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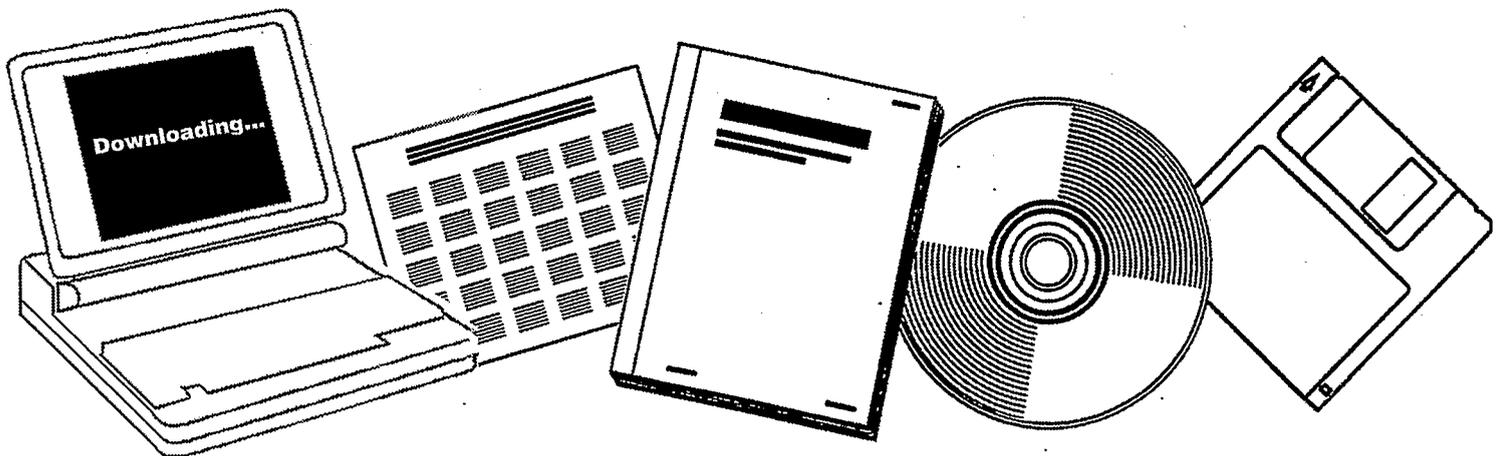
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MECHANISTIC STUDIES OF CATALYTIC METHANOL SYNTHESIS. FINAL REPORT

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FINAL REPORT

Mechanistic Studies of Catalytic Methanol Synthesis

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Abstract:

The catalytic methanol production on a Cu-Zn-oxide catalyst was studied at 17 atm and about 200C in a batch reactor. The initial rate measurement was performed for different CO₂/CO ratios in the feed. The rate was found to increase with increasing CO₂/CO, for a fixed H₂ partial pressure. This behavior was observed for catalysts at different stages of deactivation, and from 195 to 225C. Addition of a small amount of water vapor greatly suppressed the rate.

When C¹⁸O₂ was used in a feed of CO₂:CO:H₂ = 5:10:20, the initial rate of production of methanol-¹⁸O was found to be about half the rate of production of methanol-¹⁶O. In view of the much lower partial pressure of CO₂ than CO in the feed, this result suggests that the hydrogenation rate of CO₂ on a per mole basis is faster than that of CO. This is consistent with the above initial rate data. Production of C¹⁶O¹⁸O and C¹⁶O₂ were also rapid, which indicated rapid exchange of the lattice oxygen with CO₂. The production of H₂¹⁸O was also rapid, being about twice as fast as the methanol production rate. Thus under the conditions of initial rate measurements, the water-gas shift reaction is rapid.

The relative rates of hydrogenation of CO₂ and CO were also determined near chemical equilibrium by the relaxation method. Nonequilibrium thermodynamic theories were applied to describe the relaxation process. The physical meaning of the equilibrium exchange rate for a complex reaction was discovered. A method was developed to measure the equilibrium exchange rates of the simultaneous reactions in methanol synthesis.

OBJECTIVE

The objective of this work is to gather kinetic and mechanistic data for the catalytic production of methanol from a mixture of CO, CO₂ and H₂ over a Cu-Zn-oxide catalyst.

DESCRIPTION OF THE OVERALL APPROACH

Work performed in this project can be grouped into three sections. Each represents a different type of kinetic measurement. The first type is the measurement of initial rate data. These data were gathered for different CO/CO₂ ratio in the feed, at 17 atm, and from 195 to 225C. The second type is isotope labeling experiment. C¹⁸O₂ was used as a component of the feed. The third type is relaxation experiment. In this, the theories of nonequilibrium thermodynamics were used to describe the relaxation toward equilibrium of the reaction system, which consists of a mixture of CO, CO₂, H₂, H₂O, and methanol. Equilibrium exchange rates were calculated from the relaxation data. These three approaches are separately described below.

I. THE RATE OF METHANOL PRODUCTION ON A COPPER-ZINC OXIDE CATALYST.
THE DEPENDENCE ON THE FEED COMPOSITION

Introduction

Methanol synthesis on a copper-zinc oxide catalyst has been extensively studied with respect to the solid state properties of the catalyst (1-4), the adsorption properties (5), the reaction mechanism (6-9), and the kinetics (10-12). In a very extensive kinetic study, Klier et al measured the rate of methanol production in an integral reactor as a function of the CO/CO₂ ratio in the reactant feed (12). They observed a sharp maximum at a CO/CO₂ of about 28/2. The data were interpreted assuming that the active site of the catalyst undergoes a redox reaction with the gas phase CO and CO₂. When the CO₂ content is too low, the reduced and inactive form of the active site dominates. When the CO₂ content is too high, the competitive adsorption of CO₂ blocks the active site. Thus an optimum CO/CO₂ ratio is observed. Using this model and the assumption that methanol is formed by the reaction of adsorbed CO with adsorbed H₂, a rate expression was derived which fitted the experimental rate data well. Furthermore, reasonable values of adsorption enthalpies and entropies could be calculated using the kinetic model.

Because of the use of an integral reactor in Klier's study, the carbon conversions were relatively high, especially in the experiments at higher temperatures in which the methanol yield approached the equilibrium yield. The high conversion introduced a number of possible complications to the kinetic measurement. The rate of the reverse reaction of methanol decomposition could be significant and could contribute to the observed kinetics. The rate of the competing water-gas shift reaction could be high and result in the production of water the effect of which has to be examined. The large change in the gas phase composition along the reactor also could complicate analysis of the data. To obtain the kinetics of the methanol synthesis reaction without these complications, we performed initial rate measurements using a batch reactor. Results of the study are reported here.

Experimental

All measurements were conducted in a constant volume stainless steel reactor with a volume of 63 mL. The inside of the reactor was made up of two connecting concentric cylindrical sections. The inside diameter and the height of the bottom section were 6.5 and 2.6 cm, respectively, and those of the upper section were about 3.5 and 2.7 cm, respectively. The content of the reactor was stirred by a magnetically driven fan which had blades at two different levels. The lower blades were about 1 cm above the catalyst bed, and the upper blades were about 1.5 cm above the lower blades. The lower blades were extended almost to the perimeter of the reactor. The extent of mixing in the reactor was determined by monitoring the response of the mass spectrometer signal to a step change in the gas composition in the reactor without any catalyst. Typically, the response was like an exponential decay, and the signal relaxed to within the noise level of the measurement in about two minutes. At the top of the reactor was a leak valve (Varian Vacuum Products) which fed a small amount of the reaction mixture into a mass spectrometer chamber. A UTI 100 C quadrupole mass spectrometer was used. The selection of mass numbers and the collection of data were performed by an Apple II plus computer interfaced with the mass spectrometer. One mass intensity was collected every five seconds, and all five components (CO , CO_2 , H_2 , CH_3OH and H_2O) were monitored in every experiment by monitoring masses 44, 31, 28, 18, 15 and 2. These intensities were converted to mole fractions in the reactor after correcting for the cracking patterns and the sensitivity factors which were independently determined. In all experiments, the mass 15 intensity could be accounted for by the cracking of CH_3OH . Thus CH_4 was not detected as a significant product.

