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Methanol Synthesis from $CO/CO_2/H_2$ over $Cu/ZnO/Al_2O_3$ at Differential and Finite Conversions

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Methanol production from $CO/CO_2/H_2$ over a $Cu/ZnO/Al_2O_3$ catalyst has been compared in an internal recycle reactor (finite conversion) and a differentially operated tubular reactor. From experiments at differential conversion it was found that the intrinsic rate of CO_2 hydrogenation was approximately 20 times faster than the intrinsic rate of CO hydrogenation. The rate of methanol production at differential conversion increased almost linearly with respect to the CO_2 concentration, indicating that there is negligible inhibition by CO_2 in the absence of products. With 1–4% CO_2 in the synthesis gas, the methanol production rate was found to be substantially greater at finite conversion than at differential conversion, which is evidence for a promoting influence by the product water. With >4% CO_2 in the synthesis gas there was increasing loss of methanol production at finite conversion, and under CO_2/H_2 in particular there was an order of magnitude difference between methanol production at finite and differential conversions. This effect was due to inhibition of CO_2 hydrogenation associated with the presence of product water. © 1998 Academic Press

1. INTRODUCTION

Cu/ZnO type catalysts are active for methanol synthesis under CO/H_2, $CO/CO_2/H_2$, and CO_2/H_2. Numerous workers have found that there is a clear maximum in methanol synthesis activity at low (2–5%) CO_2 concentrations with conditions in the range 0.1–10 MPa and 225–285°C (1–10). This kinetic phenomenon would appear to be connected to two issues: the direct carbon source of methanol, where radiotracer experiments have shown that CO_2 rather than CO hydrogenation is the main synthesis route (11–13), and the state of the active Cu site, where the CO/CO_2 redox may be responsible for providing key oxidised sites (1, 13–15).

However, the kinetic effect of CO_2 appears to be different under very low conversion conditions. With very high space velocities of the synthesis gas, the methanol production rate has been found to increase continuously with respect to the CO_2 concentration (7, 9), and similar trends have been reported for the initial rates of methanol synthesis in batch reactors (3, 16), suggesting that the products as well as the CO_2 affects the catalytic activity at finite conversions. The influence of water in particular is well known (16–20).

The objective of this study was to elucidate the separate effects of the CO/CO_2 ratio and the products on the catalytic activity for methanol synthesis. This has been achieved by a comparison of methanol production rates from $CO/CO_2/H_2$ at finite and differential conversion[1] over the same catalyst under the same conditions with the same source of synthesis gases. The experiments at finite conversion were carried out in an internal recycle "gradientless" reactor, such that the catalyst bed was uniformly exposed to the product gas phase. Therefore, it has been possible to determine the catalytic activity at a measured product concentration. For experiments at differential conversion, rigorous experimental procedures have been adopted to limit the influence of products on the catalytic activity and to eliminate secondary reactions involving the water–gas shift reaction. As such, it has been possible to measure the forward rates of CO and CO_2 hydrogenation.

2. EXPERIMENTAL

2.1 Catalyst Preparation

The preparation of $Cu/ZnO/Al_2O_3$ was based on an ICI proprietary procedure (21) involving a two-stage precipitation. The precipitate was washed and calcined at 300°C for 6 h. Pellets were formed with a density of 2 g/cm^3 (using a small amount of graphite powder), before being crushed and seived to small granules. The nominal composition of the catalyst was 60% CuO, 30% ZnO, 10% Al_2O_3 (w/w), the industrial standard (2). The actual composition of the calcined catalyst measured by AA was 60.3% CuO, 28.6% ZnO, 10.8% Al_2O_3, with 420 ppm Na_2O. The BET surface area of the calcined catalyst was 115 m^2/g with an average pore diameter of 17.2 nm.

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[1] "Differential conversion" applies when the conversion of reactants to products is so low that, if effect, the catalyst is only exposed to the feed gas mixture. The effects of products are eliminated and the intrinsic forward rate of reaction for the given feed gas can be measured.

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The temperature-programmed reduction (10°C/min) of the calcined catalyst under dilute (5%) H_2 revealed a CuO reduction peak beginning at approximately 205°C with the maximum reduction rate at 255°C. The Cu metal surface area of the reduced catalyst was measured using the pulse N_2O decomposition technique (14). Assuming a Cu atom density of 1.46×10^{19} atoms/m^2, the Cu surface area was 25 ± 1 m^2/g, corresponding to a Cu dispersion of 6.4%.

