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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 potassium methoxide and Cu-chromite loading on the MeOH formation rate was investigated. The rate obtained with Cu-chromite was compared to that using Cu-ZnO as catalyst. Work also continued on the modification of the experimental equipment to permit on-line monitoring of liquid and gas compositions.

2.0 INTRODUCTION

An experimental investigation of a novel process for converting synthesis gas to methanol is being carried out. This new process was developed in our laboratory. It has significant advantages over the conventional gas phase synthesis in that the recycle of unreacted material can be virtually eliminated and lower temperatures will suffice. 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 catalyst 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

Principle research objectives are,

- 1) To determine the effect of alternate catalysts on the synthesis. This will include copper chromite catalysts impregnated with alkali metals such as potassium, rubidium and cesium as well as their use as homogeneous catalysts in the form of methoxides or similar salts. The use of various copper chromite catalysts with different compositions will be studied; e.g. substituting barium for manganese in copper chromite catalyst has a beneficial effect.
- 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, we investigated the effect of KOME and Cu-chromite loading on the rate of MeOH synthesis. KOME is a carbonylation catalyst. The carbonylation reaction is at equilibrium with a constant mole fraction of about 4% MeF in the liquid phase at steady state⁽³⁾. The hydrogenolysis of MeF is the rate determining step. If KOME has no role to play in the hydrogenolysis reaction then the amount of KOME added should not influence the MeOH formation rate. The rate of MeOH formation as a function of KOME loading at constant loading of Cu-chromite is shown in Figure 1. The nature of the plot indicates that there exists an optimum concentration of KOME (1:6 wt. ratio of KOME to Cu-chromite in our case). This fixes an operating point for this process. There seems to be a definite interaction between the two catalysts; KOME influencing the hydrogenolysis activity of Cu-chromite. It may be that the potassium adsorbs on the Cu-chromite surface and promotes its activity. Analogous to these results, Bybell et al.⁽⁴⁾ found a sharp maximum in their study of Cs loading for enhancement of MeOH productivity on Cu/ZnO catalysts. At the lower potassium loading the potassium may be promoting the activity of Cu-chromite while above the optimum concentration the potassium may block some of the active hydrogenolysis sites resulting in decreased activity. The methoxide ion would presumably act as a counter ion to stabilize the K^+ on the Cu-chromite surface. It is

interesting to note that unlike alkali impregnation on Cu/ZnO catalysts, no higher alcohols were detected in any of the runs.

The effect of the amount of Cu-chromite catalyst on the rate of MeOH formation was studied. Since the hydrogenolysis reaction is the rate determining step, doubling the amount of the catalyst should double the rate. The results for the rates obtained at different loadings of the two catalysts, keeping their ratio the same are presented in Figure 2. The MeOH synthesis rate was found to increase by a factor of 1.2, when the amount of catalyst is doubled. It was also observed that with an increase in the catalyst concentration the amount of water in the reaction mixture increased. Since H₂O is a deactivating agent, it may be the cause of the deviation from linearity. It is possible that an interaction between the alkali methoxide and the Cu-chromite catalysts could have a role to play in this strange behavior. Other possible causes such as mass transfer effects were eliminated by Liu et al.⁽¹⁾ who found that there exists no mass transfer limitations in the reactor.

Cu/ZnO is used as a catalyst in the commercial gas phase direct MeOH synthesis. Their operating conditions are in the range of 250-270°C and 50-70 atm.^(4,5) Alkali metals such as Cs and K have been found to promote MeOH activity under these reaction conditions. Reaction studies with Cu-ZnO at lower temperatures have never been done. We compared the rate of MeOH formation using a mixed catalyst consisting of KOMe and Cu-chromite and a combination

of K₂O and Cu-ZnO under our reaction conditions of 150°C and 60 atm. The progress of the reaction for the two catalyst combinations is shown in Figure 3. The activity of K₂O/Cu-chromite is almost 8 times higher than K₂O/Cu-ZnO. It must be kept in mind that Cu-chromite is a good hydrogenolysis catalyst while Cu-ZnO is not. This may also perhaps indicate that MeOH is formed by MeF hydrogenolysis and not by direct hydrogenation of CO under our reaction conditions.

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 nature of the reaction with alternate catalysts. Mathematical equations will be written to account for the non-linear behavior of the rate with the Cu-chromite concentration. The effect of other operating parameters such as temperature, pressure and feed H_2/CO flow rate on the MeOH synthesis rate will also be investigated.

6.0 REFERENCES

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Figure 1: Rate of Methanol Synthesis vs KOMe Loading

Figure 2: MeOH Synthesis Rate at Different Heterogenous Catalyst Loading

FIGURE 3: Rate of MeOH Synthesis on Cu-chromite and Cu-ZnO catalysts

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