>Ethanol Selectivity (%)</td>
<td>1.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
The activity is roughly twice that observed for a standard methanol catalyst in the old reactor system configuration and selectivities to total alcohols are about 2-4% lower. Tube to tube variation appears to be minimal.

4.1.4 Tests With 11-DAN-115

Catalyst 11-DAN-115 (a K/Pd promoted Zn/Cr/Mn spinel oxide prepared via ammonium hydroxide precipitation) was tested in our reconfigured reactor system. This catalyst was used earlier for our process parameter design. The test conditions chosen were at a lower syngas ratio (1:2) and lower space velocity (6000 GHSV) than the standard conditions. Under these conditions the catalyst produced 72-89 g/kg-hr of total alcohols (total alcohol selectivities of 34-45%) with an isobutanol rate of 11-14 g/kg-hr and a MeOH/i-BuOH product mole ratio of 5-6.

The catalyst is not very active or efficient and parallels our observations made during the process parameter design using this catalyst.

The operating temperature was lowered to 375°C after 20 hrs on stream and overall rates fell. The syngas ratio was then switched to 1:1 and activities and conversion increased dramatically — see below:

<table>
<thead>
<tr>
<th></th>
<th>400°C (a)</th>
<th>375°C (a)</th>
<th>375°C (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol Activity (g/kg-hr)</td>
<td>89</td>
<td>65</td>
<td>1048</td>
</tr>
<tr>
<td>Hydrocarbon Activity (g/kg-hr)</td>
<td>112</td>
<td>61</td>
<td>2749</td>
</tr>
<tr>
<td>Total Alcohol Selectivity (%)</td>
<td>35</td>
<td>40</td>
<td>23</td>
</tr>
<tr>
<td>Isobutanol Rate (g/kg-hr)</td>
<td>14</td>
<td>6</td>
<td>57</td>
</tr>
<tr>
<td>MeOH/i-BuOH product mole ratio</td>
<td>6</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>Estimated Conversion (%)</td>
<td>18</td>
<td>16</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>

(a) Syngas Ratio (H2/CO) = 1:2
(b) Syngas Ratio (H2/CO) = 1:1

The temperature was then lowered to 350°C, then 325°C. Not surprisingly, at 325°C activities fell by over half with total alcohol selectivities remaining low (see table below):
<table>
<thead>
<tr>
<th>Parameter</th>
<th>375°C (a)</th>
<th>350°C (a)</th>
<th>325°C (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol Activity (g/kg-hr)</td>
<td>1048</td>
<td>1060</td>
<td>371</td>
</tr>
<tr>
<td>Hydrocarbon Activity (g/kg-hr)</td>
<td>2749</td>
<td>1858</td>
<td>508</td>
</tr>
<tr>
<td>Total Alcohol Selectivity (%)</td>
<td>23</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>Isobutanol Rate (g/kg-hr)</td>
<td>57</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td>MeOH/i-BuOH product mole ratio</td>
<td>1</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Estimated Conversion (%)</td>
<td>&gt;80</td>
<td>&gt;85</td>
<td>80</td>
</tr>
</tbody>
</table>

(a) Syngas Ratio (H₂/CO) = 1:1

We have now abandoned the ammonium hydroxide precipitation method in catalyst preparation.

4.1.5 Tests with 10-DAN-54

We have concentrated our efforts on testing our most promising isoalcohol catalyst, 10-DAN-54 (a K/Pd promoted Zn/Cr/Mn spinel oxide), in our reconfigured reactor system. Two separate charges of 10-DAN-54 have been started up and have produced reasonably consistent numbers under standard test conditions (400°C, 1000 psi, 12000 GHSV and syngas ratio = 1:1). This catalyst produces 200-252 g/kg-hr of total alcohols (total alcohol selectivities of 57-68%) with an isobutanol rate of 94-130 g/kg-hr and a MeOH/i-BuOH product mole ratio of 3. For the second charge, both space velocity (GHSV) and temperature were varied.

**Space Velocity:** At lower space velocities, productivities fall, but higher alcohols are favored, resulting in a higher proportion of higher alcohols vs. methanol (MeOH/i-BuOH product mole ratio falls from 3.2 to 1.7 on going from 12000 to 3000 GHSV).

Methanol formation is fast with respect to higher alcohol synthesis (HAS), as HAS results from consecutive reactions from methanol. Methanol formation is so fast under reaction conditions that it is essentially controlled by chemical equilibrium. Thus, long residence times favor HAS.

The isobutanol rate is still a respectable 48 g/kg-hr at GHSV = 3000.

**Temperature:** The rate of HAS increases with increasing temperature because of the more favorable kinetics, whereas the methanol equilibrium is disfavored by thermodynamics. Thus higher temperatures favor isobutanol over methanol. The concern here is that the syngas that no longer reacts to form methanol can now form hydrocarbons rather than higher alcohols, so a trade-off may exist in manipulating this variable to promote HAS.
At temperatures of 380°C and 400°C, the MeOH/i-BuOH product mole ratio stays constant at 3.6-3.8; in contrast, at 420°C, this ratio becomes 1.0 showing that HAS is favored at the higher temperature. However, selectivity to total alcohols falls from 48-57% down to 34%; hydrocarbon formation is also favored by higher temperatures and this effect appears to outweigh the benefit of increased isobutanol formation vs. methanol.

