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SYNTHESIS OF METHANOL BY A NOVEL METHOD

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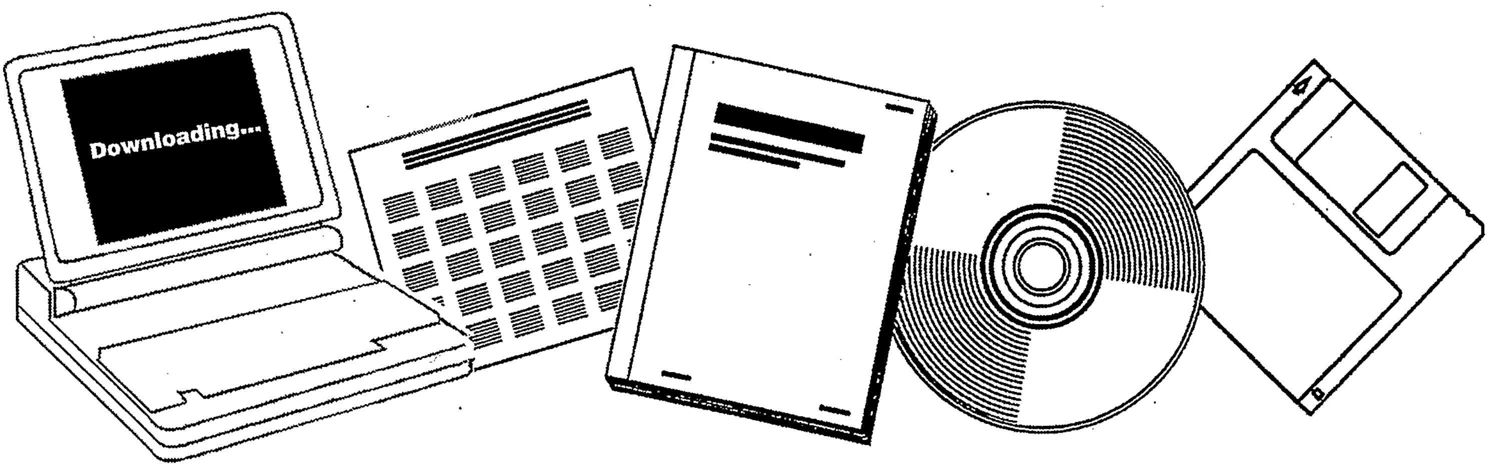

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THE SYNTHESIS OF METHANOL BY A NOVEL METHOD

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ABSTRACT

A new method for synthesizing methanol from CO and H_2 in a slurry reactor is described and some recent experimental results are presented. At the temperatures and pressures used (100-160°C, 50 atm) the methanol product remains in the liquid phase and constitutes the bulk of the liquid phase. Small amounts of other products (less than 6% total) are also present. Methanol is both a reactant and a product. The reaction is believed to proceed in two steps. In the first, methanol is carbonylated to methyl formate, and then the methyl formate is hydrogenated to methanol. A homogeneous catalyst such as potassium methoxide is used for the carbonylation reaction and a heterogeneous catalyst such as copper chromite is used for the hydrogenation reaction. Rates for the concurrent reaction (both reactions taking place in the same reactor) are greater than predicted from studies of the individual reactions. The improved performance can be explained by an interaction between the two catalysts in the surface layer adjacent to the heterogeneous catalyst.

INTRODUCTION

Methanol (MeOH) 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 gasoline, 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. Significant expansion of MeOH production might be required if oxygenated transportation fuels are needed to satisfy environmental concerns.

MeOH is made commercially from a mixture of CO and H_2 (synthesis gas) which is obtained by partial oxidation of methane, coal, petroleum, or other carbonaceous material. The overall reaction from synthesis gas is

$$CO + 2H_2 = CH_3OH \qquad (1)$$

The reaction is usually carried out in the gas phase using a Cu-Zn catalyst[2] at a temperature of 240-260°C and 50-100 atm. Some CO_2 (typically 5-10%) is present and is beneficial for the reaction. The chief disadvantages of the gas phase reaction are the low conversion per pass (5-15%) and the need for good temperature control of the reaction mixture because of the high exothermic heat of reaction with possible damage to the catalyst if hot spots develop. Higher per pass conversion with better heat transfer can be obtained by slurrying the catalyst with a heavy oil and carrying out the reaction in the liquid phase[3].

We have developed a new synthesis for MeOH--one which gives per pass conversions of over 90% at a reaction temperature of 100-160°C and a pressure of 40-60 atm. The high conversion is possible because, under these conditions, the methanol product remains in the liquid and can be continuously removed from the reactor. Little or no gas need be removed if the feed gas contains the stoichiometric H_2/CO ratio of 2.0. The reactor product contains about 95% MeOH and 5% methyl formate (MeF) plus small amounts of dimethyl ether and other products (less than 1%). In this paper, we will first describe the synthesis, then present some typical data, and finally propose an explanation for an unexpected interaction found in the reaction.

THE CONCURRENT SYNTHESIS

An indirect route for producing MeOH from synthesis gas was proposed by Christiansen[4] in 1919. It consisted of two reactions in series, and we refer to it as the two-step synthesis. In the first step, a molecule of MeOH is carbonylated to produce methyl formate.

$$CH_3OH + CO = CH_3OOCH \qquad (2)$$

This reaction is used industrially today 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. The active catalyst for the carbonylation reaction is reported by Tonner et al.[5] to be the methoxide ion MeO^-. It reacts with CO to give a formate ion which then reacts with methanol to give MeF and regenerate the methoxide ion. They found increased catalytic activity of the alkali alkoxides with decreased ionization potential of the alkali cation, the lowervalues presumably producing more MeO^- ions. The molecules CO, H_2O, and CO_2 have been found to inhibit the reaction by removing catalyst as insoluble formates and carbonates.[6,7]

In the second step, the MeF produced in the first reaction is hydrogenated to two molecules of MeOH.

$$CH_3OOCH + 2H_2 = 2CH_3OH \qquad (3)$$

One molecule replaces the MeOH consumed in the carbonylation reaction, and the other is product. The reaction can be carried out in the vapor or liquid phase using a heterogeneous catalyst such as copper chromite. For liquid phase hydrogenolysis, temperatures of 140-180°C and pressures of 40-60 atm are used. CO is known to deactivate the catalyst[6].

Rate equations for reactions 2 and 3 have been determined in our laboratory[6] and by other investigators[5,7,8]. 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 the reactions do not interfere with one another. 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. In fact, there are several reasons why the concurrent reaction should fail.

1. The temperatures normally used for each reaction differ by almost 100°C. A compromise temperature must be used--one which might well be unsatisfactory for both reactions.

2. Water and CO_2 are known to deactivate the carbonylation catalyst by forming insoluble alkali metal formates or carbonates. We found it necessary, for example, to carefully dry the methanol before carrying out the carbonylation reaction[6].

