

QUARTERLY TECHNICAL PROGRESS REPORT
NUMBER 23

THE ECONOMICAL PRODUCTION OF
ALCOHOL FUELS FROM
COAL-DERIVED SYNTHESIS GAS

CONTRACT NO. DE-AC22-91PC91034

REPORTING PERIOD:
April 1, 1997 to June 30, 1997

SUBMITTED TO:

Document Control Center
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

SUBMITTED BY:

West Virginia University Research Corporation
on behalf of West Virginia University
617 N. Spruce Street
Morgantown, WV 26506

June, 1997
Revised February 1998

U.S. DOE Patent Clearance is not required prior to the publication of this document.

Table of Contents

| | |
|---|----|
| Executive Summary | 3 |
| 1.1 Introduction | 4 |
| 1.2 Accomplishments, Results and Discussion | 4 |
| 1.2.1 Laboratory Setup | 4 |
| 1.2.2 Molybdenum-Based Catalyst Research | 4 |
| 1.3 Conclusions and Recommendations | 10 |
| 1.4 Future Plans | 10 |

Executive Summary

During this time period, we finished the kinetic study on the reduced Mo-Ni-K/C catalyst. Experimental work on this project is essentially over. We are continuing the development of kinetic models for this catalyst. We are also continuing with the quantitative analyses of TPR spectra from K-Mo/C catalysts. We request a meeting with USDOE to consider plans to follow up the current work.

1.1 Introduction

The objective of Task 1 is to prepare and evaluate catalysts and to develop efficient reactor systems for the selective conversion of hydrogen-lean synthesis gas to alcohol fuel extenders and octane enhancers.

Task 1 is subdivided into three separate subtasks: laboratory and equipment setup; catalysis research; and reaction engineering and modeling. Research at West Virginia University (WVU) is focused on molybdenum-based catalysts for higher alcohol synthesis (HAS). Parallel research carried out at Union Carbide Corporation (UCC) was focused on transition-metal-oxide catalysts. This research has been completed and is not reported on here.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory Setup

No major changes were necessary during this reporting period.

1.2.2 Molybdenum-Based Catalyst Research

We have finished the kinetic study on the reduced Mo-Ni-K/C catalyst. The experimental data were obtained on a tubular fixed-bed microreactor. These data have been reported in Technical Progress Report (TPR) 22. The concept of “gross” production rates was adopted for the development of the model used earlier for the sulfided Mo-Co-K/C catalyst (see Monthly Status Report [MS] 60), and this is continued here. Also similar to the case of the sulfide catalyst, we first developed exponential models to determine the statistically significant variables for each model for the gross production rates of significant alcohols and total hydrocarbons. A nonlinear regression procedure provided in SigmaPlot® was used to fit the exponential models. The value of the F-statistic was used to test the significance of the models, while the significance of the parameter estimates was tested using the value of the t-statistic. Then we developed the final models, which include only the statistically significant variables and which are of the Langmuir-Hinshelwood (L-H) type.

The exponential models for methanol (MeOH) and ethanol (EtOH) have been reported in TPR 22. For MeOH, we showed that all terms, including the partial pressures of CO, H₂ and MeOH, are statistically significant. For EtOH, however, none of these terms appear to be statistically significant in the first pass. We report first the development of Langmuir-Hinshelwood (L-H) models for MeOH and EtOH.

The L-H expression for the gross production rate of MeOH was initially written as:

$$r_{g,MeOH} = \frac{A_m e^{-\frac{E_m}{R} \left(\frac{1}{T} - \frac{1}{T_{cp}} \right)} \left[\left(\frac{P_{CO}}{P_{CO,cp}} \right) \left(\frac{P_{H_2}}{P_{H_2,cp}} \right)^2 - k_z \frac{K_{cp}}{K_{eq}} \left(\frac{P_{MeOH}}{P_{MeOH,cp}} \right) \right]}{\left[1 + K_A \left(\frac{P_{CO}}{P_{CO,cp}} \right) + K_B \left(\frac{P_{H_2}}{P_{H_2,cp}} \right)^2 + K_C \left(\frac{P_{MeOH}}{P_{MeOH,cp}} \right) \right]^n} \quad (1)$$

