HOMOGENEOUSLY CATALYZED SYNTHESIS GAS TRANSFORMATIONS TO OXYGENATE FUELS

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HOMOGENEously catalyzed Synthesis gas
Transformation to Oxygenate Fuels

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Abstract

At Brookhaven National Laboratory (BNL), the ongoing oxygenates synthesis program is addressing the catalytic synthesis gas conversion to liquid fuels and fuel additives. The major thrust of this effort is to enhance carbon conversion, reaction rates, product selectivity and overall process efficiency. To this effect, a series of liquid phase homogeneous catalysts have been developed and successfully utilized in the synthesis of methanol and other oxygenates. This paper identifies advantages and uncertainties associated with these newly developed catalysts. The effect of system parameters on the overall process scheme is discussed.
INTRODUCTION

The scheduled implementation of the 1990 Clean Air Act will require increased use of oxygenate fuels and fuel additives in the coming years. Though commercial technologies to generate desirable oxygenates utilizing heterogeneous catalysts already exist, these processes may not be economical under desired conditions. The conversion of plentiful coal and natural gas to liquids through synthesis gas (the indirect route) is being actively pursued at BNL by the development of liquid phase homogeneous catalysts (1,2). Though the industrial knowledge base in homogeneous catalysis is limited to a few commercial processes (3), the overall advantages inherent to homogeneous systems may help faster commercialization of technologies based on these systems. This paper describes the overall process considerations associated with the BNL Methanol Synthesis Catalyst. The discussion extends to the synthesis of other oxygenates utilizing homogeneous catalysts developed at BNL.

METHODOLOGY

The data were collected in a 0.5 L AE stirred batch reactor as well as in the BNL Continuous Gas Flow Reactor unit operating in plug-flow and CSTR modes. The reactor schematics, kinetic, batch, and continuous data collection and analyses procedures are already described (1,2).

The data from previously completed kinetic runs (2) were utilized to construct an empirical kinetic model utilizing the Ultramax® optimization software package. The variables included in the model were: volume of solution, methanol and catalyst concentrations, reaction temperature and stirring speed. Based on these variables, a kinetic model was proposed using a Fixed-Point-Centered-Quadratic with high and low constraints for each variable selected from the experimental data.

The recycle mimic run was conducted in the batch reactor by conducting five consecutive syngas charges of 750 psig each, distilling off the synthesized methanol and repeating this entire process twice. The catalyst performance during cycles was then compared.

RESULTS AND DISCUSSION

The LLTMeOH Technology Update

The BNL methanol synthesis catalyst system falls into a general category of "homogeneous" systems. In a typical homogeneous system, the catalyst is completely dissolved in the solvent medium and, unlike heterogeneous catalysts, each molecule of the catalyst is utilized. The salient features of the BNL catalyst system include:

- The liquid phase operation permits better heat management.
The catalyst operates well between 50-150°C where an almost 100% syngas conversion to methanol is thermodynamically allowed at relatively low pressures.

The BNL catalyst shows an unprecedented activity for methanol synthesis with rates up to an order of magnitude higher than those attained with known heterogeneous systems.

With balanced gas, a high (> 95%) selectivity to methanol is observed under conditions where methyl formate reaction is suppressed.

At pressures as low as 100 psi, the catalyst is active for methanol synthesis.

An important feature of the system is its ability to achieve high gas conversion per pass. This eliminates the expensive recycle step.

The catalyst appears inert to N₂ under the operating conditions. This feature permits partial oxidation with air during syngas manufacture. The elimination of an oxygen separation unit is expected to result in a substantial saving.

Unlike heterogeneous systems, the present two-phase (gas/liquid) homogeneous system is better defined and lends itself to a mechanistic study.

The aforementioned features make the BNL catalyst system attractive for potential commercial applications.

**Kinetic Model.** In a previous study (2), the effect of reaction variables on reaction rate was studied and a rate expression derived (Equation 1):

\[
-dP_{CO}/dt = k_0(P_{CO})(C_{Base})^{2.84}(C_{TMC})^{0.72}(\exp\{-0.27[C_{MeOH}]\})
\]  

where \( k_0 \) is kinetic rate constant, \( P_{CO} \) is partial pressure of carbon monoxide, \( C_{Base} \) (1.0-4.0 M), \( C_{TMC} \) (0.01-0.10 M), and \( C_{MeOH} \) (10-24 M) are base, transition metal complex and methanol concentrations respectively. Based on the experimental kinetic data, an empirical model utilizing the Ultramax® software program was constructed. Twelve additional kinetic runs, predicted by this model, were conducted. The pseudo first-order rate constants (k) were derived by plotting the logarithmic partial pressure of CO against time. The predicted and measured rate constants were in excellent agreement (Table 1). The prediction error was 0.031 min⁻¹ and the R-squared value was 98.5. These data show that the proposed kinetic model is valid over a wide range of reaction conditions and as such could be used for scale-up.