3. Carbon dioxide and CO deactivate the hydrogenolysis catalyst, and CO must be present in large amounts if the reactions are carried out concurrently because CO is one of the reactants.

4. Since both CO and H_2 are present, the presence of any H_2O or CO_2 will guarantee the presence of the other through the water gas shift reaction. 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.

5. Undesired side reactions might occur as the result of combining the reactions.

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, that the catalysts remain active for more than 200 hours, and that small amounts of CO_2 and H_2O are tolerated[9]. The selectivity to MeOH is high--greater than 95% with the principal by-product being MeF--the equilibrium amount at the reaction conditions. In addition small amounts of dimethyl ether (less than 0.4%) are produced. No higher alcohols are found and only trace amounts of other products have been detected.

In the next section some typical experimental results are presented and then a mathematical model for the reaction is proposed.

EXPERIMENTAL

Reactions are carried out in a 300 or 1000 ml autoclave. A diagram of the experimental apparatus is shown in Figure 1. In a typical run, MeOH and the two catalysts are charged to the reactor. The reactor is heated to 170°C and H_2 is passed through the reactor for 16 hours to reduce the hydrogenolysis catalyst in situ. Then a H_2/CO feed mixture is 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[9].

The results of a typical run are shown in Figure 2 where the rate of MeOH synthesis is plotted versus time of reaction. The heterogeneous catalyst is copper chromite (Calsicat, 81C-83B). The soluble catalyst is potassium methoxide (KOMe). The rate of formation of MeOH is based on hydrogen consumption. The rate is low initially and rises to a maximum at about 40 hours. It should be noted that the concentration of MeF in the liquid starts at zero and rises to a steady state value at about 40 hours. The composition of MeF in the reactor then remains constant at approximately the equilibrium value.

Figure 3 shows the rate at which CO and H_2 are converted in a typical run. After about 40 hours, the rate of conversion of each is essentially constant and equal as is expected since the feed ratio is stoichiometric ($H_2/CO=2$). The level of conversion depends on the rate at which gas is removed from the reactor with lower rates giving higher conversions. An important difference in the conversion rates occurs during the first 40 hours. Hydrogen conversion starts at zero and steadily increases to the steady state value, while CO conversion starts high and decreases to the steady state value.

We have tested other soluble and heterogeneous catalysts. Relative reaction rates obtained using a copper chromite heterogeneous catalyst and two different soluble catalysts at the same reaction conditions are shown in Table 1.

Table 1
Effect of Soluble Catalyst
on Rate of Formation of Methanol
(Cu-Cr Heterogeneous Catalyst)

Soluble Catalyst	Relative Reaction Rate at 40 Hours
Potassium Methoxide	100
Sodium Methoxide	68

The copper chromite-KOMe combination shows a significantly higher reaction rate than the copper chromite-NaOMe combination. This result is puzzling because the mole fraction of MeF in the liquid is the same in each case and essentially equal to the equilibrium composition for the experimental conditions. Since the MeF-MeOH reaction is close to equilibrium, the soluble catalyst should have little effect unless it is somehow participating in the heterogeneous reaction. The same phenomenon is shown in a different way in Figure 4 where the rate of formation of MeOH is plotted versus ratio of soluble to heterogeneous catalyst. In each case, the MeF composition is the same and essentially at equilibrium, yet the rate varies with the amount of soluble catalyst.

ANALYSIS OF CONCURRENT SYNTHESIS

Our studies of the concurrent MeOH synthesis described above show that there are significant differences between the actual performance and that predicted assuming that the reaction proceeds through the carbonylation and hydrogenolysis reactions given by equations 2 and 3. These can be summarized as:

1. The reaction rate for the concurrent production of MeOH is significantly higher that that calculated from kinetic data obtained from the individual reactions.

2. CO deactivation of the hydrogenolysis reaction is reduced.

3. The amount and type of soluble catalyst affects the rate of MeOH formation but not the mole fraction of MeF in the reactor liquid.

4. The soluble catalyst is not removed by formation of formates, carbonates or other insoluble salts. In fact, the reaction proceeds using potassium formate and carbonate as the soluble catalyst--although at a reduced rate.

At least two explanations for these discrepancies are possible. One is that the reaction is essentially the two step mechanism outlined above--carbonylation to MeF in the liquid followed by hydrogenolysis of MeF on the hetereogeneous catalyst--and that the differences noted above are due to the changed environment in which the reactions take place.

A second explanation is that MeOH formation takes place through a different pathway--one which does not require that MeF be formed homogeneously in the liquid phase. This latter pathway would probably involve adsorption of the soluble catalyst as well as CO and H_2 on the heterogeneous catalyst with subsequent reaction at or near the surface. The MeF appearing in the liquid could be formed by a homogeneous side reaction and would be at the equilibrium composition.

The essential difference in these two paths is that in the first the carbonylation reaction takes place homogeneously and is an essential step in the reaction sequence. In the second, any homogeneous carbonylation is a side reaction and not essential to the formation of MeOH. We believe that the experimental evidence points to the former. Referring to Figure 3, it can be seen that on introducing CO into the reactor it begins to react rapidly while H_2 does not. At the beginning only MeF is being formed. As the MeF mole fraction increases in the liquid, H_2 consumption and thus MeOH formation increases. These data strongly suggest that the MeOH formation follows the MeF composition and that MeF is an essential step in the reaction pathway.

Based on this observation, we have developed a mathematical model which we believe explains why the concurrent synthesis does not appear to be a simple combination of the carbonylation and hydrogenolysis steps considered separately.

MODEL FOR CONCURRENT SYNTHESIS

A overall description of the proposed model is given here. A more complete development including equations has been made and will be reported in a subsequent publication. The basic assumptions for the model follow:

1. The reaction proceeds in two steps--the first being carbonylation and the second hydrogenation.

2. The carbonylation reaction takes place homogeneously in the liquid and the hydrogenation occurs on the surface of the heterogeneous catalyst.

3. The carbonylation reaction is rapid compared to the hydrogenation reaction.

4. Mass transfer from gas to liquid is rapid compared to reaction rates, and the liquid phase is well mixed and of uniform composition.

5. MeF mole fraction in the bulk liquid is the equilibrium composition for the reaction conditions. This is a consequence of assumptions 3 and 4 and the fact that catalyst loading is low. It has been verified experimentally.

6. The hydrogenation reaction takes place on the surface of the heterogeneous catalyst.

In order to reach the surface MeF must diffuse to the surface of the catalyst. It is this region adjacent to the catalyst surface that is of prime interest. MeF is disappearing at the surface, and there must be a concentration gradient from the bulk liquid composition to the surface concentration. Since the MeF concentration decreases in the surface layer, it will be below the equilibrium value for the homogeneous reaction, and reaction with CO will occur. It seems quite possible that all or most of the homogeneous reaction is taking place in this layer. When reaction occurs, CO is depleted, and there must be diffusion from the bulk liquid into the surface layer. The net effect is that the concentration of CO near the surface layer is less than the equilibrium values in the bulk liquid.

