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SYNTHESIS OF METHANOL IN A METHANOL-RICH LIQUID PHASE

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ABSTRACT

A novel method for synthesizing methanol from CO and H_2 in a slurry reactor is described and experimental results are presented. At the temperatures and pressures used (100-160°C, 50 atm) the methanol product is liquid and constitutes the bulk of the liquid phase. Small amounts of methyl formate (4 to 5%) and other products (less than 1% total) are formed. A heterogeneous catalyst (copper chromite) and a homogeneous catalyst (an alkali salt) are used in a single reactor. It appears likely that the reaction proceeds in two steps--carbonylation of methanol to methyl formate and then hydrogenation of the formate to two moles of methanol. Experiments were carried out in a 300 ml autoclave with continuous gas feed and intermittent liquid withdrawal. In situ reduction of the copper chromite was found to be as effective as external reduction and was used in all runs. A barium-promoted copper chromite showed substantially less deactivation than a manganese promoted one. Of six homogeneous catalysts tested the most effective was potassium methoxide, although some reaction occurred with all the homogeneous catalysts used. The rate of reaction 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.

INTRODUCTION

Methanol (MeOH) is an important industrial chemical. It is widely used as a solvent; as a precursor for many important two carbon chemicals; as the starting material for Mobil's MTG process for producing high octane fuel; as a raw material for octane enahancers such as methyl tertiary-butyl ether (MTBE)[1]; and as a transportation fuel either alone or mixed with hydrocarbons. The use of MeOH in transportation fuels may increase greatly if alternative oxygenated fuels are required to satisfy environmental concerns. The increased demand would require significant expansion of MeOH production, and there is general interest in new processes for MeOH synthesis. We have developed a novel process for producing MeOH from synthesis gas (a mixture of CO and H_2) in our laboratories, and in this paper, we report some recent findings.

THE DIRECT AND THE TWO-STEP SYNTHESES

The leading industrial process for synthesis of MeOH from CO and H_2 is carried out in the gas phase using a Cu-Zn-Cr catalyst at a temperature of 240-260°C and 50-100 atm[2]. We refer to it in this work as the direct synthesis. The overall reaction is given by

$$CO + 2H_2 = CH_3OH \tag{1}$$

The actual reaction path is more complicated and is the subject of continuing research. At reaction conditions, the equilibrium conversion is about 50%, but per-pass conversions are much lower--typically 5-15%--primarily to limit heat generation and possible catalyst damage if temperatures are allowed to rise. The unreacted synthesis gas must be separated from the product and recycled through the reactor.

An alternate route for producing MeOH from synthesis gas was proposed by Christiansen[3] in 1919 and consists of two reactions in series. We refer to this as the two-step synthesis. In the first step, a molecule of MeOH is carbonylated to produce methyl formate (MeF).

$$CH_3OH + CO = CH_3OOCH \tag{2}$$

This reaction is used industrially to manufacture MeF. Typical reaction conditions are 60-90°C and 30-50 atm. The reaction takes place in a liquid solution of MeOH and MeF in which an alkali metal alkoxide catalyst is dissolved.

In the second reaction, MeF is hydrogenated to two molecules of MeOH, one of which replaces the MeOH consumed in the carbonylation reaction.

$$CH_3OOCH + 2H_2 = 2CH_3OH \tag{3}$$

A heterogeneous catalyst such as copper chromite is used, and the reaction can be carried out in the vapor phase or liquid phase. For liquid phase hydrogenolysis, temperatures of 140-180°C and pressures of 40-60 atm are used. We have studied each reaction in our laboratory[4]. These papers also contain brief summaries of other relevant work published on the two reactions.

THE CONCURRENT SYNTHESIS

There are obvious disadvantages to the two-step synthesis as outlined above in that two reactors and two separation systems would be required. Carrying them out concurrently in one reactor would clearly be superior provided that the reactions proceed at an adequate rate and that interference between the reactions does not occur. We define using a single reactor for both reactions as the concurrent synthesis and it is the subject of this paper. It should be noted that it is not at all obvious that the reactions can be carried out concurrently in a single reactor. The temperatures normally used for each reaction differ by almost 100°C; undesired side reactions might occur; H_2O and CO_2 deactivate the carbonylation catalyst by forming insoluble alkali metal formates or carbonates; and CO_2 and CO deactivate the hydrogenolysis catalyst. Tolerance to CO_2 and H_2O is important since it is expensive to remove CO_2 to very low levels in synthesis gas generation, and the presence of CO_2 and H_2 will produce H_2O via the water gas shift reaction.