**Continuous Gas Flow Data.** The performance of a catalyst under continuous flow conditions yields valuable information. To this effect, the BNL catalyst was tested in the BNL Continuous Gas Flow Unit. In the plug-flow mode, a run in 90% triglyme/10% methanol with 7.0 wt% catalyst loading, yielded data shown in Table 2. A 40% increase in methanol concentration in the final solution measured in the collection tank quantified the amount of syngas consumed with 98% selectivity to methanol. The remaining consumed syngas was accounted for by methyl...
formate production. The methanol productivity was 45.7 G-mol MeOH/Kg.cat-hr. An average 61% syngas conversion per pass over a three-hour period is encouraging but in no way represents an optimized value. It is expected that optimization of reaction parameters will match the catalyst performance normally observed in batch mode. Efforts are under way to correlate batch and continuous gas flow data. The effect of rate of gas/liquid mixing on reaction rate is presently being studied.

**Catalyst Life.** This aspect is important to the overall economics of any process. With the present system, due to non-availability of a test unit with a recycle capability, no direct measurement of catalyst life has been made. The measurement of this parameter was all the more critical because the batch mode data collected with the BNL Catalyst System indicated that the gas consumption rate decreased with time. This decrease has been attributed to the negative effect of methanol concentration and is represented by the negative exponential term in the rate equation (Equation 1). To confirm this deduction, a multicharge three-cycle run was conducted in the 0.5 L AE batch reactor. The run conditions were: 200 mL glyme/MeOH solvent, 14% catalyst loading, H₂/CO = 1.85, 120°C, 1200 rpm, P₁ = 750 psig. This five-charge run yielded batch rates of 29, 57, 56, 52, 41 psi/min respectively. The total gas consumption yielded a theoretical methanol value and the equivalent amount was distilled off from the reactor after cooling the reactor. The second five-charge run batch rates were 25, 33, 32, 27, 23 psi/min respectively and 27 mL methanol was then distilled off the reactor. The third five-charge run gave batch rates of 30, 35, 30, 23, 18 psi/min. These data suggest that the rate slow-down during multi-charge runs appears to be caused by methanol accumulation. Relatively higher rates observed during the first five-charge cycle are attributed to the catalyst conditioning. The data from second and third cycles are more consistent. At the end of the run, the integrity of the cosolvent was also confirmed within limits.

**The Overall Process.** The foregoing discussion relates to several process uncertainties associated with the present BNL Methanol Catalyst System. These data are being put into perspective to address additional issues related to the scale-up of the present system. The high gas conversions measured in batch mode need to be confirmed in the Continuous Gas Flow Unit operating in CSTR mode. The catalyst life issue needs to be fully addressed.

**The LLTMF Technology Update**

Another version of the BNL Methanol Synthesis Catalyst maximizes carbon conversion in synthesis gas by synthesizing methyl formate via the Liquid Low Temperature Methyl Formate (LLTMF) synthesis technology, presently under development at BNL. Several solvents are being screened for compatibility, and reaction parameters are being optimized for enhanced methyl
formate selectivity. A successful development of this process is expected to result in a very attractive one-pot synthesis of methyl formate directly from synthesis gas.

CONCLUSIONS

The application of homogeneous catalysis in synthesis gas conversion to oxygenates has resulted in the development of a series of homogeneous catalysts. The data presented in this paper are summarized below:

- A kinetic model has been developed for the BNL Methanol Catalyst System. An empirical model, constructed utilizing the Ultramax® software confirms the derived rate expression over a wide range of conditions. The prediction error for the rate constant was 0.031 min⁻¹ and the R-squared was 98.5.
- Under continuous gas flow conditions, the average gas conversion was 61% per pass over a three-hour period in plug-flow mode. The methanol productivity was calculated to be 45.7 G-mol MeOH/Kg. cat-hr.
- The data from a three-cycle batch run (each cycle consisting of five charges of 750 psi per charge) established that the accumulation of methanol is one parameter responsible for decreased rate under batch conditions.
- The negative methanol effect corresponds to the negative exponential term in the rate expression.
- The collected data with the BNL catalyst is being integrated to study the feasibility of a scale-up.
- The BNL Methyl Formate Synthesis Catalyst is being evaluated for one-pot synthesis of methyl formate from synthesis gas.

ACKNOWLEDGEMENTS

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REFERENCES

Table 1

The Actual Versus Predicted k Values for the BNL Methanol Catalyst System

0.5 L AE Zipperclave Batch Reactor

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<th>Model k</th>
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Table 2
Data Summary of a Continuous Gas Flow Run with the BNL Methanol Synthesis Catalyst

Run Conditions

Solvent: 90% Triglyme/10% Methanol
Catalyst Loading: 7.0 wt%
Syngas: $H_2/CO = 1.85$
P = 350 ± 3 psig at T
T = 98 ± 1°C (Top)/110 ± 1°C (Bottom)
Initial Volume of Catalyst Solution in Reactor = 100 mL
Space Velocity = 4675 L/Kg cat-hr
Catalyst Make-Up Rate = 0.20 L/hr
On-line Time = 3 hr 0 min

Data Analysis

Gas Conversion

Average = 61%
Maximum = 67%
Minimum = 57%
Final $H_2/CO$ = 2.17
Theoretical MeOH = 0.93 G-mol

MeOH Concentration in Catalyst Solution by Volume

Initial = 10.0%
Final:
  Reactor = 13.9%
  Collection Tank = 14.4%
MeOH Selectivity = 98%
MeOH Productivity = 45.7 G-mol MeOH/Kg cat-hr
END

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