A qualitative explanation for the effects noted in the previous section is given below. In each case a comparison is made between the situation observed with the individual reactions and that with the concurrent reaction with the object of explaining the difference.

1. Higher rate of reaction for concurrent reaction than for individual reactions. The rate limiting step for MeOH production is the hydrogenolysis reaction, and the rate of reaction will be higher when the surface concentration of MeF is higher. If the carbonylation reaction is not taking place in the surface layer (the case when only the hydrogenolysis reaction occurs), the MeF concentration will drop (probably linearly) from the bulk concentration to the surface concentration. If the carbonylation reaction is taking place (the concurrent reaction), there will be additional reaction in the surface layer which will yield a higher value of the surface concentration for MeF. The higher surface concentration would be expected to produce a higher reaction rate. The interactive effect of the two reactions results in more of the MeF reaching the surface with resultant higher reaction rate.

2. Decrease in CO deactivation. If no homogeneous catalyst is present, the CO near the heterogeneous hydrogenolysis surface will be essentially that in the bulk liquid. However, if homogeneous catalyst is present, reaction will take place in the surface layer, and the CO concentration will be less than that in the bulk liquid. The net effect is to reduce the CO concentration at the surface and thus to reduce its deactivating effect.

3. Amount and type of homogeneous catalyst affect rate of MeOH formation. As noted above, the amount and type of homogeneous

catalyst should not affect the rate of MeOH formation since MeF is in equilibrium in the bulk liquid. However, it is not in equilibrium in the surface layer, and therefore the homogeneous catalyst can affect the rate of MeF formation and thus the rate of MeOH production.

4. Decreased sensitivity to CO_2 and H_2O deactivation of homogeneous catalyst. Removal of homogeneous catalyst by formation of formates and/or carbonates has been reported for the carbonylation reaction. This does not occur or at least is greatly reduced for the concurrent reaction. The presence of hydrogen in the surface layer and the presence of a hydrogenolysis catalyst may serve to convert formates or carbonates to methoxides.

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%). The reaction seems to proceed in two steps—the first is the carbonylation of MeOH to MeF and the second is the hydrogenolysis of MeF to MeOH. The concurrent rate of reaction is higher than that predicted from the individual reactions and the increased rate can be explained by interactions which occur on or near the surface layer adjoining the heterogeneous catalyst. Work is ongoing to determine optimal operating conditions, evaluate better catalyst combinations, and develop mathematical models.

ACKNOWLEDGMENT

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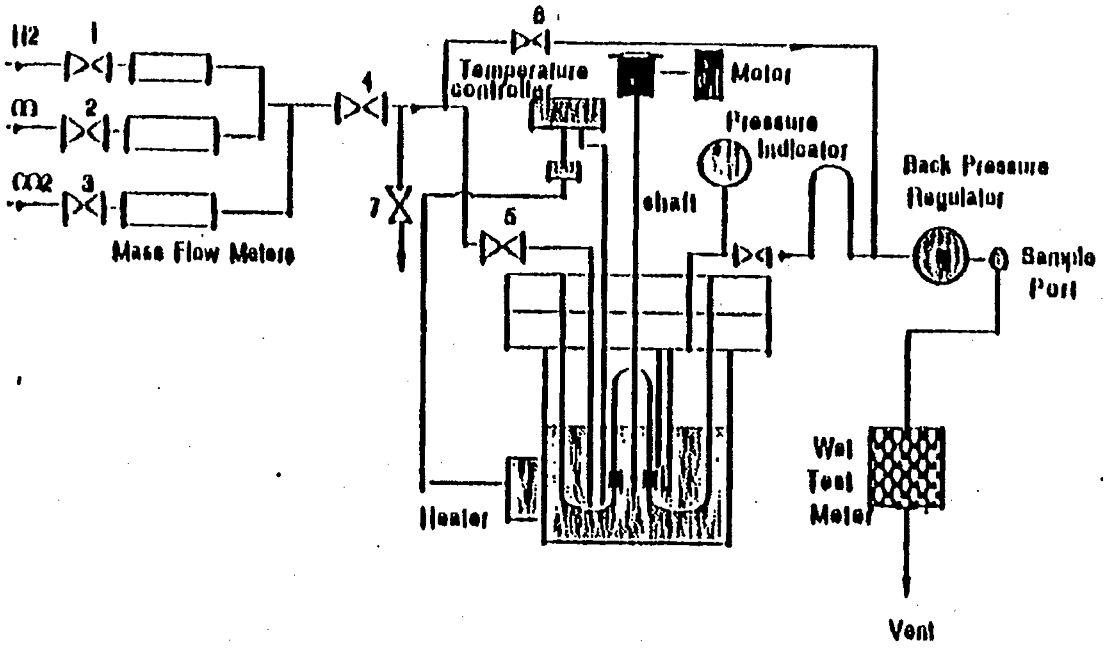

Figure 1. Schematic diagram of experimental apparatus.

