

Methanolization under pressure of carbon oxides and their mixture on Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts. Role of carbon dioxide.

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The hydrogenation of carbon oxides into methanol is a reaction known for a long time. Formely it was believed that methanolization of CO<sub>2</sub> proceeded via the intermediacy of CO (1). More recently, Bashkirov et Al.(2) have shown that reduction of CO<sub>2</sub> into CO and methanol could not be consecutive reactions since they both took place when contact time tended to zero; they reported as Temkin et Al.(3) that methanol formation from CO decreased dramatically if the presence of CO<sub>2</sub> or water was strictly eliminated from the reactive gases. Then it was concluded that methanolization of CO<sub>2</sub> proceeded through a direct pathway whereas that of CO involved the intermediacy of CO<sub>2</sub> through the water gas shift reaction. On the contrary, Klier et Al.(4) proposed that the role of CO<sub>2</sub> in a mixture of carbon oxides is to keep the catalyst in an oxidation state favourable to CO hydrogenation which was regarded as the main reagent leading to methanol. We report here some results which support the hypothesis of Bashkirov but do not exclude the oxidative role of CO<sub>2</sub>.

#### EXPERIMENTAL

The CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> (65/25/10) catalyst used is an industrial one prepared by precipitation of nitrates mixture by potassium carbonate at pH 7. Its surface area is about 50 m<sup>2</sup>/g. 5mg of this catalyst diluted in 500 mg of quartz powder are introduced in a 1/4" differential flow reactor and reduced for 12 hr at 300°C in a hydrogen stream (3l/hr; heating rate: 3°C/mm). Then the mixture of reactive gases (CO + 2H<sub>2</sub>, CO<sub>2</sub> + 3H<sub>2</sub>, or 23CO + 7CO<sub>2</sub> + 70H<sub>2</sub>) kept in a pressurized steel container is passed through the catalytic bed (22bar, 2l/hr), depressurized downstream the reactor in a heated upstream pressure regulating valve and chromatographically analyzed on line.

Higher conversion experiments are performed in a 3/8" integral flow reactor (22bar, 2l/hr, 2,2g of catalyst); downstream the reactor, the products are partially trapped at ambient temperature and effluent gases are analyzed as above. All reactive gas mixtures are used with their residual moisture.

#### RESULTS AND DISCUSSION

The results obtained in the differential flow reactor (22bar, 2l/hr, 5mg of catalyst) are represented in the figure. As observed under atmospheric pressure (5), the formation of methanol under 22bar, from either CO or CO<sub>2</sub> shows a maximum versus temperature. The maximum obtained from CO<sub>2</sub> is higher and situated at a lower temperature than that from CO. Moreover the only significant by-product from CO<sub>2</sub> is CO, whereas hydrocarbons and higher alcohols are formed in important proportions

from CO. Thus the methanolization of  $\text{CO}_2$  under the present conditions proves to be more active, more selective and to proceed at a lower temperature than that of CO. These results support the hypothesis of Bashkirov (2) according which  $\text{CO}_2$  can be hydrogenated directly into methanol, without the intermediacy of CO; indeed the methanolization of  $\text{CO}_2$  proceeds at a temperature which does not allow significant hydrogenation of CO. Thus the hydrogenation of CO and  $\text{CO}_2$  must involve two distinct reaction pathways, the latter being more rapid. Nevertheless these results are in disagreement with those of Klier et Al. (4) who observed that hydrogenation of CO into methanol was more active and selective than that of  $\text{CO}_2$  and concluded in the opposite way. The difference in catalyst composition and preparation may be the reason of such a divergence since Sneed et Al. (6) observed that the ratio of methanol formation maxima from CO and  $\text{CO}_2$  could be reversed by changing the nature of the catalyst.

Experiments were also performed in the integral reactor (22bar, 21/hr; 2,2g of catalyst), whose results are reported in table 1.