The entire reactor was situated in an oven equipped with forced air

circulation. The temperature gradient along the reactor was less than 2 C. At the beginning of each series of experiments, a mixture of CO, CO₂, CH₃OH and H₂ at about 17 atm (1 atm = 101.3 kPa) was introduced into the reactor to calibrate the mass spectrometer sensitivity factors. This was repeated three times before rate measurements were made and was done twice at the end of the series. For the rate measurements, a mixture of the desired composition was prepared in a premixer before being expanded into the reactor. A transducer (Viatran) measured the reactor pressure before and after the experiment, and was isolated from the reactor during reaction. All experiments were conducted at 16.8 ± 0.2 atm pressure which decreased by less than 0.2 atm throughout the experiment. Each experiment lasted for 30 to 35 min. The experiments in each series were performed one after another immediately after evacuation of the gas mixture of the previous run, and introduction of the gas mixture for the new run. Between series of experiments, the catalyst was left in contact with the reaction mixture at 1 atm at reaction temperature.

The catalyst was prepared according to the method of Herman et al (1). It was precipitated from a copper nitrate (Alfa) and zinc nitrate (Alfa) solution (total cation concentration was 1 M) by the dropwise addition of a 1 M sodium carbonate (Alfa) solution at 85 to 90 C to a final pH of about 7. The resulting mixture was cooled for 2 h while stirring. The precipitate was then filtered and washed with glass distilled water five times, dried in air at 72 C, then calcined in air at 350 C for 3 h. Between 150 and 350 C, the calcination temperature was raised by 50 C every 30 min. The resulting catalyst was a black powder of 80-120 mesh. Its BET area was 21 m²g⁻¹, which was reduced to 18 m²g⁻¹ after use. Its CuO/ZnO ratio was 30/70 by weight, assuming that the precipitation of Cu and Zn was complete. The catalyst was loosely spread out in a teflon tray placed at the bottom of the reactor to form

a bed of less than 3 mm thick. It was reduced with a 2% H₂ in N₂ mixture at 1 atm and 250 C. Reduction at 200 C gave the same results. Two methods of reduction were used. In one, the reduction was performed in a batch system and a fresh charge of H₂/N₂ was introduced every 30 min. after the previous charge was evacuated. This procedure was repeated eight times. At the end of the eighth time, the catalyst was left in the H₂/N₂ mixture overnight. The reduction was considered complete because for one charge of catalyst, this reduction procedure was repeated after the catalyst was used in experiments. The activity of the catalyst after the repeated reduction remained the same. In the second method, the catalyst was reduced in a flowing stream of H₂/N₂ mixture for 12 h. This method was used only once and it produced a catalyst that was slightly more active than the first method. Otherwise the behavior of the catalysts was independent of the reduction method.

H₂ (Air Products, high purity), CO₂ (Linde, bone dry), and CO (Linde, high purity) were used without further purification. H₂O was introduced by vaporizing liquid doubly distilled water that was purified by pumping. A premixed mixture of 4.28% CO₂, 32.5% CO, and 63.22% H₂ (Airco) was used in every series of experiments as a test on the deactivation of the catalyst.

Results

Since the activity of the catalyst depends on its oxidation state which in turn depends on the composition of the gas mixture, preliminary experiments were performed to test for the reproducibility of the system by introducing a reactant feed of the same composition in consecutive experiments. It was found that for a fresh charge of catalyst, reproducible rates were obtained after two or three experiments. However, a slow deactivation was observed when the rates were compared from day to day. An example is shown in Table 1. The activity of the catalyst decreased by about 60% before a steady state was reached.

While the activity changed, the dependence of the rate on the feed composition did not change. Such deactivation was not noticed among the experiments within each series (in one day). An example is shown in Table 2. In these experiments, the composition of the reactant feed was randomly varied, and the initial rate of methanol production varied smoothly with the composition (see also Fig. 2).

As described, each series of experiments began with three calibration runs for the mass spectrometer. In the first one or two rate measurements immediately after the calibration, the methanol production rate was found to be higher than the steady state rates. The excess methanol was attributed to the displacement of adsorbed methanol by the feed gases (probably CO_2). Once this excess adsorbed methanol was displaced, reproducible rates were obtained as is shown by the data in Table 2.

Because the catalyst was placed in a tray at the bottom of the reactor, there was no forced convection through the catalyst bed. Transport of reactants and products in and out of the bed had to be by diffusion. The influence of catalyst bed diffusion on the measured rate was minimized by making the bed as thin as possible to less than 3 mm thick. The absence of such influence was confirmed by measuring the initial rate using different amounts of catalysts (i.e. different bed thickness). Such experiments were conducted at both 198 C and 225 C. In both cases, the steady state rate of a catalyst was first obtained using a H_2 - CO_2 feed mixture (70:30). Then about half of the catalyst was removed. The remaining catalyst was again reduced in a H_2/N_2 mixture, and the rate measurements were performed using the same feed. It was found that the initial rate of methanol production was reduced by about 60%. This proportional decrease in rate suggested that catalyst bed diffusion was much faster than the chemical transformation rate. That the rate was

reduced by slightly more than half was attributed to the deactivation of the catalyst after exposure to air and the second reduction. Diffusion limitation in the catalyst pores was not tested. However, we believe that pore diffusion limitation was not important because 1) the catalyst used has a low BET area and therefore large pores, 2) the catalyst was a fine powder, and 3) the rate of methanol production was slow. In fact, because of the slow reaction rate, the heat released by the reaction was small and there was no temperature gradient in the catalyst bed.

An example of the data showing the partial pressures of the components in the reactor is shown in Fig. 1. They were calculated from the mass spectrometer intensities by first correcting for the cracking pattern and the mass spectrometer sensitivities, and then normalizing the data to fit the mass conservation equations. The data for all the other experiments were similar to these except for different magnitudes and signs of the slopes. The rate of change of the H_2 partial pressure was always negative because it was a reactant. That for the CH_3OH partial pressure was always positive because it was a product. That for H_2O was positive if it was not being introduced in the feed, and could be either negative or positive if it was introduced in the feed, depending on whether the CO/CO_2 ratio was high or low, respectively. Similarly, the rates of change of CO and CO_2 partial pressures depended on the feed composition.

The dependence of the initial rates of CH_3OH production on the CO/CO_2 ratio in a 70% by volume of H_2 , 30% $CO + CO_2$ feed is shown in Fig. 2. The CO/CO_2 ratios were varied randomly in these experiments. The 225 C data were obtained with a fresh charge of catalyst, and the 195 C data were obtained with a steady state catalyst. The difference shown in the rates between the two temperatures were larger than the real difference because of the deactivation phenomenon described earlier. The trend was clear, however, that independent

of the degree of deactivation, the rate was higher at a higher CO_2 partial pressure. Similarly to CH_3OH , the initial rates of H_2O production also increased with increasing CO_2 partial pressure. This is illustrated by the data in Table 2. It is due to the increased rates of reverse water gas shift and of hydrogenation of CO_2 to methanol and water with increasing CO_2 pressure.