where $K_{cp} = \frac{P_{MeOH, cp}}{P_{CO, cp} (P_{H_2, cp})^2}$

The parameter K_{eq} in Equation (1) represents the equilibrium constant for MeOH synthesis from CO and H₂, and is obtained from Chemical Equilibrium Software (CHEMEQ.BAS) developed by Sandler. The parameters A_m and E_m are the pre-exponential factor and the activation energy respectively. The parameters K_A , K_B and K_C in the denominator represent the adsorption coefficients. The temperature dependences of the adsorption coefficients are neglected. The parameter k_z is a fugacity correction factor whose temperature dependence is also neglected. Equation (1) is similar to the expression used for MeOH production over the sulfided catalyst, as reported earlier. However, the form of Equation (1) proved to be unsatisfactory, as is described in detail in MS 68. The final form used is:

$$r_{g,MeOH} = \frac{A_m e^{-\frac{E_m}{R} \left(\frac{1}{T} - \frac{1}{T_{cp}} \right)} \left(\frac{P_{CO}}{P_{CO,cp}} \right) \left(\frac{P_{H_2}}{P_{H_2,cp}} \right)^2}{\left[1 + K_A \left(\frac{P_{CO}}{P_{CO,cp}} \right) + K_B \left(\frac{P_{H_2}}{P_{H_2,cp}} \right)^2 \right]^n} \quad (2)$$

with:

$$A_m = 135.4 \text{ mol/h/kg-cat.} \quad (3a)$$

$$E_m = 45.00 \text{ KJ/mol} \quad (3b)$$

$$K_A = 0.6940 \quad (3c)$$

$$K_B = 0.9475 \quad (3d)$$

The L-H rate expression for EtOH is given by the following equation:

$$r_{g, EtOH} = \frac{A_e e^{-\frac{E_e}{R} \left(\frac{1}{T} - \frac{1}{T_{cp}} \right)} \left(\frac{P_{MeOH}}{P_{MeOH, cp}} \right)}{\left[1 + K_M \left(\frac{P_{MeOH}}{P_{MeOH, cp}} \right) \right]^n} \quad (4)$$

In this equation, A_e and E_e are the pre-exponential factor and the activation energy respectively, and K_M is the adsorption coefficient of MeOH. Nonlinear regression gives the following parameter values (for $n=1$):

$$A_e = 20.35 \text{ mol/h/kg-cat.} \quad (5a)$$

$$E_e = 88.17 \text{ KJ/mol} \quad (5b)$$

$$K_M = 0.7309 \quad (5c)$$

The independent variables considered for the production rate of propanol (PrOH) were the reaction temperature, the partial pressures of CO, H₂ and EtOH. The expression for the gross production rate of PrOH can be written in exponential form as:

$$r_{g, PrOH} = A_3 \exp[-(E_3/R)(1/T-1/T_{cp})] (P_{CO}/P_{CO, cp})^{a3} (P_{H_2}/P_{H_2, cp})^{b3} (P_{EtOH}/P_{EtOH, cp})^{c3} \quad (6)$$

The nonlinear regression (provided in SigmaPlot®) was used to obtain values of these parameters. The best-fit values for Equation (6) have been tabulated in MS 69. However, the t-statistic for each parameter showed that none of the terms in Equation (6) is statistically significant, except the pre-exponential and the temperature terms. Hence, we adopted the procedure of dropping the least significant term and re-regressing, repeating the process until every remaining term in the rate expression was significant. The result showed that only the EtOH-dependence term is significant in addition to the pre-exponential and the temperature terms. Therefore, the following equation was adopted for the L-H model of PrOH production:

$$r_{g, PrOH} = \frac{A_p e^{-\frac{E_p}{R} \left(\frac{1}{T} - \frac{1}{T_{cp}} \right)} \left(\frac{P_{EtOH}}{P_{EtOH, cp}} \right)}{\left[1 + K_E \left(\frac{P_{EtOH}}{P_{EtOH, cp}} \right) \right]^n} \quad (7)$$

In this equation, A_p and E_p are the pre-exponential factor and the activation energy respectively, and K_E is the adsorption coefficient of EtOH. Nonlinear regression gives the following parameter values (for $n = 1$):

$$A_p = 11.24 \quad \text{mol/h/kg-cat.} \quad (8a)$$

$$E_p = 49.93 \quad \text{KJ/mol} \quad (8b)$$

$$K_E = 0.9139 \quad \text{dimensionless} \quad (8c)$$

These values are much better than values obtained for $n = 2$ and $n = 3$ in Equation (7). The t-statistic values indicate that every term in Equation (7) is statistically significant. Therefore, the model given by Equations (7) and (8) is acceptable.