Table 1: Conversion of carbon oxides into methanol( $x\%$ ) and methanol concentrations measured( $C\%$ ) or theoretical equilibrium values( $C_{eq}$ ) at determined temperatures.

Reagents	T °C	$x\%$	$C\%$	$C_{eq}$
$\text{CO} + 2\text{H}_2$	246	11,8	4,5	11
$\text{CO}_2 + 3\text{H}_2$	225	7,2	3,5	3,8
$2\text{CO} + 7\text{CO}_2 + 7\text{OH}_2$	230	31,3	11,6	12

The theoretical equilibrium values of methanol concentrations were calculated from relations reported in reference 4.

It can be seen that the thermodynamic equilibrium is nearly reached in the case of  $\text{CO}_2$  or CO,  $\text{CO}_2$  mixture, but not with CO. These results confirm the high reactivity of  $\text{CO}_2$  already observed in differential conditions which are governed by kinetics; in the integral reactor the  $\text{CO}_2$  conversion is lower than that of CO because of thermodynamic limitations.

As was reported by Klier (5) and other workers (1), the CO, $\text{CO}_2$  mixture leads to the best results; according to the former the role of  $\text{CO}_2$  in such a mixture is to keep the catalyst in an oxidized form  $\text{Cu}^{\text{I}}$  which would favour CO hydrogenation. In the light of our results we can propose a complementary explanation: taking into account its high reactivity,  $\text{CO}_2$  may well be the main reagent leading to methanol. Each reduced  $\text{CO}_2$  molecule leads to one of methanol and one of water; this latter can react in the presence of CO according to the water gas shift reaction which is kinetically and thermodynamically favoured under the present conditions. Thus, the equilibrium  $\text{CO}_2 + 3\text{H}_2 = \text{MeOH} + \text{H}_2\text{O}$  can be displaced to the right and then the low thermodynamic limitations in the case of pure  $\text{CO}_2$  can

be overstepped. In order to evaluate the realism of such a proposal, the influence of water content on the methanolization of CO was studied under atmospheric pressure ( table 2 ).

Table 2: Influence of water content in CO + 2H<sub>2</sub> mixture on CO hydrogenation at 220°C ( 1bar, 2l/hr, 175mg of catalyst ).

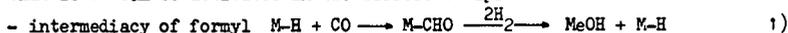
Water content	.5ppm (a)	residual moisture	6000ppm	2%
Methanol concentration ( ppm )	60	400	500	300

(a) dehydration of gas is performed by trapping in acetone-dry ice bath.

It must be pointed out that for each water content, CO<sub>2</sub> is obtained almost quantitatively from reaction of water and CO. Thus no kinetic limitation can restrict the conversion of CO into CO<sub>2</sub> during the hydrogenation of CO, CO<sub>2</sub> mixtures.

The results in table 2 show that methanolization rate of CO is very low in the absence of water; but traces of water are sufficient to reactivate the process; in this case the intermediacy of CO<sub>2</sub> is unlikely because of its low partial pressure. Higher water contents inhibit methanol formation probably for kinetic reasons.

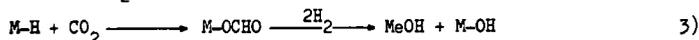
These results support the mechanism already proposed by Sneed et Al.(6), that is CO can be activated in two different ways:



This process may occur mainly in the absence of water and proves to be very slow; it may also lead to C-C bond formation.



The same formate intermediate shown by Deluzarche et Al.(7) by chemical trapping can be formed from CO<sub>2</sub>:



The processes 2 and 3 prove to be rapid according to our results. The M-OH species which allows rapid activation of CO may be an oxidized form of copper as proposed by Klier (4); in agreement with these workers the conservation of such a species may involve the presence of CO<sub>2</sub> or water as can be illustrated by equations 3' and 4



### CONCLUSION

The comparative study of hydrogenation under pressure of CO and CO<sub>2</sub> has shown that CO<sub>2</sub> leads to methanol more rapidly, more selectively and at a lower temperature than CO. These results support the hypothesis of Bashkirov which suggests that methanolization of CO<sub>2</sub> proceed without the intermediacy of CO.