The dependence of the initial rate of methanol production on the partial pressure of water in the feed was also investigated. The results are shown in Figs. 3 and 4 for the 195 C and 225 C experiments. The data in each of these figures were obtained in one series of experiments in which the water partial pressure was varied randomly. The dotted lines in the figures show the rates in the absence of water. For the 225 C data, experiments with no water were performed with 63% H_2 instead of 70% H_2 . The rates thus obtained were used to confirm the normal behavior of the catalyst. The dotted line shown was drawn using data from other series of experiments using 70% H_2 feed compositions.

Discussion

It has been established that the rate data reported here were free of influence by mass and heat transfer processes. They were initial rates at the feed compositions that were introduced into the reactor. Over the 30 min. interval when the rate data were gathered, the conversion was low (< 15%) such that in all cases examined, except when the feed did not contain CO , the partial pressure of methanol increased linearly with time. This indicated that the gas composition in the reactor only changed slightly, and that the reverse reaction of methanol decomposition was not important in these measurements. When only CO_2 and no CO was used, the methanol formation rate was the highest and a carbon conversion of 15% was reached. Coupled with the fact that the equilibrium partial pressure of methanol was the lowest, the reverse reaction

of methanol decomposition was the most likely in these experiments. As shown in Fig. 1, however, the methanol pressure increase showed at most a slight curvature.

Since the experiments were performed in a batch reactor, the catalyst might not have reached a truly steady state. This could be particularly important if the nature and the activity of the catalyst vary sensitively with the gas phase composition. Results in this study, however, did not support this possibility. In every sequence of experiments performed, the gas phase compositions were varied randomly. After accounting for the catalyst deactivation, the rates of methanol formation for the same feed composition were always reproducible, and did not depend on the preceding experiment. Therefore we believe that the data represented the true behavior of the catalyst.

Data in Figs. 3 and 4 showed the inhibition effect of water. The extent of inhibition increased with increasing water partial pressure. This suggested that water is competitively adsorbed on the active site of the catalyst. The suppression of activity should not be due to deactivation by oxidation by water of the catalyst. This is because CO_2 is a stronger oxidizing agent than water, yet addition of CO_2 enhanced and not suppressed the reaction.

The increase of the rate with increasing CO_2 pressure shown in Fig. 2 is somewhat surprising in view of the results of Klier et al (12) who showed that on essentially the same catalyst, the methanol formation rate reached a maximum at a CO/CO_2 ratio of about 28/2. There are a number of differences between their measurements and ours. First, their experiments were performed at a higher pressure of 75 atm. The catalyst could behave differently although this does not seem likely. At higher pressure, condensation of methanol, water and CO_2 in the catalyst pores is possible. If such condensation did occur, diffusional effect would influence their observed kinetics. Second, their

experiments were conducted in an integral reactor and their conversions were much higher than ours. It is possible that the reverse reaction of methanol decomposition occurred in their experiments. In other words, the decrease in rate beyond the maximum on increasing CO_2 pressure could be a consequence of the much lower equilibrium methanol yield at a high CO_2 pressure. This equilibrium limitation was not present in our experiments. Third, because of the integral nature of their reactor, the gas phase composition changed along their reactor. In particular, because of the production of water by the water gas shift reaction, the rate of methanol production they measured did not correspond to the feed composition in the same way as that in our experiments. Since the rate of water production increased with the CO_2 content in the feed (see Table 2) and that water inhibited the reaction, this could result in the decrease in methanol formation rate with increasing CO_2 content in their experiments. While these are possible explanations of the differences, the answer can only be obtained by a detailed study of the effect of the different operating conditions.

In conclusion, using initial rate measurements, methanol synthesis on a Cu-Zn-O catalyst was found to be enhanced by CO_2 and suppressed by H_2O . The observation pointed to the important role of CO_2 , but it did not provide any mechanistic information. The large difference in the dependence of the rates on the feed composition obtained in this study and in an earlier study using an integral reactor pointed to the sensitivity of the catalyst behavior to the gas phase environment. It also illustrated once again the danger of deriving mechanistic information from kinetic data.

Acknowledgement

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TABLE 1. SLOW DEACTIVATION OF THE Cu-Zn-O CATALYST.

Catalyst weight = 0.4197 g

Gas composition: H₂/CO/CO₂ = 63.22/32.5/4.28

T = 225 C

P = 17.0 ± 0.1 atm

Initial CH₃OH Production rate

(10⁻⁵ moles/min-g)

Date

Nov. 14	1.80 (fresh catalyst)
Nov. 16	1.73
Nov. 23	0.86
Nov. 25	0.74
Nov. 29	0.85
Dec. 3	0.75

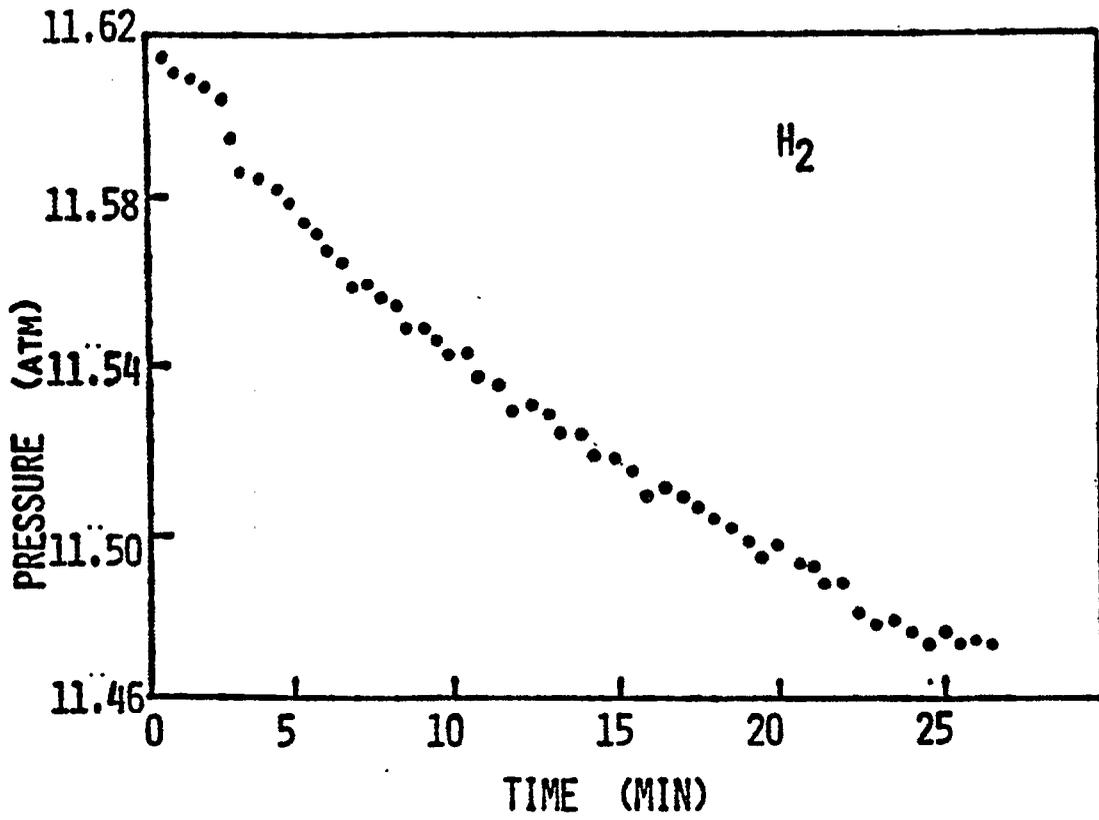
TABLE 2. RATES OF METHANOL AND WATER FORMATION IN ONE SERIES OF EXPERIMENTS.
 Cu-Zn-O (30/70). P = 16.9 ± 0.1 atm, T = 228 C, 0.2810 g catalyst