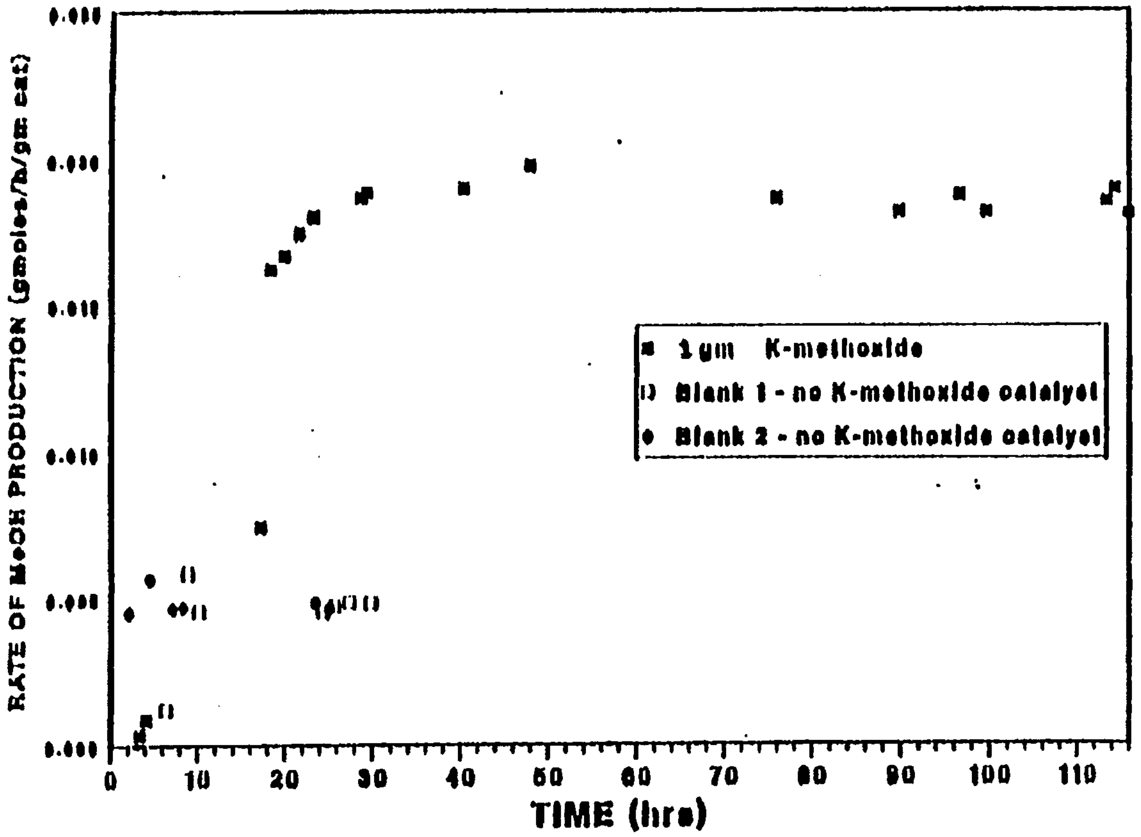

Figure 2. Variation of methanol production rate with time in a typical experiment. The heterogeneous catalyst is copper chromite, and the homogeneous catalyst is potassium methoxide. Reaction conditions: 150°C, 63.5 atm, H_2/CO ratio 2.0, 3 g copper chromite, 1 g KOMe, feed rate 105 cc/min.

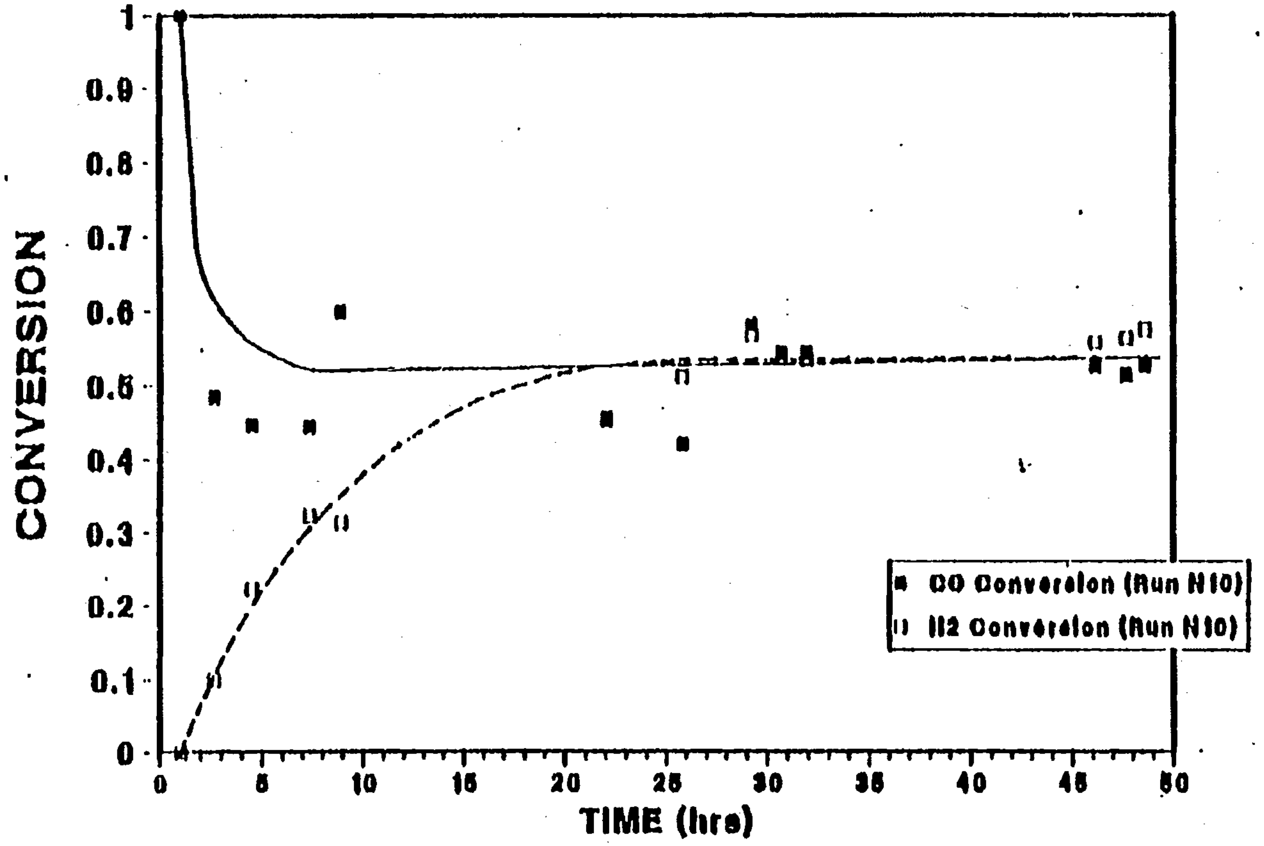

Figure 3. Change in conversion of CO and H_2 during a typical experiment. The heterogeneous catalyst is copper chromite and the homogeneous catalyst is potassium methoxide. Reaction conditions: 150°C, 63.5 atm, H_2/CO ratio 2.0, 3 g copper chromite, 1 g KOMe, feed rate 105 cc/min.