Moreover the hydrogenation of CO proves to be dramatically dependent of the presence of CO<sub>2</sub> or water; the role of these products may be to keep the catalyst in a suitable oxidized form. At high conversion the hydrogenation of CO in CO,CO<sub>2</sub> mixtures may also proceed at least partially through water gas shift reaction via the intermediacy of CO<sub>2</sub>.

### REFERENCES

- 1/ G. NATTA Catalysis, Emmett (Reinhold New-York) III, 349, 1955
- 2/ A.N. BASHKIROV et Al. Kinetics and Catal. 16, 704 and 706, 1975, *ibid* 17, 380 and 1132, 1976
- 3/ V.D. KUZNETSOV, F.S. SHUB and M.I. TEMKIN *ibid* 23, 788, 1982
- 4/ K. KLIER et Al. J. Catal. 74, 343, 1982
- 5/ R. BARDET, J. THIVOLLE-CAZAT, Y. TRAMBOUZE J. Chim Phys 78, 135, 1981
- 6/ B. DENISE and R.P.A. SNEEDEN J. Mol. Catal. 17, 359, 1982
- 7/ A. DELUZARCHE et Al. React. Kinet. Catal. Lett 16, 207, 1981

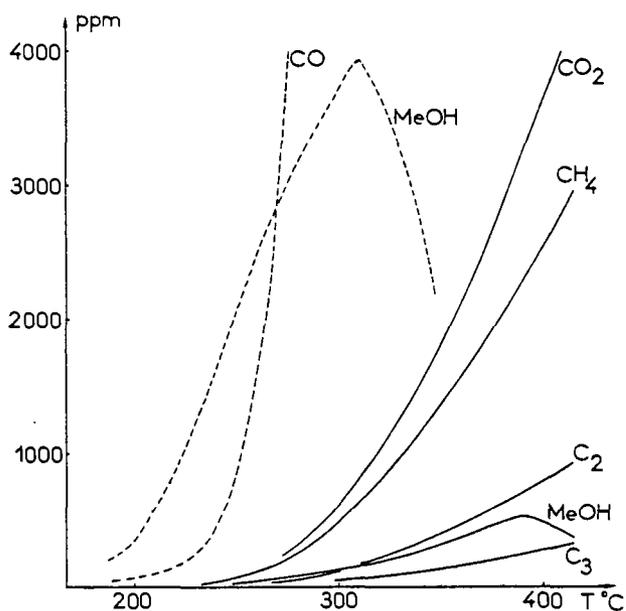


Figure: Evolution of products concentration versus temperature, during CO (—) or CO<sub>2</sub> (---) hydrogenation (22bar, 2l/hr, 5mg of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst).

The Effect of CO<sub>2</sub> and H<sub>2</sub>O in the Methanol Synthesis Reaction on Cu-Zn-O

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Introduction:

Methanol production over a copper-zinc oxide catalyst has been extensively investigated recently. With regard to the effect of the feed composition, Klier et al. reported a detailed measurement of the rate of methanol production as a function of the CO/CO<sub>2</sub> ratio (1). They observed a sharp maximum at a CO/CO<sub>2</sub> of about 28/2. Later, they also reported the effect of H<sub>2</sub>O in the feed. Again, an optimum H<sub>2</sub>O partial pressure was observed (2). The data were interpreted with the change in the active site concentration on varying feed composition, and competition of the active site by CO<sub>2</sub> and water.

Since these data indicated a strong dependence of the kinetics on the gas composition, it became interesting to try to determine the kinetics at well-controlled gas compositions. This can be achieved either by using a differential flow reactor, or by using a batch reactor and performing initial rate measurements. This paper describes results of the latter approach.