Experiment	<u>Initial gas Composition (%)</u>			<u>CH₃OH rate</u>	<u>H₂O rate</u>
	<u>H₂</u>	<u>CO</u>	<u>CO₂</u>	<u>(10⁻⁵ moles/min-g)</u>	<u>(10⁻⁵ moles/min-g)</u>
11-F	63.22	32.5	4.28	1.54	1.33
11-G	63.22	32.5	4.28	1.60	1.41
11-H	59.23	30.45	10.32	1.50	3.09
11-I	70.05	27.74	2.21	1.27	1.30
11-J	69.73	12.24	18.03	2.00	9.88
11-K	70.25	20.95	8.80	1.50	3.33
11-L	69.99	0	30.01	2.49	11.24
11-M	70.02	16.22	13.76	1.70	4.57

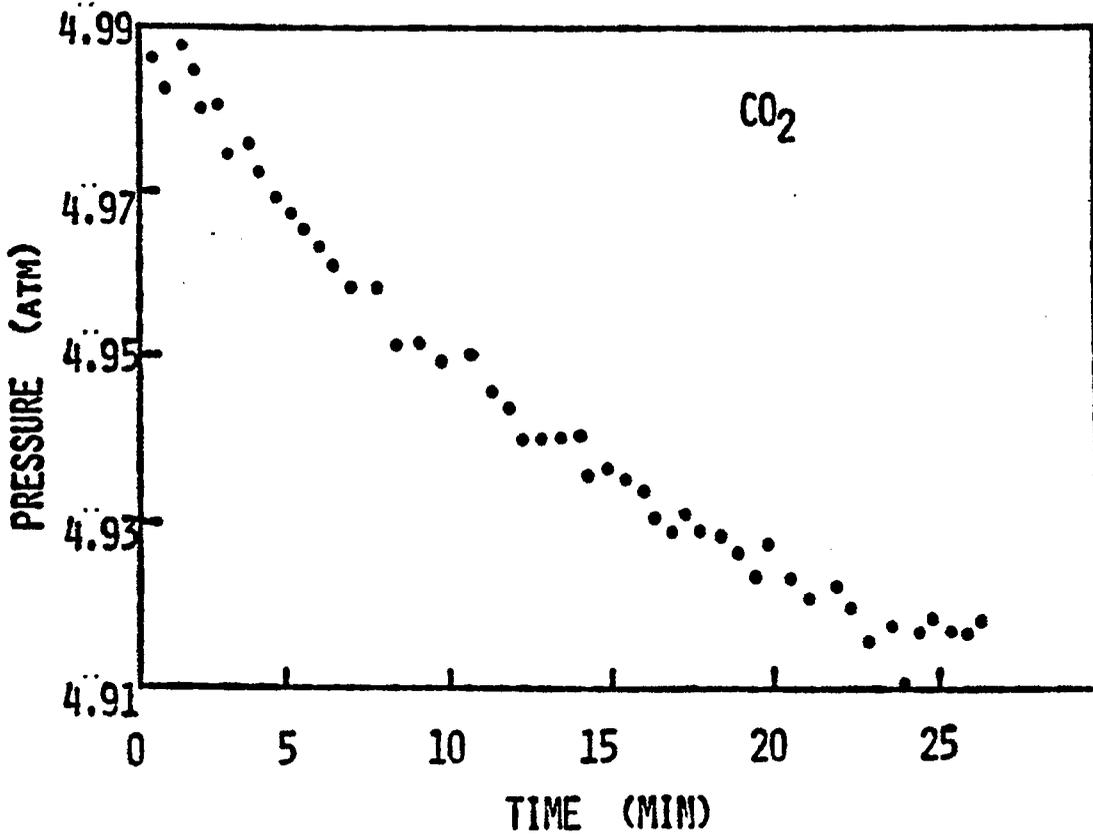
Figure Legend

- Fig. 1: The partial pressures of gases in the reactor as a function of time. Reaction conditions: 16.65 atm, 198 C, a feed composition of 70% H₂, 30% CO₂; a: H₂; b: CO₂; c: CO; d: CH₃OH; e: H₂O. 0.3578 g of catalyst was used.
- Fig. 2: The initial rates of methanol production as a function of the CO/CO₂ ratio in the feed. Feed compositions: 70% H₂, 30% CO + CO₂. The 225 C data were for a fresh charge of catalyst. The 195 C data were for a steady state catalyst.
- Fig. 3: The influence of water on the initial rates of methanol production at 198 C. Other reaction conditions: 17 atm, a feed composition of 70% H₂, 30% CO + CO₂ + H₂O. Numbers in the brackets denote the initial partial pressures of H₂O. 0.3578 g of catalyst was used.
- Fig. 4: The influence of water on the initial rates of methanol production at 225 C. Other reaction conditions: 17 atm, a feed composition of 70% H₂, 30% CO + CO₂ + H₂O. Numbers in the brackets denote the initial partial pressures of H₂O. The dotted line denotes the rate in the absence of water. 0.2810 g of catalyst was used.

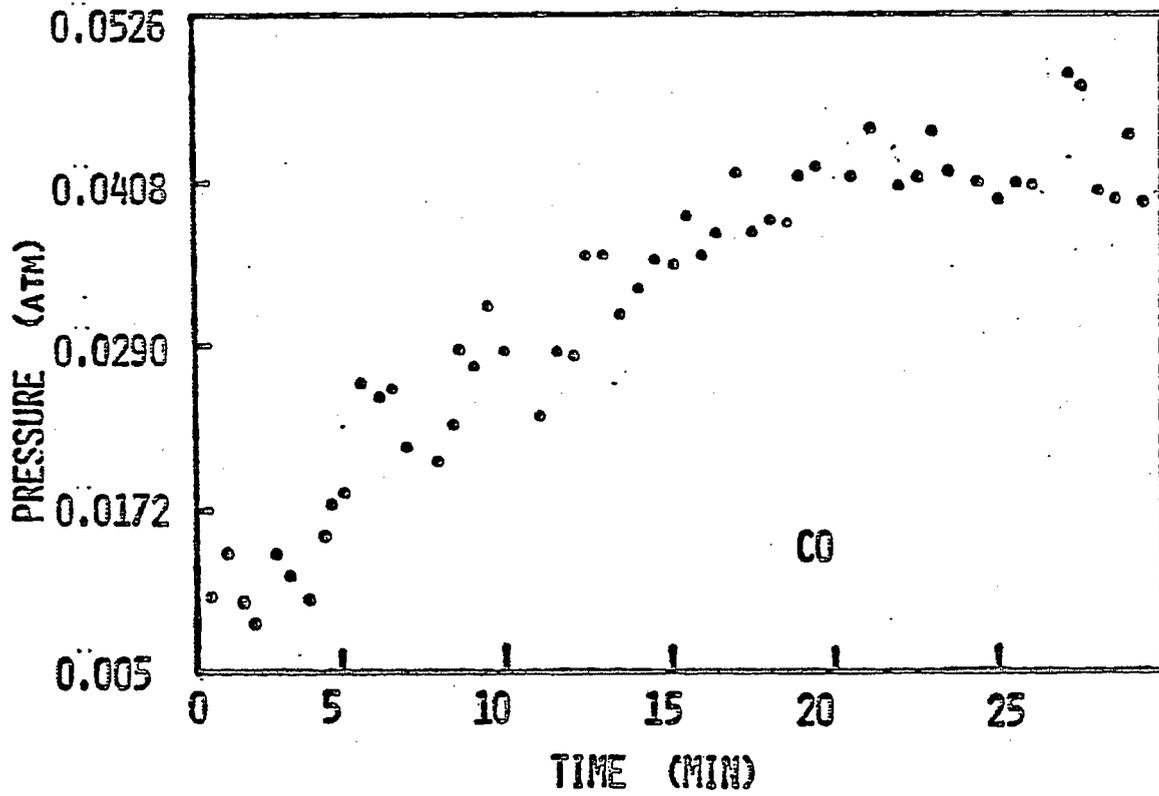
(a)