Similarly, the exponential rate expression for butanol (BuOH) was originally written as:

$$r_{g,\text{BuOH}} = A_4 \exp[-(E_4/R)(1/T-1/T_{cp})] (P_{\text{CO}}/P_{\text{CO,cp}})^{a_4} (P_{\text{H}_2}/P_{\text{H}_2,\text{cp}})^{b_4} (P_{\text{PrOH}}/P_{\text{PrOH,cp}})^{c_4} \quad (9)$$

The nonlinear regression gives the following best-fit values of parameters:

$$A_4 = 2.268 \quad \text{mol/h/kg-cat.} \quad (10a)$$

$$E_4 = 46.90 \quad \text{KJ/mol} \quad (10b)$$

$$a_4 = 0.1129 \quad \text{dimensionless} \quad (10c)$$

$$b_4 = -0.3642 \quad \text{dimensionless} \quad (10d)$$

$$c_4 = 0.2681 \quad \text{dimensionless} \quad (10e)$$

Once again, the value of the t-statistic indicates that none of the terms in Equation (9), except the pre-exponential term A_4 , is statistically significant. The same procedure as described above was used to determine the statistically significant variables. However, the situation is more complicated this time. When we drop the least significant term one by one until only one pressure-dependence term (the partial pressure of PrOH) is left, the t-statistic still shows that the last pressure-dependence term is not statistically significant. That indicates that the production rate of BuOH is sufficiently small, and the change in the partial pressure of PrOH is sufficiently small, in the range of experimental conditions used here, that the changes are overshadowed by the statistical error expected. In that case, the final model for BuOH production rate becomes:

$$r_{g,\text{BuOH}} = A_B \exp[-(E_B/R)(1/T-1/T_{cp})] \quad (11)$$

where A_B and E_B are pre-exponential factor and the activation energy for BuOH production, respectively. The best-fit values of parameters for this equation are:

$$A_B = 2.154 \quad \text{mol/h/kg-cat.} \quad (12a)$$

$$E_B = 69.77 \quad \text{KJ/mol} \quad (12b)$$

Even though the dependence of the BuOH rate on the PrOH pressure is statistically negligible, there are physical reasons to include this term. If one would prefer to take the pressure dependence into account, the best equation could be:

$$r_{g, BuOH} = \frac{A_B e^{-\frac{E_B}{R} \left(\frac{1}{T} - \frac{1}{T_{cp}} \right)} \left(\frac{P_{PrOH}}{P_{PrOH, cp}} \right)}{\left[1 + K_P \left(\frac{P_{PrOH}}{P_{PrOH, cp}} \right) \right]^n} \quad (13)$$

In this equation, K_P is the adsorption coefficient of PrOH. The best-fit values of parameters for Equation (13) are (for $n=1$):

$$A_B = 16.1 \quad \text{mol/h/kg-cat.} \quad (14a)$$

$$E_B = 56.92 \quad \text{KJ/mol} \quad (14b)$$

$$K_P = 6.116 \quad \text{dimensionless} \quad (14c)$$

These values are better than those obtained when $n = 2$ and $n = 3$ in Equation (13).

For pentanol (PeOH), hexanol (HexOH) and heptanol (HepOH), the production rates are measurable by our reaction system. However, the measured values are too low, relative to the statistical error, to allow for the development of reliable models.

We are continuing to analyze quantitatively the spectra from temperature-programmed reduction (TPR) of K- and Ni-doped C-supported Mo-based catalysts. During the period of this report, we have studied the effects of impregnation sequence and of calcination for Ni-doped C-supported Mo catalysts. Results with the K-doped catalysts have been reported earlier (Technical Progress Report 22).