2.2. *Measurement of Catalytic Activity*

Methanol synthesis at finite conversion was investigated in an internal recycle reactor (reactor volume 300 cm^3, catalyst basket volume 100 cm^3). An impeller speed of 1500 rpm ensured that there was a well mixed gas phase, such that the catalyst was almost uniformly exposed to the product gas phase.[2] A 5- to 10-g catalyst charge was used along with glass beads as diluent. Three external band heaters and associated thermocouples inside the reactor ensured accurate temperature control without gradients (a flow and control diagram can be found elsewhere (22)). Experiments at differential conversion were carried out in a downflow tubular microreactor. The 6-mm internal diameter reactor was charged with ∼5 mg catalyst for experiments under CO_2/H_2, giving a bed length of approximately 1 mm. Packing of inert SiC above (175 mm) and below (100 mm) the catalyst with the same particle size ensured the flow was well distributed. The control thermocouple was placed within the catalyst bed, and additional thermocouples approximately 10 mm above and below the catalyst bed confirmed that there was no temperature gradient.

All experiments were carried out at a temperature of 250°C. The pressure was 5 MPa in the internal recycle reactor and 4.5 MPa in the tubular reactor. The additional pressure in the internal recycle reactor allowed for 10% He which was added to the synthesis gas as an internal analytical standard. Premixed gases, CO_2/H_2 and CO/H_2 (20% : 80% in each case), were mixed to enable the CO_2 concentration in the feed to be varied while maintaining fixed concentrations of total carbon oxides and H_2. The catalyst was reduced *in situ* under flowing H_2 (5% in N_2) raising the temperature by 1°C/min to 215°C and holding for 12 h. Subsequently, the pressure and temperature were raised to the set values before the initial activity was measured.

The effluent pipes from both reactors were trace heated to prevent condensation of products and were connected directly to a Perkin Elmer 8500 gas chromatograph for online analysis using a TCD and H_2 as a carrier gas. The only compounds detected were He, CO, CH_4, CO_2, H_2O, and CH_3OH. The methanol yield was calculated by:

$$\mathrm{CH_3OH\ yield\ (internal\ recycle\ reactor)} = (\mathrm{CH_3OH/He})_{\mathrm{product}}/(\mathrm{CO/He} + \mathrm{CO_2/He})_{\mathrm{feed}}$$

$$\mathrm{CH_3OH\ yield\ (tubular\ reactor)} = (\mathrm{CH_3OH})_{\mathrm{product}}/(\mathrm{CO} + \mathrm{CO_2} + \mathrm{CH_4} + \mathrm{CH_3OH})_{\mathrm{product}}$$

No activity was found in the absence of catalyst. An impeller speed ≥1000 rpm in the internal recycle and a flow rate ≥240 ml/min (stp) in the tubular reactor were demonstrated to be sufficient to prevent extraparticle mass transfer limitation. Catalyst particle size ranges of 250–500 μm for the internal recycle reactor and 106–250 μm for the tubular reactor were found to be suitable to prevent any limitation from intra-particle diffusion. The reproducibility of kinetic data was ±6% from the result for the internal recycle reactor and ±4.5% from the mean result for the tubular reactor. The use of He in the internal recycle reactor allowed mass balances in carbon and oxygen (calculated relative to the amount of C or O converted) to be checked. In all kinetic experiments the balances closed to within ±7.5%, in 95% of experiments the balances were within ±5% (mass balances were not possible in the tubular reactor given the low conversions).

3. METHANOL SYNTHESIS AT FINITE CONVERSION IN THE INTERNAL RECYCLE REACTOR

Kinetic data throughout this paper were obtained as initial activity measurements (i.e., the initial rate or yield of methanol production) using a fresh charge of catalyst each time. In this way it was intended to capture the effect of the gas phase composition on the kinetics of methanol synthesis and avoid interference by catalytic deactivation which is also a function of the gas phase composition. To establish the validity of initial activity measurements, methanol synthesis activity was monitored over extended periods. From the deactivation profiles given in Fig. 1, initial rate of deactivation was found to be ∼1.5%/hour with CO_2/H_2, ∼2%/hour with $CO_2/CO/H_2$ (2% CO_2), and ∼4%/hour with CO/H_2. We stress that these initial rates of deactivation were low relative to absolute differences in activity of the catalyst with different synthesis gases.