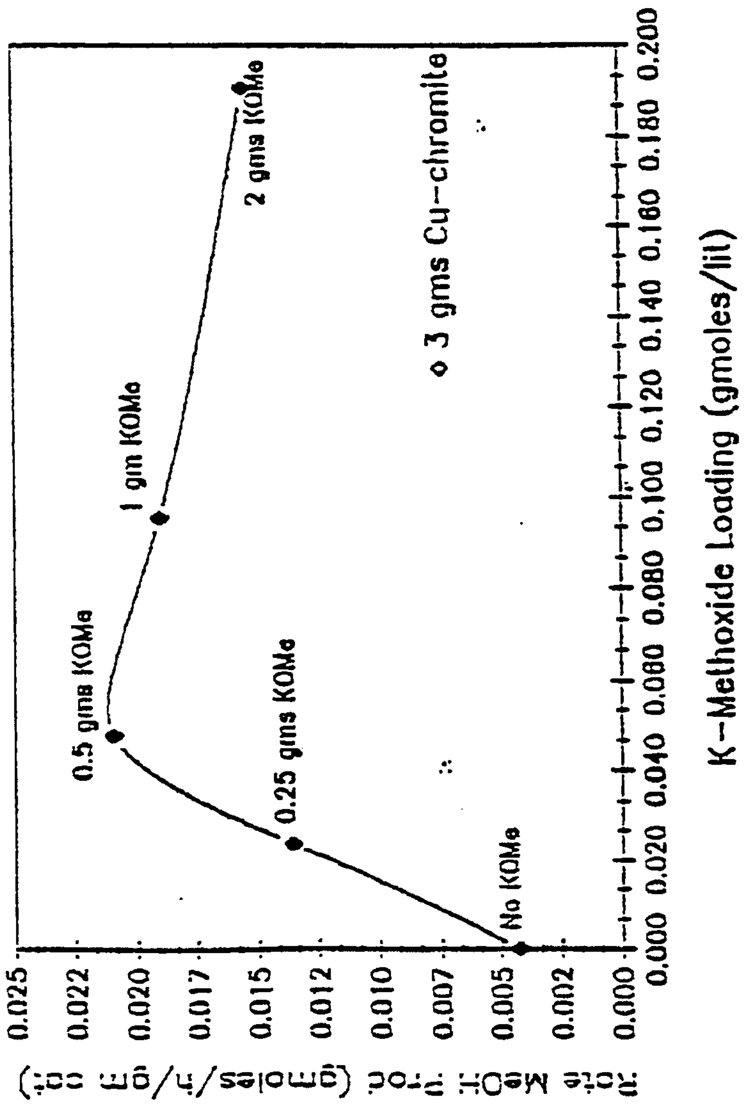

Figure 4. Variation of methanol production rate at 40 hours with ratio of homogeneous to heterogeneous catalyst. Reaction conditions: 150°C, 63.5 atm, H_2/CO ratio 2.0, 3 g copper chromite, feed rate 105 cc/min.

A NOVEL SYNTHESIS OF METHANOL

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ABSTRACT

Commercial methanol synthesis processes are characterized by high pressures and temperatures with low per pass conversion. A novel liquid phase synthesis of methanol from CO and H_2 at about 100°C lower than present commercial processes, with little or no recycle, is reported. The reaction may proceed in two steps--the carbonylation of methanol to methyl formate and the hydrogenolysis of methyl formate to two moles of methanol. High methanol synthesis rates are obtained. The process is tolerant to CO_2 and H_2O with about 94% selectivity to methanol.

Reaction studies with different catalyst systems are reported. High MeOH formation rates are obtained with a mixed catalyst comprised of sodium and potassium methoxide and copper chromite. An interaction may exist with the two catalysts; potassium seems to promote the activity of Cu-chromite. Studies on these various catalysts are being carried out to elucidate the nature of the reactions involved in the MeOH synthesis. The effect of variation in process parameters such as temperature, pressure, feed H_2/CO ratio and catalyst loading are also investigated. The process is tolerant to fluctuations in the feed H_2/CO ratio.

INTRODUCTION

Social and environmental concerns arising out of CO and hydrocarbon emissions due to use of gasoline as a transportation fuel have led to a growing demand for alternate cleaner burning fuels such as methanol.[1] One route for the synthesis of methanol from synthesis gas involves the carbonylation of methanol to form methyl formate (MeF) and the successive hydrogenolysis of methyl formate to give two moles of methanol (MeOH) as shown in reactions 1 and 2.[2]

$$CH_3OH + CO \rightleftharpoons HCOOCH_3 \qquad (1)$$

$$HCOOCH_3 + 2H_2 \longrightarrow 2CH_3OH \qquad (2)$$

Essentially all MeOH produced today is made by the <u>direct</u> gas phase CO hydrogenation process at temperatures of 200-300°C and pressures of 50-110 atm using Cu/ZnO based catalysts[3]. Methane is the main source of syngas though coal gasification is also used to some extent[2]. The outlet MeOH concentration is restricted to 5-6 mole% due to heat transfer limitations (ΔH_{298}=91 kJ/mol), leading to a high recycle ratio.

In comparison, this novel synthesis is carried out at milder conditions of 100-150°C and pressures of 40-65 atm. The two steps were first proposed by Christiansen[4] in 1919. Aker Engineering reported a two component liquid phase catalytic system to convert synthesis gas to a mixture of methanol and methyl formate in a single step at 383°K and 0.5 MPa pressure in the absence of CO_2,

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H_2O and sulfur compounds[5]. The only experimental evidence is provided by Inyanitov et al.[6] who showed that reactions can occur in a single reactor, using NaOMe and Cu-chromite as catalysts.

We have succeeded in carrying out the two reactions described above in a single slurry reactor, operated in a semi-continuous manner. Preliminary results on reaction studies were reported by Liu et al.[7]. In spite of potential deactivating species like CO_2 and H_2O, the <u>concurrent</u> (concurrent = both reactions carried out in the same reactor) reaction using a mixed catalyst comprised of KOMe and Cu-chromite gives high MeOH production rates with low rates of deactivation. In this paper, we report experimental findings for this new synthesis of MeOH.

BACKGROUND

The homogenous carbonylation of MeOH using NaOMe or KOMe as catalyst and liquid phase hydrogenolysis of MeF using Cu-chromite as catalyst have been studied individually. Liu et al.[8] found that CO_2 and H_2O inhibit the carbonylation reaction due to the formation of insoluble K salts, while CO and H_2O deactivate the copper chromite. They also presented kinetic expressions for each reaction.

Due to the favorable thermodynamics of the two individual processes, up to 95% conversion can be obtained with about 94% selectivity to MeOH. One of the salient features of this concurrent process is that no higher alcohols are produced. Vedage et al.[9] found that the presence of alkali on copper in Cu-ZnO catalysts enhances MeOH formation rate but higher alcohols have invariably been formed, decreasing selectivity towards methanol. Klier et al.[10] reported alkali promotion of the water gas shift reaction on a Cu-Zn surface. A bifunctional base - hydrogenation catalyst has been reported by Union Carbide[11]. It consists of a Cu^+ and an alkali methoxide; the hydrogenation component is believed to be copper hydride (CuH).

Liu et al.[7] found that the MeOH formation rate using a mixed catalyst comprised of KOMe and Cu-chromite was higher than that calculated using a kinetic rate expression obtained by combining the two individual rate equations. This suggests that the effect may not be a simple summation of the two individual steps.

<u>EXPERIMENTAL</u>

A 300 cc. stainless steel autoclave was cleaned and charged with 150 cc. of MeOH and the catalyst. The catalyst was reduced in situ in the liquid phase using pure H_2 flowing at 25 cc/min at 170°C and a pressure of 63 atm., for 16 hours. Liu[12] found that there were no mass transfer limitations in this reactor system. This has the advantage of eliminating an external reduction step. A schematic of the experimental setup is shown in Figure 1.