We have studied the concurrent reaction using a 300 ml batch autoclave. A schematic diagram of the experimental apparatus is shown in Figure 1. In a typical run, MeOH and the two catalysts are charged to the reactor and the copper chromite is reduced in situ for 15 hours at 170°C using H_2. The H_2/CO feed mixture is then introduced into the reactor at a preset rate. Unreacted gases are removed through a back pressure regulator which acts to maintain the desired reactor pressure. More complete descriptions of the apparatus and experimental procedures have been published[5].

We have found that, in spite of the potential difficulties outlined above,

- the concurrent reaction proceeds at a good rate at 160°C and 50 atm in the presence of CO.
- the catalysts remain active for more than 200 hours.
- small amounts of CO_2 and H_2O are tolerated.
- selectivity to MeOH is high--greater than 95%.
- the principal by-product is 4-6% MeF--the equilibrium amount at the reaction conditions.
- small amounts of dimethyl ether (less than 0.4%) are produced.
- only trace amounts of other products are found.

The reactions take place in the liquid phase, and the methanol product remains in the liquid. The reactants (H_2 and CO) must dissolve in the liquid and be transported to the reaction sites. We use high stirring rates and have determined that mass transfer does not limit the reaction rate. The methanol product remains in the liquid phase at the conditions used for the reaction. This can be seen from examination of Figure 2 which is a plot of temperature versus pressure for the formation of MeOH from a H_2/CO mixture in which the reactant ratio is 2.0. The equilibrium line in the diagram is the locus of conditions for which the vapor pressure of methanol is equal to the equilibrium methanol partial pressure for the reaction. At temperatures and pressures to the left and above this line the vapor pressure of MeOH is less than the equilibrium value for the reaction, so any product MeOH will remain in the liquid phase. To the right and below the equilibrium line, MeOH product will vaporize and the liquid phase will disappear. A necessary condition for the concurrent reaction is that the pressure and temperature lie in the cross-hatched region.

The fact that MeOH product is obtained as a liquid is an important feature of the concurrent reaction. Since liquid can be removed from the reactor as it is formed, little or no gas need be removed. In principle, then, recycle of synthesis gas can be eliminated. The liquid product, moreover, is about 95% MeOH and 5% MeF and can be readily separated if necessary.

The results of typical runs are shown in Figure 3 where the rate of MeOH synthesis is plotted versus time of reaction. The heterogeneous catalysts are copper chromites, one promoted with manganese (United Catalyst, G-89) and the other with barium

(Calsicat, 81C-83B). The homogeneous catalyst is potassium methoxide (KOMe). The rate is low initially because there is no MeF present. As MeF is formed, the rate increases and reaches a maximum value at about 40 hours, after which the MeF concentration remains constant at approximately the equilibrium value.

CATALYST REDUCTION

The copper chromite catalyst should be reduced to obtain the active form. The method of reduction can be important. For example, Monti et al.[6] studied the hydrogenolysis of MeF after reducing the catalyst in the gas phase, while Sorum and Onsager[7] studied the same reaction using the same catalyst but with liquid phase reduction. Lower reaction rates were found by Monti et al. and were attributed to the method of catalyst reduction. We used external gas phase reduction for hydrogenolysis studies and for the initial studies of the concurrent reaction by contacting the catalyst with H_2 at 170°C for 12 hours and then adding the reduced catalyst to the reactor. Careful experimental technique was necessary to prevent contact with oxygen. A simpler procedure in which the catalyst is reduced in situ was also examined. The MeOH, copper chromite, and homogeneous catalyst were added to the reactor and heated to 170°C. Then H_2 was bubbled through the reactor for 15 hours. The reactor was then cooled to the desired temperature, and CO was added to the feed.

Results are shown in Table 1 for four runs using different methods of catalyst reduction--one with external gas phase reduction, one with in situ liquid phase reduction as described above, one with in situ liquid phase reduction in which the homogeneous catalyst was added after the reduction period, and one with no reduction period. In each case the homogeneous catalyst was KOMe.