3.1. *Methanol Synthesis with CO_2/H_2 and CO/H_2 Feeds*

In all kinetic experiments with CO_2/H_2 the major products were methanol, CO, and water. The amount of water produced was always the sum of the methanol and CO produced, or the total CO_2 converted (±7.5%), which follows from stoichiometry. In experiments with CO/H_2 methanol was the only major product. Trace product methane was detected with both feeds with a selectivity of ca. 0.5% with CO_2/H_2 and approximately double that with CO/H_2. With

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[2] The mixing characteristics of the internal recycle reactor were investigated by monitoring the residence time distribution of a tracer in the gas flow. With impeller speeds ≥1000 rpm it was found that there were no concentration gradients and the uniform concentration in the reactor was the same as the concentration in the reactor effluent.

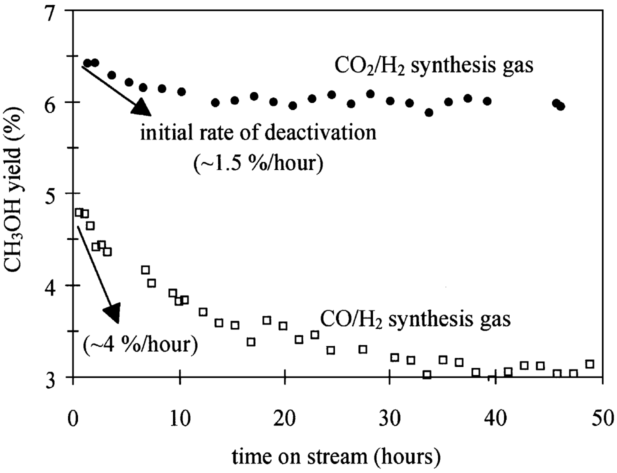

FIG. 1. Methanol production from CO_2/H_2 and CO/H_2 in the internal recycle reactor as a function of time on stream (CO_x/H_2 space velocity 1.67 mol h^{-1} g^{-1}).

CO/H_2, CO_2 and H_2O were also detected as trace products with $CH_4 > CO_2 > H_2O$.

Table 1 shows methanol production from CO/H_2 and CO_2/H_2 at various space velocities. In all cases, methanol production was not at equilibrium (under the present conditions the equilibrium methanol yield is 71% from CO/H_2 and 22% from CO_2/H_2). At high space velocity methanol production was greater with the CO_2/H_2 feed but at lower space velocity methanol production was greater with CO/H_2, which is associated with the inhibition of synthesis from CO_2/H_2 caused by the presence of the products (see below).

CO production from CO_2/H_2 via the reverse water–gas shift reaction is also shown in Table 1. At high CO_2/H_2 space velocity methanol production was greater than CO production, but at lower space velocity the selectivity switched in favor of CO production, which is associated with the relative inhibition of methanol synthesis by the products (see below). At even lower space velocity CO production approached equilibrium. The ratio of partial pressures, $CO \cdot H_2O/(CO_2 \cdot H_2)$, was 0.014, which compares to an equilibrium constant for the water–gas shift reaction of 0.012 from the literature (23).

TABLE 1

Methanol Production from CO/H_2 and CO_2/H_2 in the Internal Recycle Reactor

	CO/H_2 synthesis gas		CO_2/H_2 synthesis gas	
Space velocity (mol h^{-1} g^{-1})	CH_3OH production rate[a]	CH_3OH yield (%)	CH_3OH, CO production rate[a]	CH_3OH, CO yield (%)
6.68	—	—	49.4, 35.3	3.7, 2.6
1.67	15.8	4.7	21.7, 23.7	6.5, 7.1
0.84	—	—	16.0, 18.9	9.6, 11.3
0.21	9.7	23.2	6.6, 5.0	15.8, 12.0

[a] mmol h^{-1} g^{-1}.