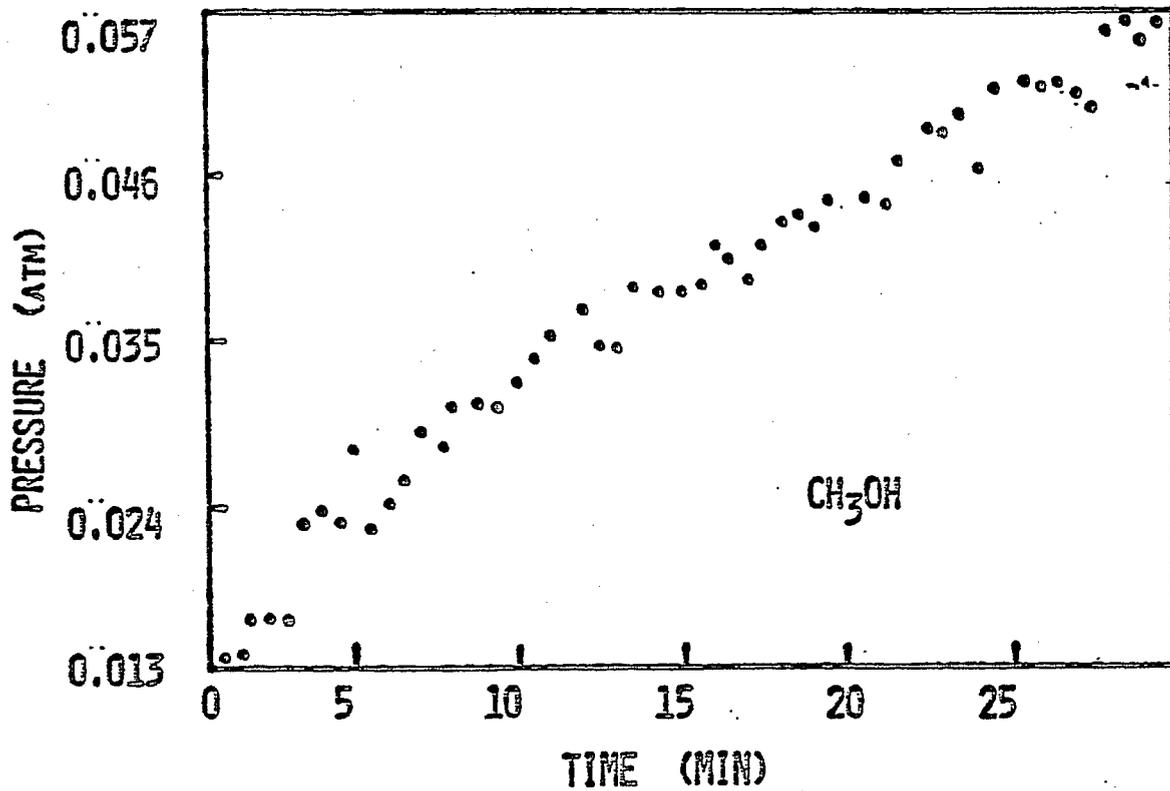
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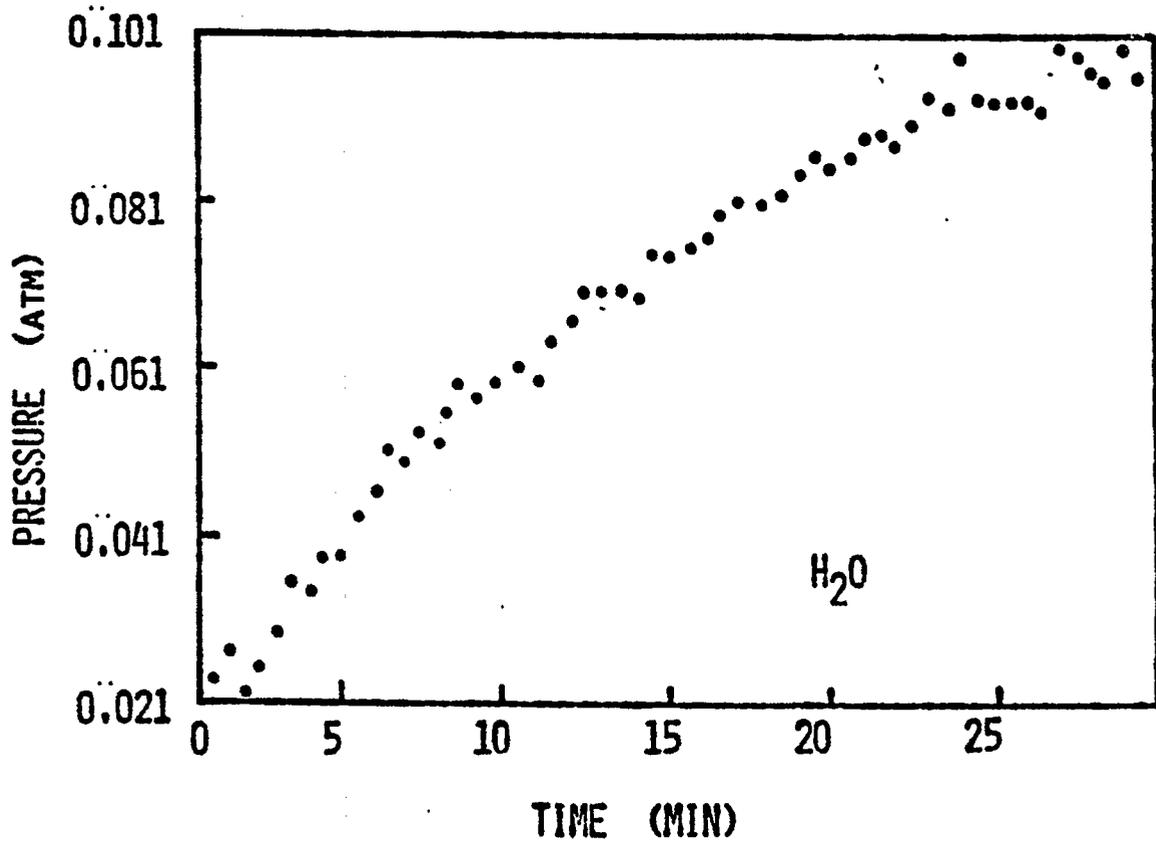
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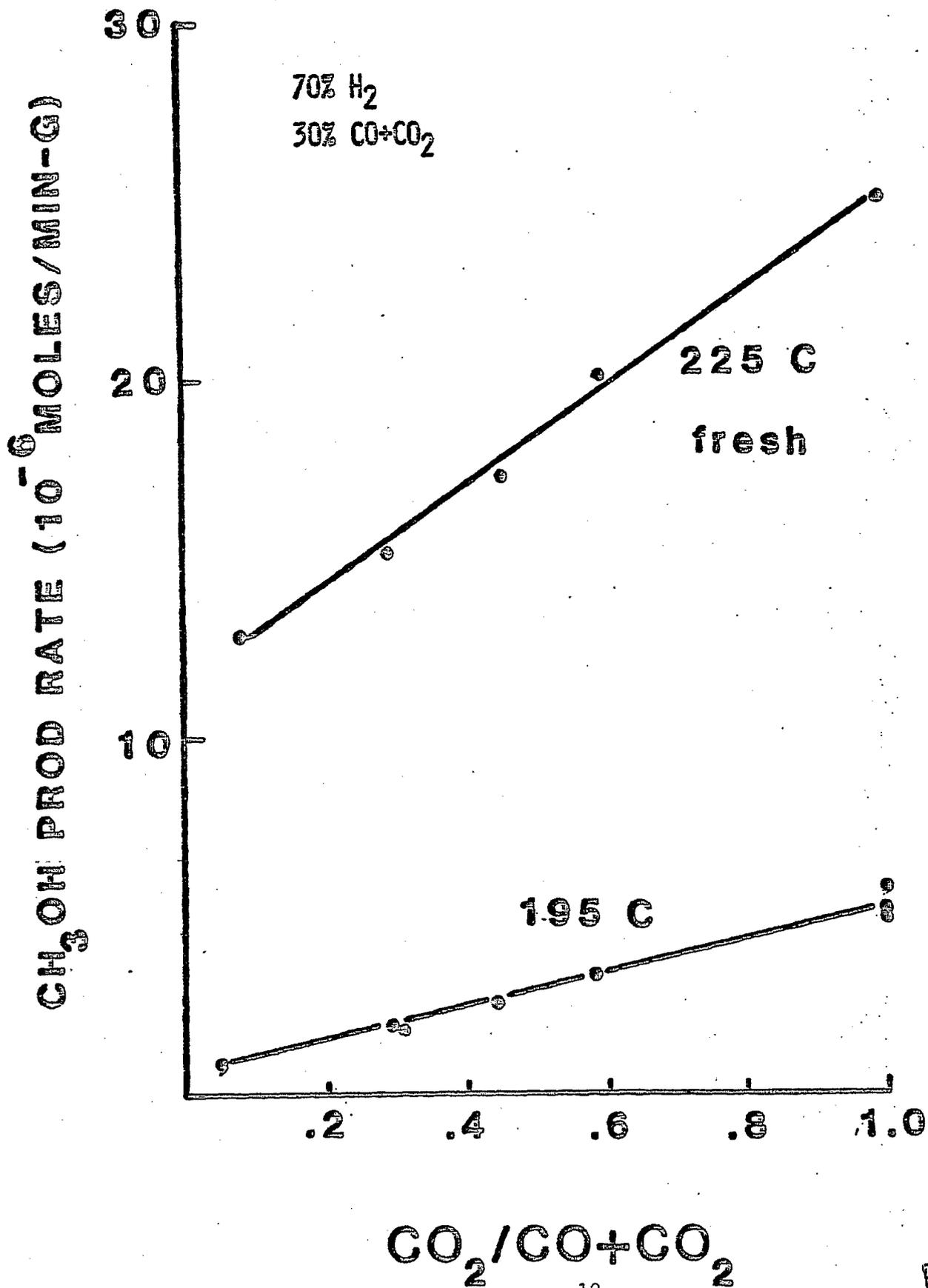


