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PROGRESS REPORT

A NOVEL PROCESS FOR MANUFACTURE OF METHANOL

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1.0 ABSTRACT

A bench-scale reactor is being used to conduct studies of the conversion of synthesis gas to methanol by a novel process. During the last quarter, the effect of operating parameters such as temperature, pressure, feed H_2/CO ratio and feed flow rate on the MeOH synthesis rate were investigated. The specific rate of MeOH synthesis was found to vary with gas feed rate -- an unexpected result. It is proposed that this is due to the presence of small amounts of an inhibiting agent which accumulates in the liquid at low flow rates. Work also continued on the modification of the experimental equipment to permit on-line monitoring of liquid and gas compositions.

Mr. Vishwesh Palekar was awarded a Master of Science Degree in Chemical Engineering for work done on this project. The title of his thesis is "A Novel Synthesis of Methyl Alcohol".

A presentation of this work was made by Mr. Palekar at the Pittsburgh-Cleveland Catalysis Society Meeting on April 18. The title of his presentation was "A Novel Synthesis of Methanol". His presentation was judged the best of the student papers presented.

2.0 INTRODUCTION

An experimental investigation of a new process, developed in our laboratory, for converting synthesis gas to methanol is being carried out. It has significant advantages over the conventional gas phase synthesis in that the recycle of unreacted material can be virtually eliminated and it operates at lower temperatures. The reaction is not significantly poisoned by CO_2 or H_2O products. It has been demonstrated that the reaction proceeds with good rates at 140°C and 6 MPa pressure. However, the nature of the mixed catalyst comprised of KOME and Cu-chromite and of the possible intermediates is not well understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst. This information should make it possible to scale up the process.

Two papers have been published^(1,2) reporting our studies - one on the individual reactions (carbonylation of methanol and hydrogenolysis of methyl formate) and the other on the concurrent reaction in which a carbonylation catalyst (e.g. potassium methoxide) and a hydrogenolysis catalyst (e.g. Cu-chromite) are used. The current work is part of a three and a half-year project which started in September, 1989.

3.0 RESEARCH OBJECTIVES

Principal research objectives are,

- 1) To determine the effect of alternate catalysts on the synthesis. This will include modified copper chromite catalysts in addition to homogeneous catalysts in the form of methoxides or similar salts.
- 2) To determine the nature of the active catalyst in this reaction and the effect of deactivating agents such as CO_2 , H_2O and CO .
- 3) To determine the rate limiting steps in this reaction so that proper scale-up is possible. The effect of catalyst loading and reactor volume are of special importance.
- 4) To develop mathematical models which can be used to predict the rates of reaction and are suitable for scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, the effect of reaction temperature, pressure and feed characteristics were studied. This information is useful in selecting a good operating point for MeOH production.

4.0.1 Effect of Temperature

The effect of temperature is manifested in the rates of the reactions, vapor pressures of the solution components, and solubilities of CO and H₂. Since the rate of the MeOH synthesis is calculated based on the gas phase concentrations of H₂, the solubility of CO and H₂ does not affect the calculated value. The concurrent reaction was run under a steady state at temperatures of 100, 125 and 150°C at a feed H₂/CO ratio of two. A plot of the effect of temperature on the rate of reaction is shown in Figure 1. The energy of activation obtained is in the order of 7.13 kcal/mole which is comparable to that of the commercial direct gas synthesis route which is of the order of 7 to 12 kcal/mole. A run was made at 80°C to check the possibility of operating at lower temperature. The reaction does proceed even at 80°C, although the rate obtained is approximately one fourth of that at 150°C. No corresponding results are available in the literature for comparison. The rates predicted by the equation obtained by Liu et al.⁽²⁾ were lower than the actual rates obtained. This may be a manifestation of the promotion effect of the alkali metal on the Cu-chromite catalyst

leading to a different and more active site due to interaction between the Cu-chromite and the alkali salt. A similar effect is described for Cu/ZnO catalysts in the gas phase direct MeOH synthesis.⁽⁴⁾

4.0.2 Effect of Pressure

The effect of pressure was studied using NaOMe as the carbonylation catalyst at a feed H_2/CO ratio of two. A linear relationship was obtained for the rate versus the total pressure. This is shown in Figure 2. Liu et al.⁽²⁾ obtained a similar result using KOMe as the catalyst. A white precipitate was obtained at the end of the run and identified by pH measurements to be sodium formate. The decreased solubility of NaOMe with decrease in pressure may also result in a decrease in the rate of MeOH synthesis.