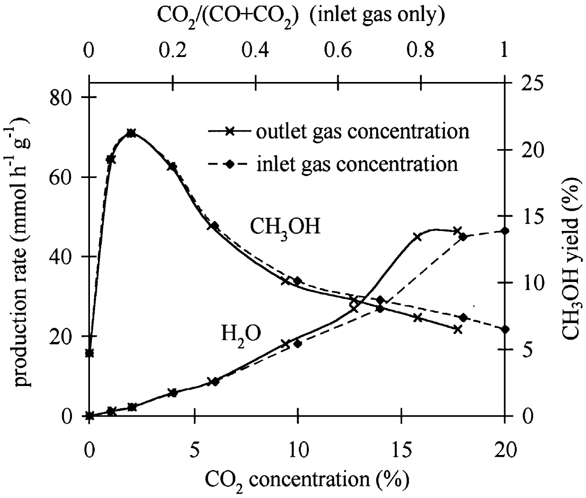

FIG. 2. Methanol and water production from $CO/CO_2/H_2$ gas mixtures in the internal recycle reactor ($CO/CO_2/H_2$ space velocity 1.67 mol h^{-1} g^{-1}).

3.2. *Methanol Synthesis with $CO/CO_2/H_2$ Feeds*

Methanol production for varying CO_2 concentrations (the total concentration of $CO + CO_2$ was always kept constant) was determined with a space velocity of 1.67 mol h^{-1} g^{-1}, such that the methanol yield was never close to the equilibrium. Figure 2 shows the results as a function of the CO_2 concentration in the synthesis gas as well as the CO_2 concentration in the product which is appropriate for a well mixed internal recycle reactor. A small CO_2 concentration resulted in a sharp increase in methanol production with a maximum at 2% CO_2, in agreement with previous studies (1–10). Increasing CO_2 concentrations resulted in decreasing methanol production. The production rate of water increased continuously with increasing CO_2. Within the tolerances for experimental error, the water production rate was equal to the CO_2 consumption rate across the range of CO_2 concentrations, which follows from stoichiometry. The water–gas shift equilibrium was obtained with 1–10% CO_2 in the synthesis gas or $0.05 \leq CO_2/(CO + CO_2) \leq 0.5$, based on the above equilibrium constant.

4. METHANOL SYNTHESIS AT DIFFERENTIAL CONVERSION

Methanol synthesis at differential conversion was measured with high space velocity of synthesis gas through the tubular reactor, making use of very low catalyst mass. Kinetic data were obtained as initial activity measurements so that the effect of the gas phase composition on the intrinsic kinetics could be determined unaffected by catalyst deactivation. The initial rate of deactivation in the tubular reactor at differential conversion gas ~7%/h under CO/H_2 decreasing to <1%/h under CO_2/H_2. These initial rates of deactivation were low relative to absolute differences in catalytic activity with different synthesis gases.

4.1. *Methanol Synthesis from CO_2/H_2*

With increased space velocities, covering two orders of magnitude, the methanol production rate in the tubular reactor increased as the conversion decreased (see Fig. 3). At space velocities above 325 mol h^{-1} g^{-1}, with methanol yields <0.33%, the rate of methanol production reached an asymptote indicating that true differential kinetics had been obtained. The asymptote, 0.22 mol h^{-1} g^{-1}, corresponds to the forward rate of CO_2 hydrogenation to methanol. This was at least one order of magnitude higher than the methanol production rate at finite conversion, which is strongly indicative of inhibition associated with a product.