**Catalyst Aging:** The catalyst was returned to start-up conditions after 102 hours and showed little deactivation:

<table>
<thead>
<tr>
<th></th>
<th>20 hrs on stream</th>
<th>122 hrs on stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ROH activity (g/kg-hr)</td>
<td>200</td>
<td>204</td>
</tr>
<tr>
<td>Isobutanol activity (g/kg-hr)</td>
<td>94</td>
<td>89</td>
</tr>
<tr>
<td>MeOH/i-BuOH product mole ratio</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>ROH Selectivity</td>
<td>68</td>
<td>48</td>
</tr>
</tbody>
</table>

The catalyst appears to keep a constant alcohol productivity with time, but hydrocarbon production increases, resulting in an overall loss in selectivity. Surface analyses will determine if this loss in selectivity is due to promoter redistribution with time.

4.1.6 Experimental

4.1.6.1 Catalyst Preparation

The ZnCrMn oxides were prepared by coprecipitating the metal nitrate salts in aqueous medium at a constant pH. An aqueous solution containing the metal nitrate salts and a basic solution were dripped slowly into ~200 mL of the basic solution using two peristaltic pumps. Care is taken to assure that the resulting solution is well stirred during the addition and the pH of the solution is monitored continuously. The flow of the basic solution is adjusted to keep the solution at a constant pH. The resulting mixture is then heated for a given time and then solid precipitate is filtered and washed with at least three liters of water, mixing well during the washing. The solid is dried at 110-120°C overnight and calcined for the desired time at the appropriate temperature. The catalysts were impregnated using the incipient wetness method.

4.1.6.2 Catalyst Testing

The reactor tubes were made from 1/4 inch stainless steel tubing that had been treated overnight with a 50/50 solution of hydrochloric acid and water. The tubes were rinsed with water for 5 minutes followed by an acetone rinse. Reactors were dried under vacuum. One gram of catalyst was mixed with 3 cm³ of glass beads until the mixture was uniform. The reactors were then loaded while tapping on the sides of reactor tube. Due to the V-like nature
of the reactor tubes, each side of the V was loaded with one-half of the catalyst mixture at a time. Glass wool was then put into place on both sides of the reactor. The catalysts were reduced with 5% hydrogen in nitrogen for four hours at the desired temperature.

The reduced catalysts were then loaded into the sand bath and the system was pressurized with nitrogen. Once the reactor reached the correct temperature, the nitrogen was turned off and the syngas feedstream was turned on and adjusted to the correct pressure.

4.1.7. Task 1 Conclusions

Reactor system modifications, undertaken to improve data quality, have been completed. The changes should help eliminate differences between the two reactors and allow for more reliable analysis of higher molecular weight products. A standard methanol catalyst has been used to calibrate the new reactor configuration.

Catalyst 11-DAN-115 (a K/Pd promoted Zn/Cr/Mn spinel oxide prepared via ammonium hydroxide precipitation) has been tested in our reconfigured reactor system. This catalyst was not very active or efficient, which parallels our observations made during the process parameter design that used this catalyst. We have now abandoned the ammonium hydroxide precipitation method in catalyst preparation.

To calibrate our new reactor system, we have retested our "best" isobutanol catalyst, 10-DAN-54 (a K/Pd promoted Zn/Cr/Mn spinel oxide, prepared via potassium carbonate precipitation) in our reconfigured reactor system. This catalyst is about twice as active and 20% less selective to alcohols in the new reactor configuration.

The effects of space velocity and temperature have also been examined for 10-DAN-54. At lower space velocities, productivities fall, but higher alcohols are favored, resulting in a higher proportion of higher alcohols vs. methanol. At temperatures above 400°C, the MeOH/i-BuOH product mole ratio approaches 1.0, but selectivity to total alcohols falls dramatically; hydrocarbon formation is also favored by higher temperatures and this effect appears to outweigh the benefit of increased isobutanol formation vs. methanol.

Future work will involve continued testing of 10-DAN-54 to examine the effects of pressure and syngas ratio on this catalyst. Surface science analyses are planned to determine if the loss in selectivity observed with time on stream is due to promoter redistribution. The procedures used in catalyst charging, pretreatment, and startup will be examined. New catalyst formulations will also be tested.
4.2. Task 2 – Engineering Studies

4.2.1. Reaction Engineering

4.2.1.1. Introduction

Task 2 work under this contract involves reaction engineering studies to examine the best catalysts identified in Task 1. New catalysts will be developed and screened in powder form in Task 1. We will develop scaleup and process strategies to make use of the best catalysts found in Task 1 and will develop kinetic models to describe their performance.

Since powders cannot be used commercially in a gas phase reactor (the type which will be used for initial screening studies), we will evaluate different strategies for utilizing new catalysts on an industrial scale. This may include pelletizing or tableting the powdered catalysts for use in gas phase reactors, using powdered catalysts in a gas-liquid-solid slurry reactor, or using solid pellets or powder in other types of three phase reactors, such as trickle bed reactors.

4.2.1.2. Reaction Engineering Activities

Task 2 research during the last quarter of 1993 was severely limited due to the temporary unavailability of personnel in the reaction engineering areas, retirements (Jean B. Cropley), and the restructuring of the Engineering Department. The re-staffing of the Engineering Department is currently in progress and will be finalized by the end of January. We hope to resume work in early February.

4.2.2. Mathematical Process Development

4.2.2.1. Introduction

Mathematical process development can be broken down into synthesis and simulation. Process synthesis determines which unit operations are needed and in what order. Once the structure is defined by the synthesis step, the process is simulated to determine the heat and material balance.

4.2.1.2. Process Synthesis Activities

Six ASPEN PLUS base case studies have been received from West Virginia University. We are in the process of constructing a base case patterned after one of these generic cases, but more detailed and specific to our envisioned process.

4.2.3. Task 2 Conclusions

Reaction engineering studies will soon begin to study the kinetics of some of our better catalysts. A base case is being developed that will be specific to our envisioned process.
END

FILED

5/14/19

DATE