4.0.3 Effect of Feed H_2/CO Ratio

The concurrent process involves H_2 and CO reacting separately in different reactions. From the overall stoichiometry, For every CO reacting, from the overall stoichiometry, two H_2 are required. The H_2/CO ratio existing in the vapor phase is an important parameter influencing the rates of individual reactions. Effects of different H_2/CO ratios on the rate of reaction were studied. Feed H_2/CO ratios of 2, 1.5 and 1 were used in this study. Steady state measurements at a feed H_2/CO ratio of 1.5 were made and then the ratio was switched to one and then to two to obviate

the effect of previous catalyst histories. The average deactivation rate was used to correct the rate to that at the end of 40 hrs. Maximum rates obtained as a function of H_2/CO ratios are shown in Figure 3. The rate of MeOH synthesis decreased with decrease in the feed H_2/CO ratio. This is consistent with the observation that CO inhibits the hydrogenolysis reaction. However, the results show that the concurrent reaction can tolerate fluctuations in the H_2/CO ratio. It must be emphasized that essentially no higher alcohols were produced for any of the H_2/CO ratios.

4.0.4 Effect of Flow Rate

The rate of MeOH production was found to be independent of mass transfer limitations in this reactor system.⁽²⁾ The rate should be independent of the inlet syngas flow rate at a stoichiometric composition in the well-stirred reactor. However, the rate was found to decrease with a decrease in the inlet synthesis gas flow rate. At a H_2/CO ratio of 2.0, the flow rate was changed from 105 cc/min. to 75 cc/min. This resulted in a small transient before achieving steady state at a MeOH production rate that was less than that for the higher flow rate. The MeOH synthesis rate at different flow rates is summarized in Table 1. The mole fractions of H_2O and CO_2 in the gas outlet increased as the feed flow rate decreased. Since both H_2O and CO_2 are known deactivating factors for the carbonylation and hydrogenolysis reaction, a buildup of these components might lead to a decrease in the rate of MeOH synthesis. At a constant rate of inhibiting by-

product formation, a decrease in the inlet flow rate will cause a drop in the MeOH synthesis rate. This is consistent with experimental observations. The change in the MeOH formation rate with inlet flow rate may be related to the finding by Liu⁽³⁾ that the MeOH synthesis rate does not change linearly with catalyst loading. The above observation seems to indicate that it would not be advantageous to operate at low inlet flow rates due to the lower MeOH formation rates obtained. This means a compromise may have to be made between syngas conversion and the rate of MeOH formation.

Table 1. Effect of Flow rate on Rate of Methanol Synthesis

Flow Rate (H ₂ /CO) cc/min.	Rate of MeOH Synthesis gmoles/h/gm. cat
3 gms. Cu-chromite + 0.5 gms. KOME	
90/45	0.02685
70/35	0.02116
50/25	0.01602
3 gms. Cu-chromite + 1 gm. KOME	
70/35	0.01905
50/25	0.0156

5.0 FUTURE WORK

Equipment modifications on the system are not complete and will be continued during the next quarter. New on-line sampling valves are being purchased and will be installed.

Studies will be carried out to investigate the activity and the nature of the reaction with alternate catalysts for MeOH synthesis. The non-linear rate with a change in Cu-chromite concentration, and the effect of flow rate will be modelled mathematically, using component mass balances.

6.0 REFERENCES

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Figure 1 : Effect of Temperature on Methanol Synthesis Rate

Figure 2: Variation of the Concurrent MeOH Synthesis Rate with Pressure

Figure 3: Variation of MeOH Synthesis Rate with H₂/CO Ratios In the Reactor

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