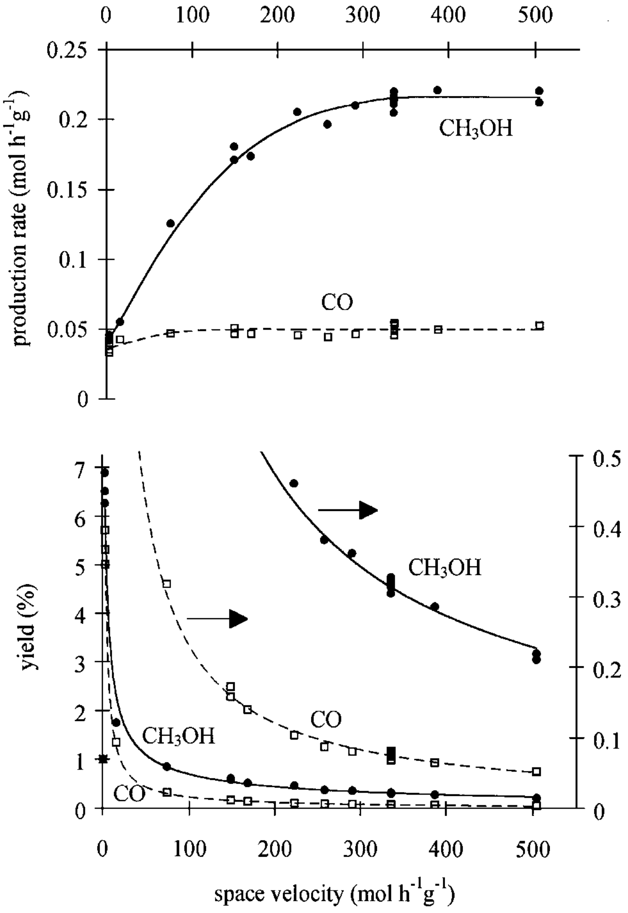

FIG. 3. Methanol and CO production from CO_2/H_2 in the tubular reactor: approach to differential conversion.

TABLE 2

Comparison of Methanol Production from $CO_2/H_2 + H_2O$ (Differential Conversion) and CO_2/H_2 (Finite Conversion in the Internal Recycle Reactor)

	H_2O concentration (mol %)	CH_3OH production rate (mol h^{-1} g^{-1})
CO_2/H_2 feed (differential conversion)[a]	0	0.22
$CO_2/H_2 + H_2O$ feed (differential conversion)[b]	2.6	0.021
CO_2/H_2 feed (finite conversion)[c]	2.8	0.022

[a] CO_2/H_2 space velocity 340 mol h^{-1} g^{-1}.

[b] CO_2/H_2 space velocity 340 mol h^{-1} g^{-1}; H_2O space velocity 8.9 mol h^{-1} g^{-1}.

[c] CO_2/H_2 space velocity 1.67 mol h^{-1} g^{-1}; H_2O production rate 0.046 mol h^{-1} g^{-1}.

The parallel production of CO by the reverse water–gas shift reaction (Fig. 3) reached differential conversion at space velocities >75 mol h^{-1} g^{-1}, with CO yields <0.33% and a production rate of approximately 0.05 mol h^{-1} g^{-1}. Hence, the intrinsic rate of CO_2 hydrogenation is four times faster than the reverse water–gas shift reaction at these conditions.

With a space velocity of ~340 mol h^{-1} g^{-1} CO_2/H_2 through the tubular reactor, the addition of 2.6 mol% water in the feed resulted in a severe loss of methanol production (see Table 2) and the inhibition was slowly reversed when the water flow was removed. Since the experiment was carried out under conditions of differential conversion, the addition of water clearly inhibits the direct CO_2 hydrogenation to methanol. (There was also a severe loss of CO production by the reverse water–gas shift reaction.)

Table 2 also gives methanol production from CO_2/H_2 at finite conversion, where the water concentration as a result of water production was similar. The two types of experiment are directly comparable; at differential conversion the catalyst was uniformly exposed to the feed concentration, whereas at finite conversion in the internal recycle reactor the catalyst was uniformly exposed to the product concentration. The similar methanol production rates show that the kinetics at finite conversion can be described by the production of methanol by CO_2 hydrogenation, and the inhibition of this reaction, by the presence of the product water.

4.2. *Methanol Synthesis from CO/H_2*

Figure 4 shows methanol production as a function of space velocity of CO/H_2 through the tubular reactor. At space velocities >15 mol h^{-1} g^{-1}, with methanol yields <0.33%, the methanol production rate became constant signifying differential reaction kinetics. Given the low amounts of impurities in the feed (CO_2 and water were present at ppm levels), CO_2 hydrogenation could not account for the methanol production. The assymptote, 10 mmol h^{-1} g^{-1}, corresponds to the forward rate of CO hydrogenation to methanol, which was over 20 times less than the forward rate of CO_2 hydrogenation.

There were two surprising features of the present results with CO/H_2. At the lowest space velocity in Fig. 4 (1.67 mol h^{-1} g^{-1}), i.e., at finite conversion, the methanol yield in the tubular reactor was ~12% less than that in the internal recycle reactor, even though the latter operates under the product gas phase concentration. This result is consistent with methanol synthesis from CO/H_2 being promoted by the presence of one of the products. With increasing space velocity of CO/H_2 through the tubular reactor, the methanol production rate decreased. A lower conversion of reactants normally leads to a greater net rate of reaction, but the converse result in Fig. 4 is again consistent with methanol synthesis from CO/H_2 being promoted by one of the products.