Experimental and Results:

Briefly, the experiments were conducted in a batch well-stirred reactor at about 200°C. The total pressure was about 17 atm. The catalyst was prepared according to Herman et al. (3). It has a CuO/ZnO of 30/70. All the data were obtained in the absence of diffusional effect. The catalyst was first reduced by H<sub>2</sub>/N<sub>2</sub>, and then preconditioned by a mixture of CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>3</sub>OH, which was also used to calibrate the mass spectrometer. The rate of methanol production was measured by monitoring the gas composition with the mass spectrometer.

Table 1 shows the initial rates of methanol production as a function of the feed gas composition.

Table 1.

T°C	Initial Gas Composition (%)				CH <sub>3</sub> OH rate	H <sub>2</sub> O rate
	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	10 <sup>-5</sup> moles/min-g	10 <sup>-5</sup> moles/min-g
228	70.05	27.74	2.21	0	1.27	1.30
	70.25	20.95	8.80	0	1.50	3.30
	70.02	16.22	13.76	0	1.70	4.57
	69.73	12.24	18.03	0	2.00	9.88
	69.99	0	30.01	0	2.49	11.24
220	71.13	26.3	1.66	0.90	0.118	-
	69.62	25.8	3.76	0.82	0.155	-
	70.45	19.80	7.23	2.52	0.138	-
	69.44	20.11	9.45	1.00	0.225	-
	69.57	11.40	18.16	0.87	0.410	-
	69.70	0	28.80	1.50	0.469	-

It can be seen from the data in the table that unlike previous results, the initial rates of methanol production increase with increasing CO<sub>2</sub>/CO ratio, and the addition of water greatly suppresses the rate. Parallel to the methanol production, the rate of water production also increases with increasing CO<sub>2</sub>/CO ratio. Similar trend was observed at a lower temperature of 197°C.

The effect of water can be explained by the competitive adsorption of water at the active site. The effect of CO<sub>2</sub>, however, must indicate other reasons. Since these were initial rate measurements, the catalyst can be assumed to be in an identical state for all the measurements, (except for a slow deactivation which did not change the dependence on the feed composition), the positive effect of CO<sub>2</sub> may indicate that the hydrogenation of CO<sub>2</sub> is faster than that of CO, or that the hydrogenation of CO is enhanced by coadsorption of CO<sub>2</sub> which may facilitate the formation of some unstable intermediates.

To investigate the rate of hydrogenation of CO<sub>2</sub> in the feed mixture, C<sup>18</sup>O<sub>2</sub> was used. Using conditions similar to those used in Table 1 with a CO/CO<sub>2</sub> ratio of about 4/1, it was found that the initial rate of production of CH<sub>3</sub>OH-<sup>16</sup>O was about as fast as the rate of production of CH<sub>3</sub>OH-<sup>18</sup>O. The results indicated clearly the importance of the hydrogenation of CO<sub>2</sub> in methanol production.

Another interesting result is on the rate of the isotope exchange reaction of CO<sub>2</sub>:



This exchange reaction proceeds at a reasonable rate in a mixture of CO<sub>2</sub> and He, and CO<sub>2</sub> and CO. The rate is greatly enhanced in a mixture of H<sub>2</sub>, CO, and CO<sub>2</sub> with the rapid production of C<sup>18</sup>O. This result can be explained by the rapid reversible water gas shift reaction, which scrambles the oxygen in CO and CO<sub>2</sub>, presumably via a formate intermediate.

#### References:

- (1) K. Klier, V. Chatikavanij, R.G. Herman, and G.W. Simmons, *J. Catal.*, **74**, 343 (1982).
- (2) K. Klier, presented in the Materials Research Society Conference, Boston MA, November 1983.
- (3) R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, J.B. Balko, and T.P. Kobylinski, *J. Catal.*, **56**, 407 (1979).