The temperature was adjusted to 150°C and controlled to within ±1°C (by a temperature controller). CO and H_2 at a H_2/CO feed ratio of 2 were metered by two on-line mass flow controllers. The reactor contents were thoroughly stirred. Gases were withdrawn from the top of the reactor through a back pressure regulator. Regular analysis of gas and liquid samples was done using an HP gas chromatograph equipped with Porapak Q and Carbosieve S columns and a thermal conductivity detector. The gas effluent was measured by a calibrated wet test flow meter. The MeOH formation rate was computed based on the gas phase H_2 consumption.

The operating conditions have to be in the cross-hatched area in Figure 2[7]. The boundary is determined by the temperature at which the vapor pressure of MeOH is equal to its equilibrium partial pressure. The conditions ensure that MeOH is produced in the liquid phase in contrast to the gas phase operating point which is used industrially. The properties of the catalysts and the operating conditions used are listed in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

(i) General Results

A number of reactions probably proceed simultaneously in the reactor including the carbonylation of MeOH to MeF, the hydrogenolysis of MeF, the water gas shift reaction (wgs) and the condensation of MeOH to give dimethyl ether (DME). Presumably, the carbonylation and the hydrogenolysis reactions proceed in series. At steady state, a constant equilibrium MeF concentration of 4% was obtained in the liquid phase. The carbonylation reaction is thus at equilibrium, and the hydrogenolysis of MeF is evidently the rate determining step. As shown in Figure 3, an average of about 35 hrs. was required for the system to attain steady state, although the wgs and the formation of dimethyl ether proceed rapidly to equilibrium. The wgs reaction dynamics results in an adjustment of the CO_2 and H_2O content in the reactor. It seems unlikely that CO_2 is a reactant because of its deactivating effect on the carbonylation catalyst.

The main byproducts formed in the reaction are H_2O, DME and equilibrium amounts of MeF. Traces of formaldehyde were found by gas analysis. At a temperature of 170°C (reduction temperature),

Table 1: Properties of Catalysts

Carbonylation Catalyst: KOMe

Type: white powder, 99% pure

Hydrogenolysis Catalyst: Cu-chromite

Type: Black powder

Surface Area, m^2/g = 103; Bulk density, g/cc = 0.64

Cu, wt% = 32.1; Cr, wt% = 29.0

Table 2: Operating Conditions for the Concurrent Synthesis

Temperature (°C)	100-150
Total Pressure (atm)	63.5
Initial Catalyst Loading	
KOMe (gmoles/lit)	0.007-0.028
Cu-chromite (gm lit)	20-40
Initial MeOH Loading (ml)	150
Feed Rate (1atm, 25°C) (cc/min)	
Stirrer Speed (rpm)	1150-1500
Feed Rate (H_2/CO)	1.0-2.0

a small amount of CH_4 are formed; it disappears as the temperature is lowered. No higher alcohols were detected for any of the runs. At 150°C the MeF equilibrium concentration is about 4%, resulting in high selectivity to MeOH. The blank run in Figure 3, suggests that Cu-chromite displays some carbonylation activity. The maximum rate obtained was almost 16% of the rate of MeOH synthesis using KOMe as the catalyst.

(ii) Effect of KOMe Loading

Different amounts of KOMe at constant Cu-chromite (3 gms) loading were used to identify any interaction between the two catalysts. The rate of MeOH formation as a function of KOMe loading is shown in Figure 4. The amount of KOMe added influences the MeOH formation rate. The nature of this plot indicates that there exists an optimum concentration of KOMe (1:6 wt. ratio of KOMe to Cu-chromite in our case). Since hydrogenolysis is the rate determining step, it seems likely that the nature of the active site is the result of an 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. Bybell et al.[13] found a similar effect and observed a sharp maximum in their study of Cs loading for enhancement of MeOH productivity on Cu/ZnO catalysts in the direct synthesis. The methoxide ion would presumably act as a counter ion to stabilize the K^+ on the Cu-chromite surface. The overall reaction is evidently not just a simple summation of the two individual reactions.

(iii) KOMe in Comparison to NaOMe

KOMe/Cu-chromite was found to be more active than NaOMe/Cu-chromite. Having a lower ionization potential, potassium (4.32 V) has the ability to generate more anions than sodium (5.12 V). However, the carbonylation reaction is essentially at equilibrium. This also seems to indicate a promoting effect of the alkali on the hydrogenolysis activity of Cu-chromite. A white insoluble precipitate of Na-formate was found in the reaction mixture after the run. The low solubility of Na-formate may also contribute to the decreased rate for NaOMe/Cu-chromite.

(iv) Effect of Cu-chromite Loading and Change in Inlet Flow Rate

A series of experiments were carried out with different catalyst loadings at constant feed rate. The MeOH synthesis rate was not linear in catalyst loading--a surprising result, since the hydrogenolysis reaction is the rate determining step; doubling the amount of the catalyst should double the rate. Possible causes such as mass transfer effects were eliminated by Liu[12].

A similar result was obtained when the gas feed rate was varied at constant catalyst loading. 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. The MeOH synthesis rate at different flow rates is summarized in Table 3.

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 feed rate is decreased. It was found that H_2O and CO_2 in the gas outlet increased in both the cases. A constant rate of inhibiting by-product formation will result in a drop in the MeOH synthesis rate. This is consistent with experimental observations. This means a compromise may have to be made between syngas conversion and the rate of MeOH formation.

Table 3: Effect of Flow Rate on Rate of Methanol Synthesis

Flow Rate (H_2/CO) cc/min	Rate of MeOH Prod. 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

(v) Comparison of Cu/ZnO with Cu-chromite Catalyst

Cu/ZnO is the commercial <u>direct</u> gas phase MeOH synthesis catalyst. Vedage et al.[9] and Sheffer et al.[14] have found that alkali metals such as Cs and K promote MeOH activity on Cu/ZnO. The rate of MeOH formation using a mixed KOMe/Cu-chromite catalyst was compared with that using a mixed KOMe/Cu-ZnO catalyst at reaction conditions of 150°C and 63 atm. The progress of the reaction for the two catalyst combinations is shown in Figure 5. The activity of KOMe/Cu-chromite is almost 8 times higher than KOMe/Cu-ZnO. It must be kept in mind that Cu-chromite is a better hydrogenolysis catalyst than Cu-ZnO. This is an indication that MeOH is formed by MeF hydrogenolysis and not by direct hydrogenation of CO under our reaction conditions. No higher alcohols were formed in case of Cu/ZnO in spite of the presence of alkali.

(vi) Effect of Feed H_2/CO Ratio

The concurrent process involves H_2 and CO reacting separately in different reactions. For every CO reacting, 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. 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 6. The rate of MeOH synthesis decreased with a decrease in the feed H_2/CO ratio. This is consistent with the observation that CO inhibits the hydrogenolysis reaction. The results show that the concurrent reaction can tolerate fluctuations in the feed H_2/CO ratio.