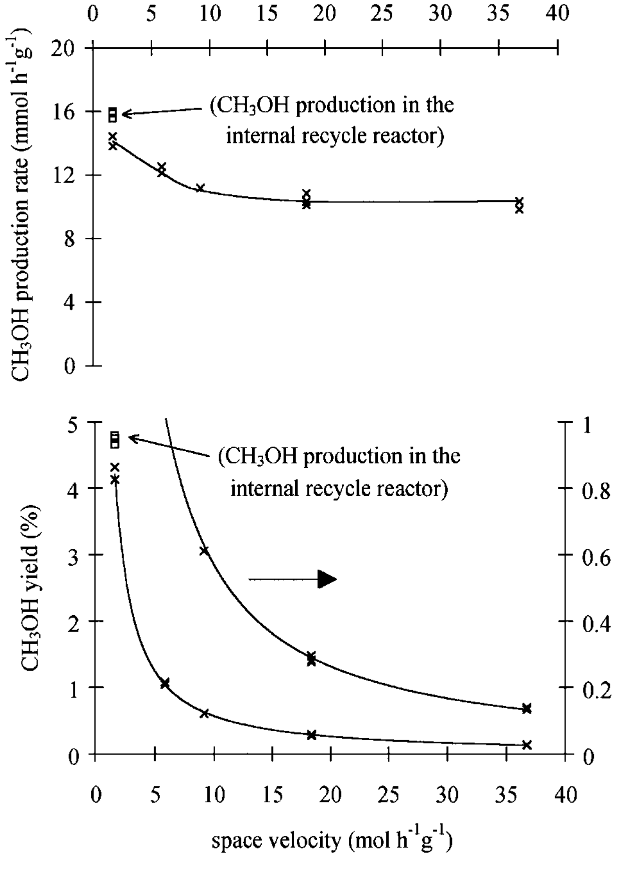

FIG. 4. Methanol production from CO/H_2 in the tubular reactor: approach to differential conversion (methanol production in the internal recycle reactor from CO/H_2 at 1.67 mol h^{-1} g^{-1} also shown for comparison).

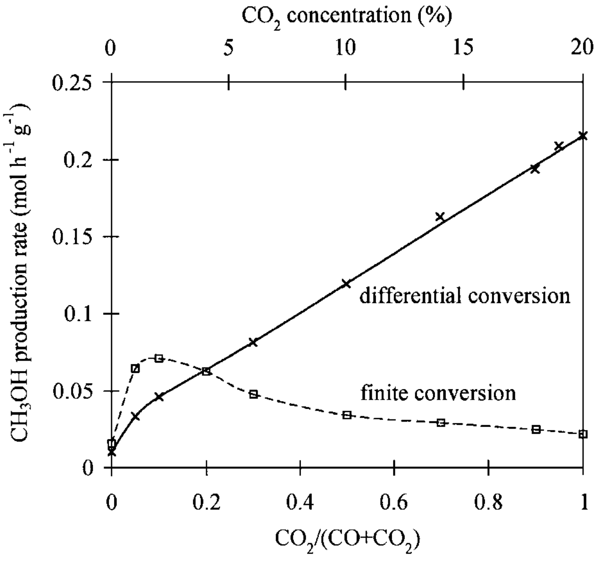

FIG. 5. Methanol production rate from $CO/CO_2/H_2$ gas mixtures at differential conversion in the tubular reactor (compared to methanol production rate from $CO/CO_2/H_2$ gas mixtures at finite conversion in the internal recycle reactor).

4.3. *Methanol Synthesis from $CO/CO_2/H_2$*

In Fig. 5 the methanol production rate at differential conversion is plotted against the CO_2 concentration in the synthesis gas. In all experiments, the space velocity was such that the methanol yield was <0.3%, which was previously found to be the requisite for differential conversion under CO_2/H_2 and CO/H_2. The rate of methanol production was almost linearly related to the CO_2 concentration. At low CO_2 concentrations there appears to be a small departure from the linear relationship toward higher methanol production rates.