#### Acknowledgement:

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MECHANISM AND INTERMEDIATES OF METHANOL SYNTHESIS OVER THE Cu/ZnO  
CATALYST IN THE PRESENCE OF WATER AND CARBON DIOXIDE

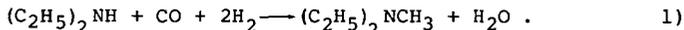
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INTRODUCTION

Since Sabatier's first experiments on heterogeneously catalyzed methanol decomposition (1), many studies have been devoted to the mechanism of both the decomposition and the synthesis of methanol, and surface intermediates such as formyl (2,3), formate (4-6), and methoxide (4,5) have been identified by IR spectroscopy and chemical trapping techniques. In a previously reported (7) study from our laboratory, it was found that the methanol synthesis rate over Cu/ZnO catalyst is greatly enhanced by small additions of water to the synthesis gas while large additions of water resulted in a decrease in synthesis rate. Comparison of the water effect with that of CO<sub>2</sub> on the synthesis rate (8) showed that water behaved as a more effective promoter at low concentrations and a more severe retardant at higher concentrations than did equimolar carbon dioxide at the same experimental conditions. Further, injection of a 65/35 mole % mixture of  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  to synthesis gas resulted in <sup>18</sup>O incorporation, the % <sup>18</sup>O in CH<sub>3</sub>OH, CO and CO<sub>2</sub> in the exit stream being 3.41, 0.60 and 3.56, respectively. These results indicated that H<sub>2</sub>O and/or CO<sub>2</sub> participate in methanol synthesis as reactants. D<sub>2</sub>O addition to the synthesis gas was employed to further determine the kinetic and mechanistic role of water, and it was observed that a significant portion of the synthesized methanol occurred as CH<sub>2</sub>DOH. No CHD<sub>2</sub>OH or CD<sub>3</sub>OH was detected, and these results indicated that water was involved in the formation of an intermediate with one single hydrogen atom. This observation was further supported by the promotion of isotopic scrambling between <sup>12</sup>C<sup>18</sup>O and <sup>13</sup>C<sup>16</sup>O by water preadsorption on the catalysts.

Chemical trapping experiments were also used (7) in identifying reactive intermediates involved in methanol synthesis. When diethylamine was continuously injected along with the synthesis gas, methylated tertiary amine was selectively obtained by the reaction:



At 215°C, H<sub>2</sub>:CO = 70:30, 75 atm and a molar feed rate of diethylamine = 14.5 mmol/2.45 g cat/hr, the yield of methyldiethylamine was 11.2 mmol/2.45 g cat/hr and 97% of the water formed during methylation of diethylamine was converted to carbon dioxide by the water gas shift reaction. Amine addition, however, was not found to affect the water gas shift reaction. The intermediate trapped by amine behaved chemically as formyl, formaldehyde or hydroxycarbene. The evidence for an aldehydic intermediate was further corroborated by utilizing it for aldol addition with propanaldehyde followed by hydrogenation to give 2-methyl-1-propanol. Although both the above trapping reactions allowed a fairly complete mechanism to be formulated, it was still deemed necessary to address some alternative trapping and side reactions, particularly those of amines with surface formates.

It is known that (9) amines react with carboxylic acids to give acid amides, which could be hydrogenated to the corresponding amines (10). In order to determine whether the added diethylamine reacted more rapidly with surface formyl or formate, the hydrogenation of N,N-diethylformamide, a suspected intermediate of the reaction of surface formate with diethylamine, was studied. It is reported herein that non-dissociative hydrogenation of N,N-diethylformamide occurs at a lower rate than the addition of synthesis gas to diethylamine 1), indicating that the amine trapped the aldehydic and not the formate intermediate under the synthesis conditions.