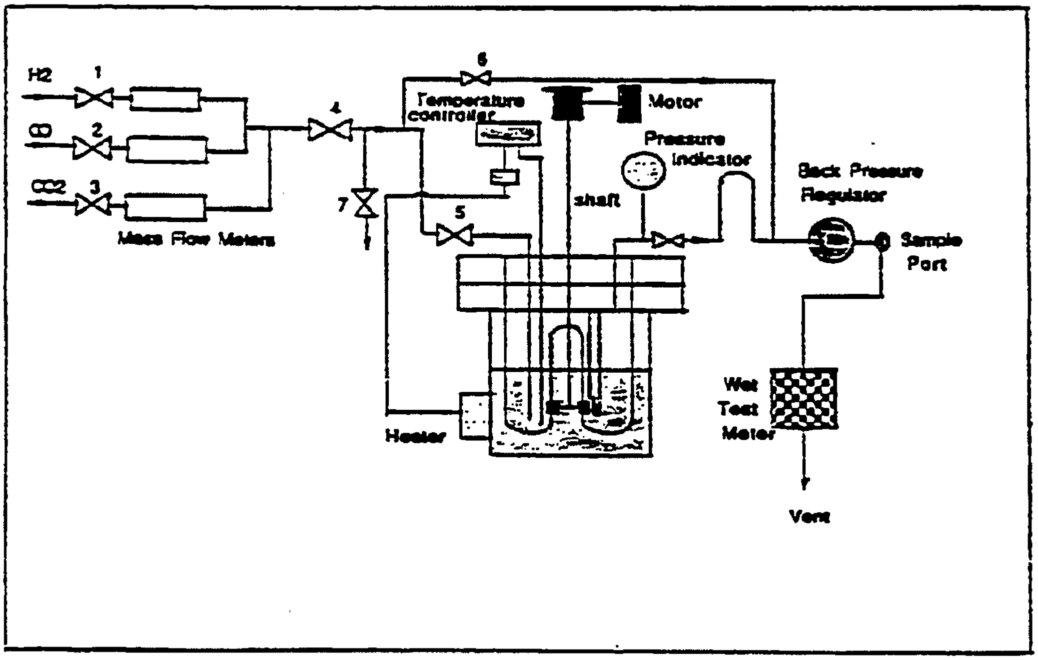

Figure 1 : Schematic of Experimental Setup

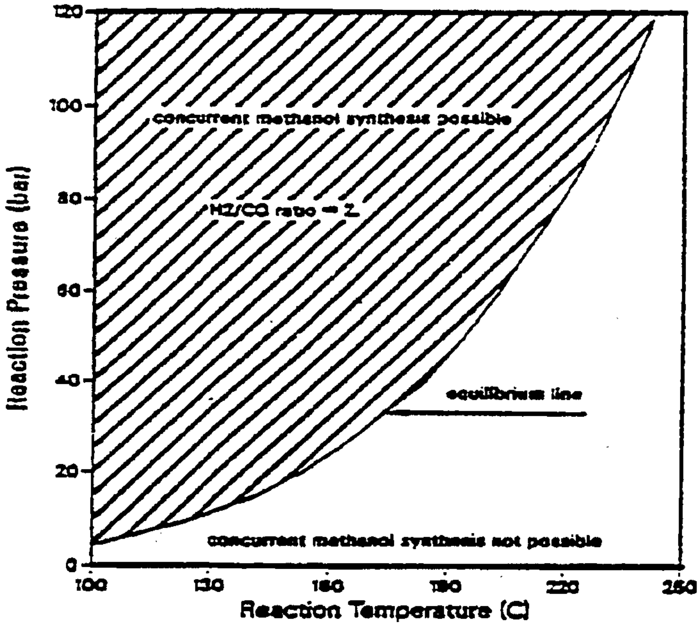

Figure 2. Thermodynamically Feasible Region for Concurrent Synthesis

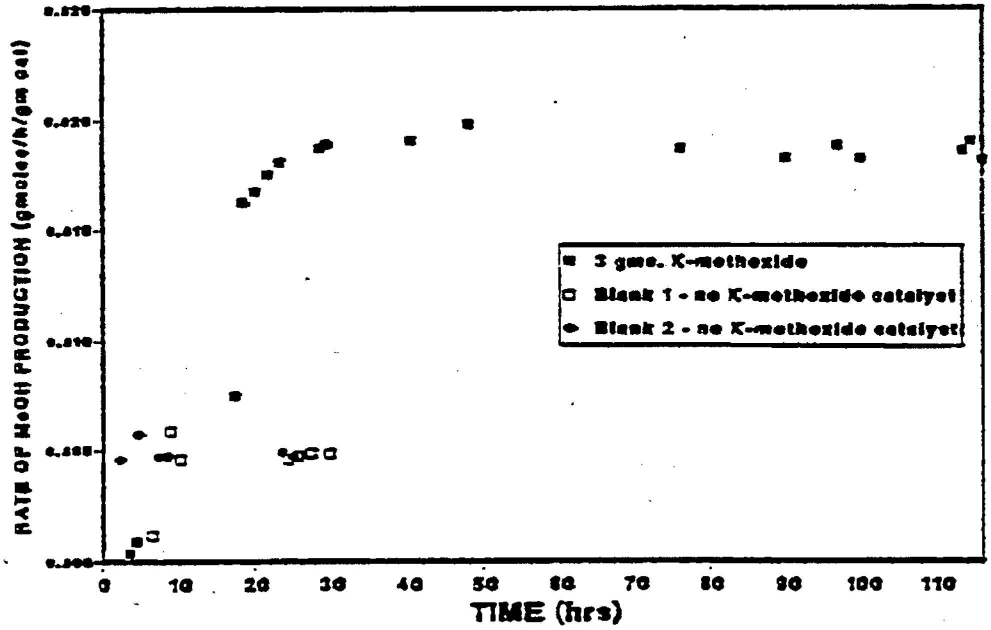

Figure 3: Rate of MeOH Synthesis vs Time

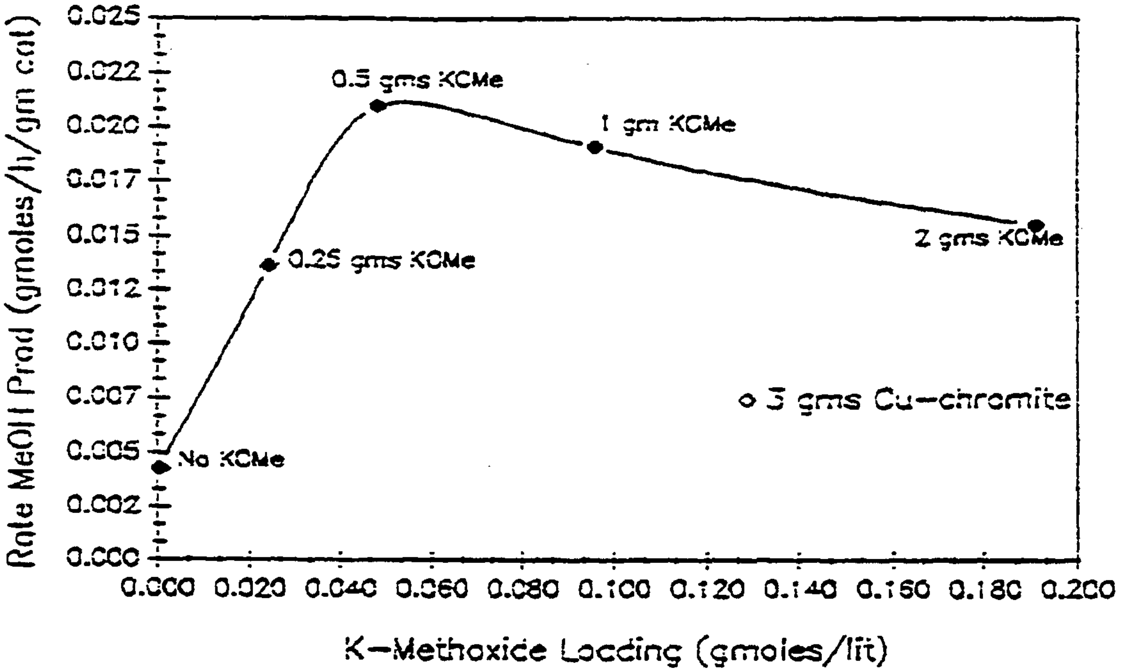

Figure 4: Rate of Methanol Synthesis vs KOMe Loading

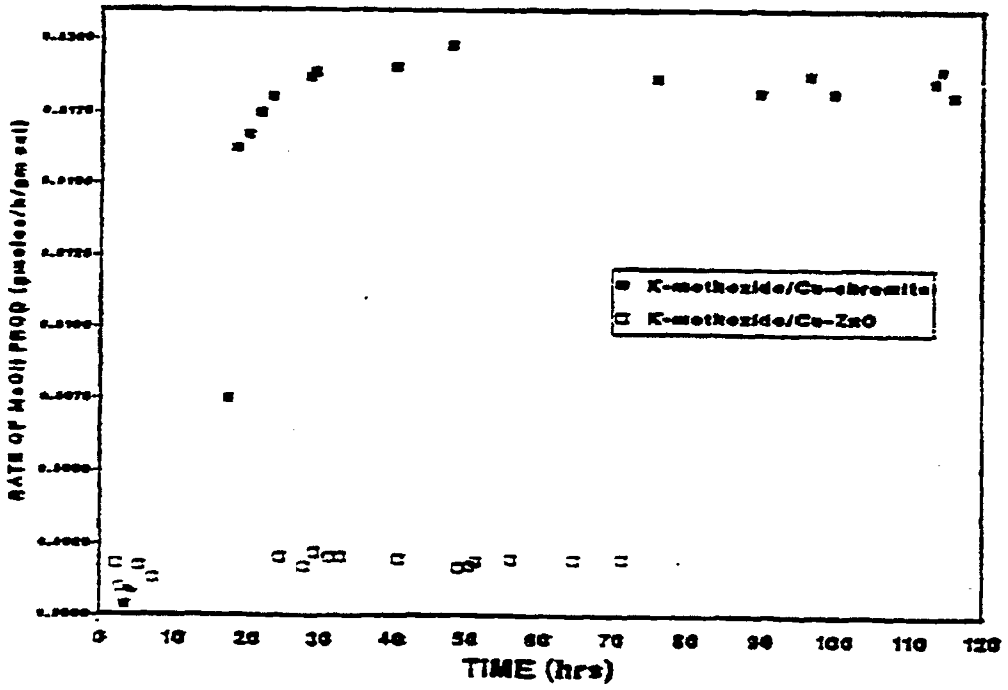

FIGURE 5: Rate of MeOH Synthesis on Cu-chromite and Cu-ZnO catalysts

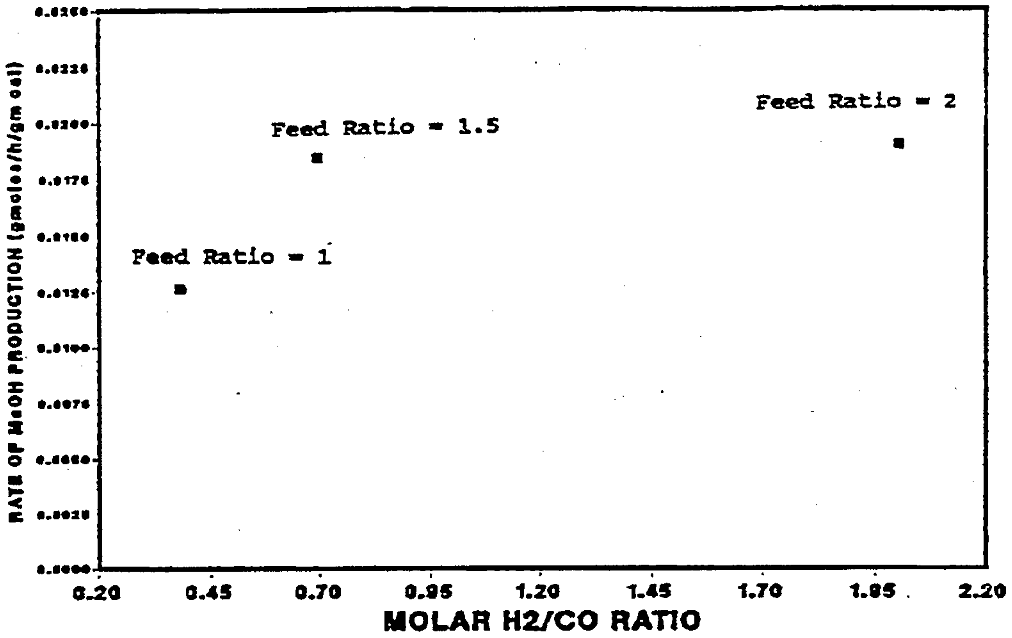

Figure 6: Variation of MeOH Synthesis Rate with H2/CO Ratios in the Reactor

CONCLUSIONS

Reaction studies on the concurrent MeOH synthesis using a mixed catalyst comprised of KOMe and Cu-chromite indicate an interaction between the two catalysts. This novel synthesis gives high selectivity to MeOH and there is little need for recycle of synthesis gas. High activity is obtained in comparison to a mixed catalyst comprised of KOMe/Cu-ZnO. The process is tolerant to fluctuations in the feed H_2/CO ratio.

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