5. DISCUSSION

5.1. *Methanol Synthesis at Differential Conversion*

At true differential conversion with conditions of 250°C and 4.5 MPa, it has been demonstrated that the forward rate of CO_2 hydrogenation over a $Cu/ZnO/Al_2O_3$ catalyst is over 20 times faster than the forward rate of CO hydrogenation. Furthermore, the approximately linear increase in the rate of methanol production as the $CO_2/(CO + CO_2)$ fraction was increased from 0 to 1 (Fig. 5) indicates that *in the absence of products* the CO and CO_2 hydrogenation reactions are approximately noncompetitive, parallel routes to methanol synthesis. Hence, CO_2 becomes the predominant carbon source for methanol production with $CO_2/(CO + CO_2)$ fractions >0.05 or CO_2 concentrations >1%. This is in broad agreement with published work of kinetic experiments at low conversions using isotope labeled CO_2. For example (12), with 1.5% CO_2 approximately half of the methanol was produced directly from CO_2 and half from CO_2, whereas with ≥4% CO_2 the predominant carbon source was CO_2 (11, 13).

The approximately linear relationship of methanol production rate to the CO_2 concentration shows that in the absence of the products there is no inhibition of the catalytic activity for methanol synthesis by CO_2. Furthermore, this trend provides no evidence of a significant promotion of methanol synthesis by a CO/CO_2 redox process (except perhaps the small positive deviation in the methanol production rate with small CO_2 concentrations). This is consistent with a number of previous studies. Muhler *et al.* (24) studied the interaction of CO and CO_2 on a $Cu/ZnO/Al_2O_3$ catalyst under methanol synthesis conditions using transient techniques and found no evidence of significant oxygen coverage. Likewise, there was no evidence of oxygen coverage on Cu(100) surfaces (25) or clean polycrystalline Cu foil (26), both of which exhibited turnover numbers under CO_2/H_2 which could be extrapolated to industrial methanol synthesis (27). We emphasise that these studies (24–26) necessarily corresponded to differential conditions and are consistent with the present work.

Previous work which has approached differential conditions in tubular reactors (7, 9) has given the impression of increasing curvature in the rate at high CO_2 levels. However, the space velocity was not increased in line with the increasing methanol production rate and therefore differential conversion was not maintained. In these studies (7, 9), and others (3, 16) reporting initial rates in batch reactors, the difference in the methanol production rates under CO_2/H_2 and CO/H_2 was much less than the present 20 times. It seems likely that the presence of products diminished this relative difference in the previous studies.

5.2. Methanol Synthesis with >4% CO_2 in the Synthesis Gas

With >4% CO_2 in the synthesis gas, an increasing departure between the rates of methanol production at finite and differential conversion was observed (Fig. 5). The loss of methanol production at finite conversion is frequently explained by overoxidation of the Cu catalyst by a CO/CO_2 redox mechanism or by strong adsorption of CO_2 leading to kinetic inhibition. However, it follows from the present results that the difference between the rates at finite and differential conversions is a consequence of the presence of the products, i.e., reverse reaction and/or inhibition associated with a product. In the internal recycle reactor, the catalyst was subject to increasing product water concentration as the inlet CO_2 concentration was increased (Fig. 2). In the extreme case of a CO_2/H_2 feed, by the addition of water at differential conversion (Table 2) we have demonstrated that the order of magnitude lower rate of methanol production observed at finite conversion can be explained entirely by the inhibition of CO_2 hydrogenation by the presence of product water. In our experiments, which were well away from equilibrium, the product methanol had a negligible effect. Consequently, the reverse reaction was not responsible for the lower methanol production at finite conversion. Of course, closer to equilibrium the importance of the reverse reaction, relative to the inhibition associated with the product, would be greater.

A number of workers have incorporated a CO_2 inhibition term in their kinetic models (1, 10, 28, 29). However, we have shown that there is no inhibition with increasing CO_2 concentration in the absence of products, whereas there is clearly inhibition when water is present. These approaches (1, 10, 28, 29) work because water production is related to the CO_2 concentration (Fig. 2). The adsorption constants for CO_2 have sometimes been obtained as negative values (e.g., 10, 29) which does not comply with the physiochemical constrains stated by Boudart (30), so that they are really no more than fitting parameters. The effect of water may be due to a H_2O/H_2 redox process, where high coverages of surface oxygen inhibit the activity of the Cu catalyst sites for CO_2 hydrogenation. In contrast, Askgaard *et al.* (27) have argued that the coverage of surface oxygen is always low and it is high coverages of formate which cause the loss in methanol production at high CO_2 concentrations. Vanden Bussche and Froment (31) have recently proposed an advanced model of methanol synthesis from CO_2 via carbonate and formate in which an explicit CO_2 inhibition term is absent and which can reproduce the evolution of the methanol synthesis rate with CO_2 concentration. Based on our results, where inhibition occurs when both CO_2 and water are present, a cooperative phenomenon involving adsorption of CO_2 and water could be the mechanism for the inhibition in which the catalyst surface would become saturated with carbonate species or resultant formate at high CO_2 levels.

