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PROGRESS REPORT

A NOVEL PROCESS FOR METHANOL SYNTHESIS

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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 (MeOH) by a novel process. In previous reports, we provided evidence for a two-step reaction in series, the carbonylation reaction taking place mainly in a non-equilibrium region in the vicinity of the copper chromite surface, and the hydrogenolysis reaction taking place on the surface of the copper chromite. Interaction between the two catalysts enhances the rate of methanol formation. In this quarter, we investigated the effect of pore diffusion on reaction rate and obtained an expression for the rate of reaction for the methanol/methyl formate concurrent synthesis.

2.0 INTRODUCTION

An experimental investigation of a new process, developed in our laboratory, for converting synthesis gas to MeOH is being carried out. It has 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 deactivated by small amounts of CO_2 or H_2O. It has been demonstrated that the reactions proceed with good rates at 150°C and 6.3 MPa pressure. The overall reaction most likely proceeds through methyl formate (MeF) as an intermediate. However, the nature of the mixed catalyst, comprised of an alkali methoxide (e.g. KOMe) and copper chromite and of the possible intermediates is not understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst(s). This information should help make it possible to scale up the process.

Two papers have been published(1,2) reporting our early work. One is a study of the individual consecutive reactions: carbonylation of MeOH to MeF and the hydrogenolysis of MeF to MeOH. The other paper describes the concurrent reaction in which a carbonylation catalyst (e.g. KOMe) and a hydrogenolysis catalyst (e.g. copper chromite) are used in the same reactor. The current work is part of a three and a half-year project which started in September, 1989.

In this report, a soluble catalyst refers to an alkali compound (e.g. KOMe) added as a powder to the reactor (the powder is soluble in MeOH); the copper chromite is referred to as a heterogeneous catalyst. In this study a "homogeneous" reaction is one which takes place in the liquid solution (not on the surface of copper chromite) and a heterogeneous reaction is one which takes place on the surface of copper chromite. It is possible that the soluble salt is adsorbed on the copper chromite and the combination then functions as the catalyst or the catalyst precursor.

3.0 RESEARCH OBJECTIVES

Principal research objectives are,

1) To determine the effect of various catalysts on the synthesis of MeOH. This will include modified copper chromite catalysts in addition to soluble 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 and H_2O.

3) To determine the rate-limiting step(s) in this reaction. 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 could be useful in eventual scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we developed a kinetic model for the rate of MeOH synthesis in the concurrent process and investigated the effect of pore diffusion limitations on the MeOH synthesis rate.

4.1 Mechanism of the Concurrent Synthesis

We have not undertaken studies aimed at identifying the reaction intermediates per se in the concurrent reaction. We believe the reaction proceeds through the formation of MeF and, based on this assumption, a plausible reaction mechanism based on information available in the literature can be proposed.

Sorum and Onsager(3) studied the hydrogenolysis of MeF on a variety of copper chromites and proposed a reaction mechanism in which the first step involved breakage of the aldehydic hydrogen from the adsorbed MeF (Equation 4). It was believed that MeOH was formed through a hemiacetal intermediate which dissociates to formyl and methoxy species each yielding MeOH by addition of H_2. In contrast, Monti et al.(4) showed that, although the formation of a hemiacetal intermediate was likely in the hydrogenolysis of MeF to MeOH (Equation 6), the MeF adsorbed on the copper chromite surface associatively without releasing the aldehydic hydrogen in the MeF (Equation 3). Trimm(5) proposed an adsorption of MeF via the pi C=O bond as being favorable. The adsorption strength on copper was greatest for MeF followed by CO followed by H_2.

At H_2 pressures greater than 70 atm and in the absence of CO, the rate of MeOH synthesis was found to be independent of H_2 partial pressure and proportional to C_{MeF}(3). Under these conditions, the rate controlling step is either the removal of the aldehydic hydrogen from adsorbed MeF(3) (Equation 4) or bond cleavage of the hemiacetal intermediate(4) (Equation 7).

The presence of CO was, however, found to inhibit both the hydrogenolysis and the equilibration of the H_2 with the surface(4). Thus, in the presence of CO or at low H_2 pressures, it is likely that the slow step in the hydrogenolysis of methyl formate to methanol involves H_2 addition to form the hemiacetal intermediate(4) (Equation 6). The rate of MeF hydrogenolysis is then a function of the H_2 surface coverage as ascertained by Liu et al.(2) and Monti et al.(4)

In the concurrent synthesis, Onsager et al.(6) perceived a totally different mechanism. They proposed that the formation of MeOH does not proceed though MeF as an intermediate, but is formed by the direct hydrogenation of CO on the copper chromite surface. The methoxide anion from the carbonylation catalyst (CH_3OK) adsorbs on the copper chromite catalyst to form a surface methoxy species which undergoes nucleophilic attack by CO to form a formate species. This reacts with adsorbed hydrogen to form the hemiacetal species which on cleavage yields MeOH and regenerates the adsorbed methoxide species. It was proposed that, in contrast to the hydrogenolysis reaction kinetics studied by Sorum and Onsager(3), in the concurrent synthesis the rate of MeOH formation was independent of the MeF concentration but a linear function of the $KOCH_3$

concentration and the total pressure. Although details are not available, it seems likely that the mechanistic step involving formation of the hemiacetal intermediate was assumed to be the slow step of the reaction.