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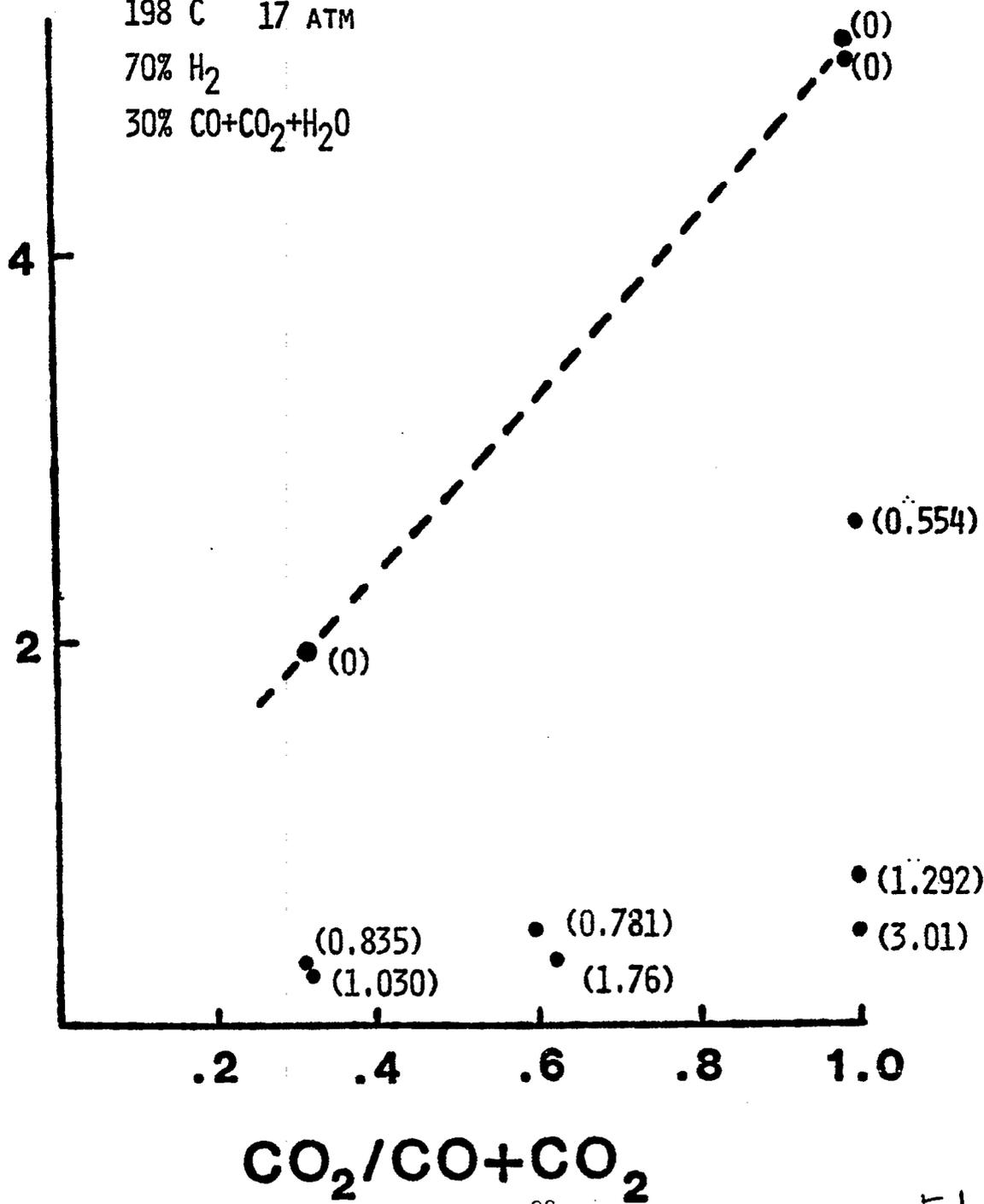
(e)