5.3. Methanol Synthesis with ≤4% CO_2 in the Synthesis Gas

The results of methanol synthesis at finite conversions in the internal recycle reactor (Fig. 2) show a well-defined maximum in production rate with 2% CO_2 (in the feed or in the product since changes in the relative pressures of CO or CO_2 were small), in agreement with many previous studies (1–10). This has been explained previously by a number of mechanisms: conversion of CO to CO_2 which is hydrogenated to methanol in a strictly sequential mechanism and/or promotion of the Cu catalyst activity by a CO_2/CO redox process. However, a striking feature of the present results (Fig. 5) is that the methanol production rates at finite conversion near the maximum were higher than at differential conversion. The same result is implicit in the work of Lee *et al.* (9). For a simple reaction one would expect the reaction rate to be greatest at differential conversion, where the partial pressure of reactants is a maximum and the reverse reaction is eliminated (this would also be true in the case where a reactant, i.e., CO_2, promotes the catalytic activity). The clear implication of the present result is that methanol production is promoted by the presence of a product, namely, water, since the promoting effect of water on methanol synthesis from CO/H_2 has been previously well documented (17–19) (the water concentrations in the internal recycle reactor with 0–4% CO_2 in the feed were between ~50 ppm and 0.4%, which falls within the range of the previous studies).

The effect of water can be explained in several ways. Surface hydroxyl groups could be directly involved in a reaction with CO to produce formate. Alternatively surface oxygen can be produced by H_2O/H_2 redox mechanism which promotes methanol synthesis from CO_2 via carbonate. The former mechanism is in accord with the isotope labelling studies of Vedage *et al.* (17) and Liu *et al.* (12). Such a process could include the possibility of bifunctional mechanisms involving Cu and ZnO (6, 32), although Burch *et al.* (33) concluded that bifunctional mechanisms are inappropriate. The involvement of a H_2O/H_2 redox process is consistent with the work of Colbourn *et al.* (34), who demonstrated that the dissociative reaction of steam evolving H_2 and adsorbed oxygen takes place readily on a polycrystalline Cu surface at temperatures similar to that of methanol synthesis. This is not necessarily in contradiction with previous studies (13–15) where the surface oxygen coverage on Cu was related to the CO_2/CO ratio in the synthesis gas: when the water gas–shift reaction is close to equilibrium, oxygen coverage can be related to either the H_2O/H_2 or the CO_2/CO ratio. From the present results alone it is not possible to discriminate between the various possibilities.

Interestingly, models based on Cu single crystal data, with negligible surface oxygen coverage, also predict synthesis rates within a factor of 2 of the observed industrial rates (25, 27). In relation to this, we note that the differential rate of methanol synthesis from CO_2/H_2 in the present work is within a factor of 3 of the rate at finite conversion with 2% CO_2 in the synthesis gas—typical industrial conditions. Consequently, models based on extrapolation from CO_2/H_2 under differential conditions, such as the single crystal work, are likely to give apparently reasonable agreement with industrial rates, although it would be coincidental and not necessarily indicative that CO_2 hydrogenation on oxygen-free Cu was the mechanism of methanol synthesis under industrial conditions.

6. CONCLUSIONS

At differential conversion the intrinsic rate of CO_2 hydrogenation was approximately 20 times faster than the intrinsic rate of CO hydrogenation and, furthermore, the rate of methanol production increased almost linearly with respect to the CO_2 concentration. Hence, in the absence of products, there is no inhibition of methanol production by CO_2 and no significant influence of a CO_2/CO redox process.

With >4% CO_2 in the synthesis gas, there was an increasing loss of the methanol production rate at finite conversion compared to that at differential conversion, which can be associated with the increasing product water concentration at finite conversion leading to inhibition of CO_2 hydrogenation. With 1–4% CO_2 in the synthesis gas, the rate of methanol production at finite conversion was greater than that at differential conversion. This is interpreted as evidence for promotion of catalytic activity for methanol production by the product water.

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