Table 1
Effect of Method of Reduction on
Reaction Rate at 40 Hours

Reduction Method	Rate mmol/min-g
Gas Phase Reduction	0.085
In Situ With KOMe	0.107
No Reduction Period	0.100
In Situ Without KOMe	0.127

The rate for gas phase reduction is somewhat lower than for the other methods. There is little difference between the reaction rates for the the second and third cases. This is not surprising since the only difference between the two is the time of CO addition. During the first 40 hours after CO addition when MeF is being formed, the CO would not be expected to interfere with the catalyst reduction since CO is also a reducing gas. A higher reaction rate was found for the last case--addition of KOMe after reduction of the copper chromite. The difference is not great, and because of inconvenience in accurately adding the homogeneous catalyst to the hot reactor, all subsequent runs were made using in situ reduction with homogeneous catalyst in the reactor.

ALTERNATE CATALYSTS

The initial catalysts used in our work were a copper chromite

(United Catalyst, G-90) with managanese promotion and KOMe. They were selected based on the results of our carbonylation and hydrogenolysis studies. We are currently investigating other catalysts. Figure 3 shows the result of replacing manganese with barium in the copper chromite catalyst. The manganese promoted catalyst activity reduces to about half its maximum value in 180 hours. One cause for this could be the presence of CO, which is known to deactivate the hydrogenolysis reaction. Since barium is less susceptible than manganese to CO pickup, a barium promoted copper chromite provided by Calsicat Division of Mallinckrodt (81C-83B) was tested and as can be seen in Figure 3, maintained high activity much longer.

Alternate homogeneous catalysts can also be used. Reaction rates for six different salts are shown in Table 2.

Table 2
Relative Reaction Rates for Alternate Homogeneous Catalysts

Homogeneous Catalyst	Relative Reaction Rate at 40 Hours
Potassium Methoxide	100
Sodium Methoxide	68
Sodium Acetate	57
Potassium Acetate	56
Potassium Carbonate	50
Potassium Chloride	24
None	22

The best of these is KOMe, and this is expected from the results of carbonylation studies. Sodium methoxide is almost as good and is often used commercially because it is cheaper. A possible explanation for the substantial rate obtained using no homogeneous catalyst is that small amounts of an alkali salt are present on the copper chromite or in the reactor.

CATALYST LOADING AND FLOW RATE

A series of experiments were carried out in which the catalyst loading was varied and the feed flow rate was varied. The results for different catalyst loadings at constant feed rate are shown in Figure 4. It is evident that the MeOH synthesis rate is not linear in catalyst loading--a surprising result since the controlling reaction should be the hydrogenolysis reaction and the rate should be directly proportional to the amount of catalyst at low loadings. This might be explained by mass transfer limitations in the liquid, but other experiments verified that at the high rate of stirring we were using mass transfer was not limiting.

A similar result was obtained when the gas feed rate was varied at constant catalyst loading. This is even more surprising since it is difficult to construct a mechanism in which the gas feed rate would affect the reaction rate. The two phenomena are related, however, in that the flow rate of gas leaving the reactor decreases when the catalyst loading is increased (more reaction) or the feed rate is decreased. The rate of reaction can vary with exit flow rate if a small amount of a deactivating agent is being produced in the reactor since it can build up to high concentrations when exit flow rates are low. As noted above, the reactor can, in principle, be operated with zero exit flow rate, and there would then be no way to remove such a deactivating agent. With high exit flow rates it would be rapidly removed from the reactor. These observations form the basis for the following equations.

Assuming that the rate of MeOH formation, R_1, is proportional to the amount of catalyst, C, and that a deactivating agent is present at concentration y, then

$$R_1 = K_1(1 - \alpha y)C \tag{4}$$

where C = Concentration of heterogeneous catalyst.

K_1 = Rate constant for MeOH formation.

R_1 = Rate of formation of MeOH.

y = Concentration of deactivating agent.

α = Deactivation constant.

and that the rate of formation of the deactivating agent is given by

$$R_2 = K_2C \tag{5}$$

where R_2 = Rate of formation of deactivating agent.

K_2 = Rate constant for deactivating agent.

It can be shown that at constant feed rate, R_1 decreases with increased catalyst loading and that at constant catalyst loading, it decreases with decreased feed rate. These conclusions are consistent with the experimental data, and work is underway to determine if this explanation is valid.

CONCLUSIONS

The concurrent synthesis is a promising alternative method for producing MeOH. There is little need for recycle of synthesis gas and the product is a liquid mixture of MeOH (95%) and MeF (5%). Work is continuing to determine optimal operating conditions and catalyst combinations.

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