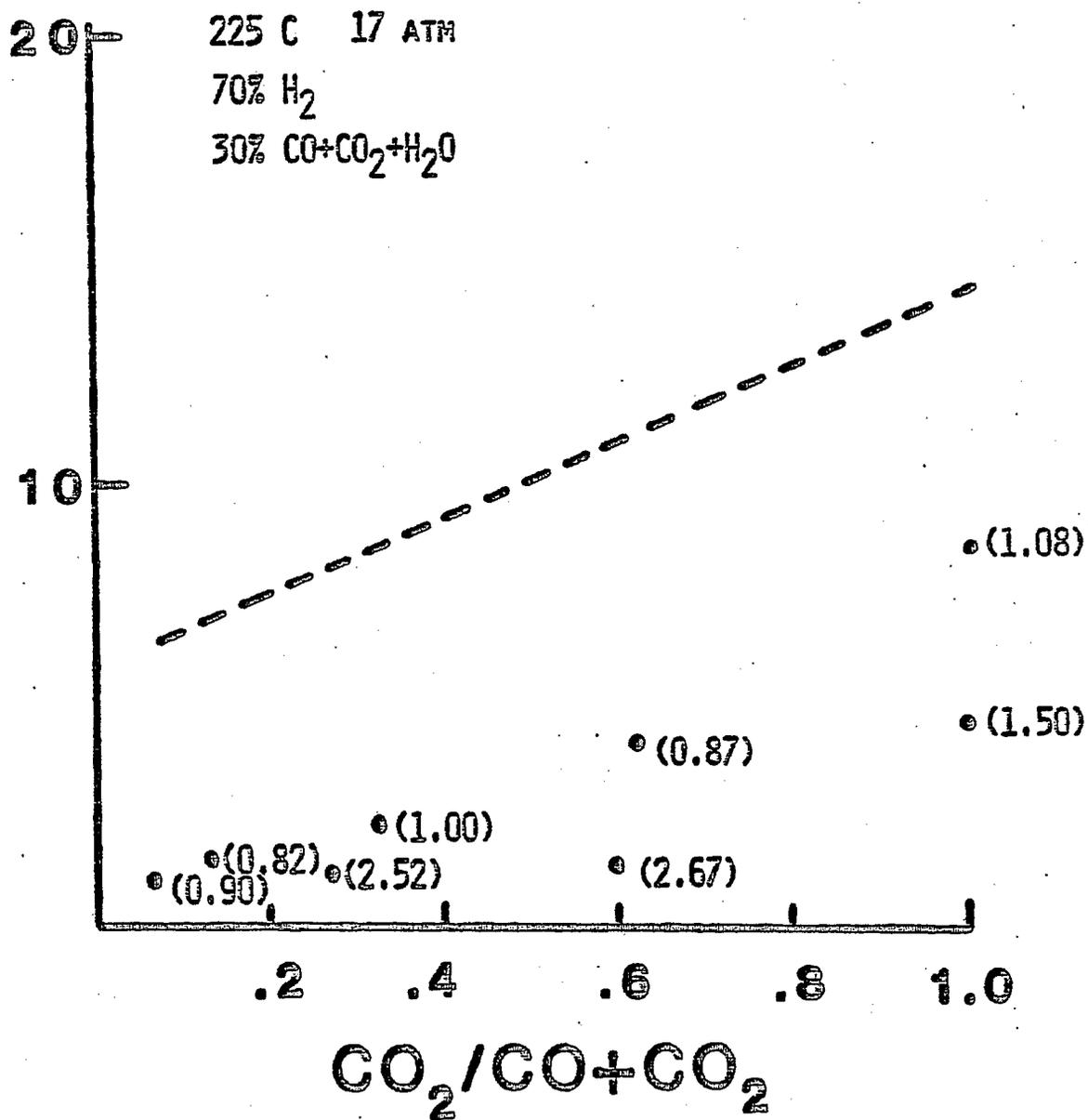
CH₃OH PROD RATE (10⁻⁶ MOLES/MIN-G)

198 C 17 ATM
70% H₂
30% CO+CO₂+H₂O



CO₂/(CO+CO₂)

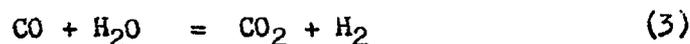
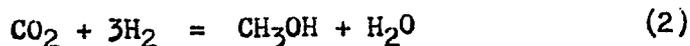
CH₃OH PROD RATE (10⁻⁶ MOLES/MIN-G)



II. C¹⁸O₂ ISOTOPE LABELING EXPERIMENT

Introduction.

Results from the previous section and from other laboratories have indicated clearly the important effects of CO₂ in the methanol synthesis reaction. In terms of the macroscopic reaction mechanism, three reactions can be readily identified:



It is of interest to identify the relative contributions of CO and CO₂ to the methanol formation. Unfortunately, because of the water-gas shift reaction (reaction 3), methanol formation from CO or CO₂ cannot be determined directly from the rate of disappearance of the reactants. It is, however, possible to obtain the information by isotopically labelling the reactant species. For example, when C¹⁸O₂ is used, methanol produced from it will be CH₃¹⁸O, while methanol produced from CO will be CH₃¹⁶OH. Therefore, measuring the rates of formation of methanol-¹⁶O and methanol-¹⁸O provides directly the rates of reactions (1) and (2). This, of course, assumes that the measurements are made before substantial isotopic exchange between CO and CO₂ occurs.

Experimental.

The same batch reactor system, as the one used in section I, was used. The catalyst, and its pretreatment before each reaction, were also the same. For reaction measurements, C¹⁸O₂ (98% pure) was first put into the premixer. It was followed by CO, and H₂ to a desired composition of CO₂/CO/H₂ of 2/28/70. The mixture was then fed into the reactor at 200C and measurement was begun.

Results.

The initial rates of production of methanol-¹⁶O and methanol-¹⁸O were determined together with C¹⁸O₂, C¹⁸O¹⁶O, and C¹⁶O₂. They were determined by monitoring the intensities of the various m/e peaks listed in Table 3. These intensities were then converted into the mole fractions after correcting for the cracking patterns and the mass spectrometer sensitivities, which were independently determined. The rate of reaction (or production) of the various species as determined from the various m/e intensities are listed in Table 3.

The rate of production of CH₃OH-¹⁸O can be taken as the rate of change of m/e = 33 or 34, and the rate of production of CH₃OH-¹⁶O as the rate of change of m/e = 31 or 32. The data in Table 3 show that depending on the peaks used, the production rates varied. We attribute this to the low signal intensity such that the background influence on the signals was large. Nonetheless, the ratio of the rates of production of CH₃OH-¹⁶O/CH₃OH-¹⁸O was estimated to be 0.3 to 1.0. Since these are initial rate measurements, it can be concluded that methanol is produced from CO₂ about twice as fast as from CO.

The data also showed that the rates of production of C¹⁶O₂ and C¹⁶O¹⁸O were very rapid. The process that led to the appearance of these products is the exchange of lattice oxygen with gas phase CO₂. The results showed that this exchange process is at least five times faster than the methanol production rate.

Finally, the rate of water-gas shift reaction was estimated from the production of H₂¹⁸O. It was found to be about the same or twice as fast as the production of methanol.

Table 3

Relative Reaction Rates with $C^{18}O_2$ Corrected for Cracking

<u>AMU</u>	<u>Parent Species</u>	<u>Rate (amps)*</u>
2	H_2	$(- 1.7 \times 10^{-9} \pm 0.7)$
17	$H_2^{16}O$	$6.2 \times 10^{-14} \pm 5$
18	$H_2^{16}O$	$- 3.9 \times 10^{-12} \pm 2.8$
19	$H_2^{18}O$	$(2.6 \times 10^{-13} \pm 0.7)$
20	$H_2^{18}O$	$(1.5 \times 10^{-12} = 0.1)$
28	$C^{16}O$	$- 7.4 \times 10^{-10} \pm 0.2$
29	$CH_3^{16}OH$	$- 8.9 \times 10^{-12} \pm 0.4$
30	$C^{18}O$	$2.8 \times 10^{-11} \pm 0.5$
31	$CH_3^{16}OH$	$6.0 \times 10^{-13} \pm 1.6$
32	$CH_3^{16}OH$	$1.2 \times 10^{-13} \pm 0.8$
33	$CH_3^{18}OH$	$(6.0 \times 10^{-13} \pm 0.3)$
34	$CH_3^{18}OH$	$(3.7 \times 10^{-13} \pm 0.3)$
44	$C^{16}O_2$	$(2.0 \times 10^{-12} \pm 0.1)$
46	$C^{16}O^{18}O$	$(8.5 \times 10^{-12} \pm 0.1)$
48	$C^{18}O_2$	$(- 7.7 \times 10^{-12} \pm 0.7)$

*Values in parentheses are identical to the uncorrected values.