We believe that the concurrent reaction proceeds predominantly through carbonylation of MeOH to MeF formate followed by the heterogeneous hydrogenolysis of the MeF to two moles of MeOH. The general mechanism is likely to be of the type listed below. In the presence of CO and equilibrium amounts of MeF and at relatively low H_2 partial pressures, formation of the hemiacetal intermediate (Equation 6) may be rate controlling.

Mechanism for the Carbonylation Reaction

$$CH_3O^- + CO \rightleftarrows CH_3OCO^- \qquad (1)$$

$$CH_3OCO^- + CH_3OH \rightleftarrows CH_3OCHO + CH_3O^- \qquad (2)$$

Mechanism for the Hydrogenolysis Reaction(3)

(S=copper chromite surface)

$$HCOOCH_3 + S \rightleftarrows [HCOOCH_3\text{-}S] \qquad (3)$$

$$[HCOOCH_3\text{-}S] + S \rightleftarrows [H\text{-}S] + [CH_3OCO\text{-}S] \qquad (4)$$

$$H_2 + 2S \rightleftarrows 2[H\text{-}S] \qquad (5)$$

$$[CH_3OCO\text{-}S] + 2[H\text{-}S] \rightleftarrows [CH_3OCHOH\text{-}S] + 2S \qquad (6)$$

$$[CH_3OCHOH\text{-}S] \rightleftarrows [HCO\text{-}S] + [CH_3OH] \qquad (7)$$

$$[HCO\text{-}S] + 2[H\text{-}S] \rightleftarrows [CH_3O\text{-}S] + 2S \qquad (8)$$

$$[CH_3O\text{-}S] + [H\text{-}S] \rightleftarrows CH_3OH + 2S \qquad (9)$$

4.2 Kinetic Modeling of the Concurrent Process

The steady state (40 hours) experimental data obtained by varying parameters for the KOMe/copper chromite system were fitted to 16 Langmuir-Hinshelwood kinetic rate expressions for integral data. Included were the models obtained by assuming one of the steps in the above mechanism to be rate controlling. The carbonylation of MeOH was assumed to be in equilibrium, while the hydrogenolysis of MeF was the slow reaction. A personal computer based statistical package NCSS was used to carry out non-linear regression to fit the data to each model. Among the statistically acceptable models, the best fit was found to be,

$$R_{MeOH} = 0.3778\exp(-3922/T)\,\frac{P_{H_2}^{1/2}C_{MeF}C_{cat,2}}{(1 + 1.019C_{MeF} + 0.085P_{CO_2})^2} \qquad (11)$$

This model was obtained by assuming formation of the hemiacetal intermediate to be the rate controlling step in the reaction. This is consistent with studies on the hydrogenolysis reaction at low H_2 partial pressures and in the presence of CO(4).

The rate of MeOH formation is proportional to $C_{H2}^{0.5}$ in Equation 11 implying that H_2 is weakly adsorbed on the copper chromite surface in the presence of equilibrium amounts of MeF and high CO in the system. The low value for the activation energy (7.8 kcal/mole) indicates the possibility of diffusional limitations in the system.

4.3 Internal Pore Diffusion Measurements

The identification of diffusion limitations is important in order to separate intrinsic reaction rates from overall reaction rates. We have previously proposed that pore diffusion limitations are likely because of the small size of the pores in the copper chromite catalyst (average pore size ≈ 40 Å)(7) and the relatively low activation energy in Equation 11. To examine this effect, the Calsicat copper chromite catalyst was sieved to obtain a particle size distribution. Three fractions were obtained, and measurements of reaction rate were made. Preliminary analysis of the data indicates little change in reaction rate with particle size, a result which, if verified, would mean that internal pore diffusion is not a limiting factor. Analysis of data is continuing.

5.0 FUTURE WORK

Studies will be carried out to investigate the activity and nature of the reactions with other catalysts for MeOH synthesis. Different salts will be investigated for their catalytic activity and to test the copper chromite regeneration hypothesis. The effect of addition of small amounts of MeF to the reaction feed will be investigated in the hope of decreasing the initial transient period. Kinetic and process modeling will be continued into the next quarter.

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