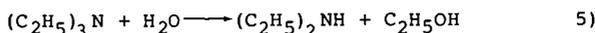
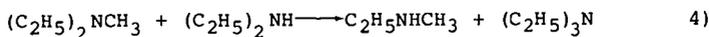
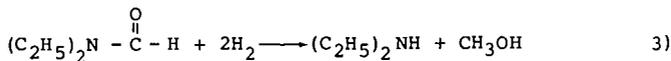
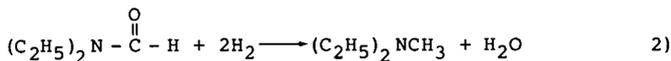
#### EXPERIMENTAL

The Cu/ZnO = 30/70 mol % catalysts were coprecipitated from nitrate solution by Na<sub>2</sub>CO<sub>3</sub>, calcined, pelletized, and reduced with 2% hydrogen in nitrogen, according to a procedure previously described in detail (11,12). A schematic of the catalytic reactor system has been presented (11), but a high pressure unit for pumping liquids into the synthesis gas stream at the reactor pressure of 75 atm has been added at the top of the reactor preheater section. The exit gas was reduced to atmospheric pressure and was sampled by an on-line Hewlett-Packard 5730A GC, coupled with a Model 3388A integrator/controller.

#### RESULTS AND DISCUSSION

The results of N,N-diethylformamide hydrogenation at 215°C and 75 atm are given in Table I. When the flow rate of N,N-diethylformamide was 10.8 mmol/2.45 g cat/hr, 62% of it was converted to diethylmethylamine and the remaining 38% was distributed among other products. When the flow rate of N,N-diethylformamide and hydrogen was doubled and tripled at 215°C and 75 atm, the yields of diethylamine and methanol increased while the yield of all other products decreased (Table I).

As indicated in Table I, the N,N-diethylformamide was completely converted to diethylmethylamine (Eqn. 2), methanol (Eqn. 3), diethylamine (Eqn. 3), methylethylamine (Eqn. 4), triethylamine (Eqn. 4), and ethanol (Eqn. 5).



The reactions given by Eqn. 4) and 5) were formulated by CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and H<sub>2</sub>O balancing. Hence, a part of diethylmethylamine and

TABLE I

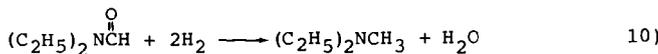
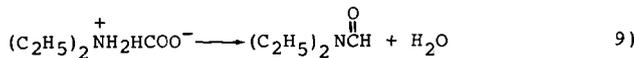
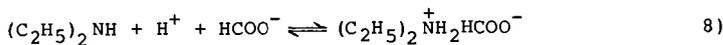
HYDROGENATION OF N, N-DIETHYLFORMAMIDE (NDEF) AT 215°C, 75 atm OVER 2.45 g of Cu/ZnO (30/70) CATALYST

Flow Rate of Substrate	Flow Rate of Hydrogen	H <sub>2</sub> O	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	MEA	DEA	DEMA	TEA	NDEF	CO	CO <sub>2</sub>	
Experiment (A) 20 $\mu$ l/min of NDEF	10.5 $\ell$ (STP)/hr		--	--	--	--	--	--	10.8	--	--	
		mmol/hr In	7.6	2.9	0.5	1.4	1.9	6.7	0.9	<0.02	<0.02	<0.02
		mmol/hr Out	34.70	13.24	2.28	6.39	8.68	30.59	4.11	<0.01	<0.01	<0.01
		Exit gas composition <sup>a</sup> (mol %)										
Experiment (B) 40 $\mu$ l/min of NDEF	21.0 $\ell$ (STP)/hr		--	--	--	--	--	--	21.6	--	--	
		mmol/hr In	13.0	7.6	0.7	1.7	6.2	12.6	1.0	<0.02	<0.02	<0.02
		mmol/hr Out	30.37	17.76	1.64	3.97	14.49	29.44	2.34	<0.01	<0.01	<0.01
		Exit gas composition <sup>a</sup> (mol %)										
Experiment (C) 60 $\mu$ l/min of NDEF	31.5 $\ell$ (STP)/hr		--	--	--	--	--	--	32.4	--	--	
		mmol/hr In	19.1	13.0	0.8	2.0	11.0	18.3	1.1	<0.02	<0.02	<0.02
		mmol/hr Out	29.25	19.91	1.23	3.06	16.85	28.02	1.68	<0.01	<0.01	<0.01
		Exit gas composition <sup>a</sup> (mol %)										