The raw TPR spectra can be fitted to two low-temperature peaks and one high-temperature peak, in addition to a peak for the reduction of the carbon support, as in the case of K-Mo/C. However, the situation is complicated for the case of the Ni-Mo/C catalyst because we have no way to distinguish the contribution of Mo reduction from that of Ni reduction. (XPS could be used for this purpose, but we do not have that capability as yet.) To solve the problem, we assume each of the two limiting cases in turn: either assume Ni is fully reduced, or assume Ni is not reduced at all.

We report the results here assuming Ni is unreducible. When K is impregnated first onto the carbon support and the catalyst subsequently calcined, the Mo valence is higher (Mo is more difficult to reduce) than the corresponding value for the calcined catalyst when Mo and Ni are

impregnated before K. This is true at both low temperature and high temperature. Further, for catalysts with Mo impregnated first, the calcined catalyst has approximately the same Mo valence after low-temperature reduction as does the uncalcined catalyst. However, after high-temperature reduction, the Mo valence decreases significantly (more Mo species are reducible) when the Mo-first catalyst is calcined than when it is not calcined.

We have also investigated the catalytic performance of the catalyst with K impregnated first. The products are exclusively hydrocarbons (in addition to CO₂). No alcohol is produced at all. One of the reasons for this poor performance could be explained by the reduction behavior of the catalyst. In our reactivity test, the catalyst is pre-treated in pure H₂ at 400°C for 12h. This is similar to the low-temperature reduction in our TPR experiment. From the TPR results presented above, the catalyst is poorly reduced at low temperature. It is possible that the active phase(s) for higher alcohol synthesis are the more-strongly reduced Mo species.

It is worth comparing this performance to that of the calcined Mo-Ni-K/C catalyst. The Mo-Ni-K/C catalyst is much better for higher alcohol synthesis, in terms of both activity and selectivity. Consistent with the hypothesis above, the Mo valence after low-temperature reduction for the calcined Mo-Ni-K/C catalyst is much smaller than the Mo valence for the calcined K-Mo-Ni/C catalyst.

We consider the experimental work on this project to be essentially finished. During this time period, several presentations were made and several manuscripts were written. A paper entitled "Formation of C₁-C₄ Alcohols from Synthesis Gas over Doped Supported Molybdenum Sulfide Catalysts" was presented at the Spring Symposium of the Tri-State Catalyst Club (TSCC) in Charleston, WV on April 8-9, 1997. A preliminary poster paper on early kinetic results, entitled "Higher-Alcohol Synthesis over Reduced Mo-Ni-K/C Catalysts: A Kinetic Study," and a preliminary poster paper on early TPR results, entitled "A TPR Study of Carbon-Supported Mo-based Catalysts," were also presented at the TSCC Meeting. A paper entitled "Kinetics of Higher-Alcohol Formation from Synthesis Gas using Statistically Designed Experiments" was presented at the 213th Meeting of the American Chemical Society (ACS) in San Francisco on April 16, 1997. Two presentations were made during the 15th Meeting of the North American Catalysis Society in Chicago IL, May 18-22, 1997. One was an oral paper entitled "Kinetics of Higher-Alcohol Formation from Synthesis Gas using Statistically Designed Experiments in a Gradientless Reactor," and the other was a poster paper entitled "Screening of Catalysts Based on Vapor-Phase Synthesized Molybdenum Sulfide for Higher-Alcohol Synthesis." We were requested to submit a manuscript for inclusion in the Special Edition of Industrial and Engineering Chemistry Research honoring Gilbert F. Froment; this paper, entitled "Screening of Alkali-Promoted Vapor-Phase-Synthesized Molybdenum Sulfide Catalysts for the Production of Alcohols from Synthesis Gas," is currently in press. A second manuscript, entitled, "A Kinetic Model for the Synthesis of High-Molecular-Weight Alcohols over a Sulfided Co-K-Mo/C Catalyst" is currently under review. Two more manuscripts are currently under preparation.

1.3 Conclusions and Recommendations

The kinetic analysis for the data over the Mo-Ni-K/C catalyst has been completed. TPR experiments on alkali-substituted Mo/C are complete. The experimental work for this project is essentially complete. The TPR data for the Ni-Mo/C are starting to be analyzed. We believe that the Mo-Ni-K/C catalyst, and the earlier-reported Co-Mo-K/C catalysts are promising catalysts for the synthesis of higher alcohols.

1.4 Future Plans

We request a meeting with USDOE to go over alternatives for research to follow up on some of our promising results.