III. THE RELAXATION METHOD FOR CATALYTIC REACTIONS.

Introduction

Relaxation towards chemical equilibrium has been a useful method to measure the kinetics of a chemical reaction (1). The usefulness relies on the fact that, according to the postulates of nonequilibrium thermodynamics (2,3), the net flux of a reaction, J , near chemical equilibrium is linearly proportional to the Gibbs free energy difference of the reaction, ΔG :

$$J = X(-\Delta G/RT) \quad (1)$$

where X is the proportionality constant known as the equilibrium exchange rate. For an elementary reaction, it has been shown that X equals the forward rate (which equals the reverse rate) of the reaction at equilibrium (2). Because of this physical significance of X , much work has been performed using the relaxation method to determine the rate constants of very fast reactions (4).

The simple relation of Eq. (1) offers another application of the relaxation method, namely, the determination of the individual fluxes of reactions in a reaction network where the number of independent chemical species is less than the number of reactions. This application could be very valuable if equation (1) can be applied to nonelementary reactions as well. This paper explores the physical meaning of X in a nonelementary reaction, and presents a method of data analysis to extract the values of X 's in a relaxation experiment.

Mathematical formulation of the relaxation process

In a reaction system that contains m number of reactions and n number of chemical species of which g are independent (the remaining $n-g$ species may be related by mass conservation equations), the ΔG of the system is given by:

$$\Delta G = \sum_j^m \sum_i^n v_{ij} \mu_i \quad (2)$$

where v_{ij} is the reaction stoichiometry of species i in reaction j . Choosing

chemical equilibrium as the standard state, for small deviation from equilibrium, the chemical potential μ_i can be expressed as:

$$\mu_i = RT \ln C_i / C_i^* \approx RT(C_i - C_i^*) / C_i^* = RT \Delta_i \quad (3)$$

where the superscript * denotes equilibrium. Combining equations (1) to (3),

the net flux of reaction j, J_j is then

$$J_j = X_j \left(- \sum_i \nu_{ij} \Delta_i \right) \quad (4)$$

Equation (4) can be used to describe the change in the concentration of each chemical species on relaxation:

$$\frac{dC_i}{dt} = \sum_j \nu_{ij} J_j = - \sum_j X_j \nu_{ij} \sum_i \nu_{ij} \Delta_i$$

It can readily be shown that this system of rate equations can be expressed in the matrix form as:

$$\frac{d\Delta}{dt} = X \Delta \quad (5)$$

where C_i^* is a diagonal matrix whose elements are C_i^* ; Δ is a vector $(\Delta_1, \Delta_2, \dots, \Delta_n)^T$

and X is an $n \times n$ matrix with elements $X_{kl} = - \sum_j \nu_{kj} \nu_{lj} X_j$.

One can see that $X_{kl} = X_{lk}$, and the matrix X is symmetric.

The meaning of X in a nonelementary reaction

Consider a series reaction $A \rightarrow B \rightarrow C \dots \rightarrow P$ in which the exchange rate of the individual elementary steps are X_1 for $A \rightarrow B$, X_2 for $B \rightarrow C$, and X_n for $P-1 \rightarrow P$, etc. The system is allowed to relax the equilibrium. The relaxation is described by Eq. (5) as:

$$\begin{bmatrix} \frac{d\Delta_A}{dt} \\ \vdots \\ \frac{d\Delta_i}{dt} \\ \vdots \\ \vdots \end{bmatrix} = \begin{bmatrix} \frac{-X_1}{C_A^*} & \frac{-X_1}{C_A^*} & 0 \\ \vdots & \vdots & \vdots \\ 0 & \dots & 0 & \frac{X_{i-1}}{C_i^*} & - \frac{X_{i-1} + X_i}{C_i^*} & \frac{X_i}{C_i^*} & 0 \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} \Delta_A \\ \vdots \\ \Delta_i \\ \vdots \\ \vdots \end{bmatrix} \quad (6)$$

In order that the relaxation can be meaningfully represented by an overall reaction $A \rightarrow P$, it must be assumed that during relaxation, the time rate of change of all intermediate species are negligibly small compared to the rate of change of A and P . This can be achieved when B^* , C^* ... $P-1^*$ are small in comparison to A^* and P^* . Under such conditions, there is only one nonzero eigenvalue λ which is much smaller than the other eigenvalues (5), and this eigenvalue can be obtained by expanding λ in an asymptotic series and keeping the first term (the constant term is zero because $\lambda = 0$ is a solution as the system is governed by one mass conservation equation). It has been shown that the solution is (5):

$$\frac{1}{\lambda} = \left(\frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n} \right) \left(\frac{1}{A^*} + \frac{1}{P^*} \right)^{-1} \quad (7)$$

If the reaction $A \rightarrow P$ is one step, the relaxation time constant can be similarly found to be:

$$\lambda = X_0 \left(\frac{1}{A^*} + \frac{1}{P^*} \right) \quad (8)$$

Comparison of Eq. (7) and (8) shows that the overall exchange rate, X_0 , is related to the individual exchange rates as:

$$\frac{1}{X_0} = \frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n} \quad (9)$$

This relationship defines the analogy between a reaction network and an electrical circuit, which is present when the reaction system is near equilibrium, and when there is no accumulation of reaction intermediates.

A method to extract equilibrium exchange rates from relaxation data

Equation (5) describes in general the relaxation behavior of a chemical reaction system. The equation can be converted into an eigenvalue problem with the following manipulation:

$$\underset{\sim}{C}^{*-1/2} \underset{\sim}{C}^* \frac{dA}{dt} = \underset{\sim}{C}^{*-1/2} \frac{dA}{dt} = \underset{\sim}{C}^{*-1/2} X \underset{\sim}{C}^{*-1/2} \underset{\sim}{C}^{*1/2} A \quad (10)$$

In this equation, $\underset{\sim}{C}^{*1/2}$ and $\underset{\sim}{C}^{*-1/2}$ are diagonal matrices whose elements are $C_i^{*1/2}$

and $C_i^{*-1/2}$, respectively. It can easily be shown that the matrix $\underset{\sim}{C}^{*-1/2} \times \underset{\sim}{C}^{*-1/2}$ is also a symmetric nxn matrix. If this system has g independent chemical species, then this matrix will have a rank of g, and there are g nonzero eigenvalues and n-g zero eigenvalues. Furthermore, because this matrix is symmetric, there are n orthogonal eigenvectors.

The procedure to obtain the equilibrium exchange rates is to first identify the n-g eigenvectors of $\lambda = 0$. They can be constructed from the mass conservation equations and then orthogonalized using a standard matrix operation. Then experiments are performed to find the remaining orthogonal eigenvectors. Once these vectors are found, the corresponding λ 's are determined from the relaxation data. Since:

$$\underset{\sim}{C}^{*-1/2} \times \underset{\sim}{C}^{*-1/2} \underset{\sim}{C}^{*1/2} \underset{\sim}{\Delta} = \underset{\sim}{C}^{*-1/2} \underset{\sim}{\Delta} \underset{\sim}{\Delta} \quad (11)$$

it follows that:

$$\underset{\sim}{X} = \underset{\sim}{C}^* \underset{\sim}{\Delta} \underset{\sim}{\Delta} \underset{\sim}{\Delta}^{-1} \quad (12)$$

where $\underset{\sim}{\Delta}$ is the eigenvalue matrix. This method is similar to that of Wei and Prater for reaction networks that follow first order kinetics (6). An example of this using the methanol synthesis reaction of a Cu-Zn-O catalyst will be given.

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