<sup>a</sup>Exit gas composition excluding hydrogen.MEA = methylethylamine  
DEA = diethylamine  
DEMA = diethylmethylamine  
TEA = triethylamine

diethylamine produced by reactions 2) and 3) was consumed by reactions 4) and 5) to produce ethylmethylamine, triethylamine and ethanol. In Figure 1, the amount of diethylmethylamine produced by reaction 2), diethylamine produced by reaction 3), methanol and water are plotted as a function of the reciprocal flow rate of hydrogen (flow rate  $N,N$ -diethylformamide =  $0.025 \times$  flow rate hydrogen). When these curves are extrapolated to infinite flow rate of hydrogen, the amounts of diethylmethylamine, diethylamine, methanol and water were 20%, 30%, 30% and 20%, respectively. This flow rate dependence study shows that there are two kinds of reactions occurring on the catalyst surface during the hydrogenation of  $N,N$ -diethylformamide: one giving rise to diethylmethylamine, and the other giving rise to diethylamine and methanol. Diethylmethylamine could be synthesized via two routes: one as in Eqn. 2) and the other by the condensation of diethylamine and methanol, produced by Eqn. 3). The results in Figure 1 indicate that the maximum amount of diethylmethylamine formed by direct hydrogenation (Eqn. 2)) was 40%.

In the following paragraphs the results of the hydrogenation of  $N,N$ -diethylformamide will be compared to the results of the methylation of diethylamine by synthesis gas (discussed in the Introduction section). This comparison is done to determine whether  $N,N$ -diethylformamide is an intermediate in methyl-diethylamine synthesis from synthesis gas and diethylamine. Over  $Cu/ZnO$  catalyst,  $14.5 \text{ mmol}/2.45 \text{ g cat/hr}$  of diethylamine reacted with synthesis gas to produce  $11.2 \text{ mmol}/2.45 \text{ g cat/hr}$  of methyl-diethylamine. When  $10.8 \text{ mmol}/2.45 \text{ g cat/hr}$  of  $N,N$ -diethylformamide, approximately equal to the methyl-diethylamine produced, was hydrogenated under conditions similar to methyl-diethylamine synthesis, the conversion to methyl-diethylamine was 62%. A comparison of these two experiments indicated that the rate of hydrogenation of  $N,N$ -diethylformamide to methyl-diethylamine was lower than the rate of production of methyl-diethylamine from synthesis gas and diethylamine. Hence, the synthesis gas and diethylamine reaction does not proceed exclusively via a  $N,N$ -diethylformamide intermediate. However, the participation of this intermediate to a lesser extent cannot be ruled out. The following path is suggested for the synthesis of methyl-diethylamine from synthesis gas and diethylamine, which proceeds via a  $N,N$ -diethylformamide intermediate.



According to this scheme, the surface formate produced by the interaction of  $CO$  and surface hydroxyls will react with diethylamine (Eqn 8)) to form an amine salt (9). Upon heating, the amine salt will be converted to  $N,N$ -diethylformamide (9), and upon hydrogenation methyl-diethylamine and water are produced (10). The flow rate

dependence study established that there are two basic pathways for the hydrogenation of N,N-diethylformamide. One gives rise to methanol and diethylamine (Eqn. 3) and the other gives rise to the direct hydrogenation product, methyldiethylamine (Eqn. 2)). At zero contact time, the contribution of the latter path is 40%. At other conditions, e.g. when 10.8 mmol/2.45 g cat/hr of N,N-diethylformamide was hydrogenated with 10.5 l(STP)/2.45 g cat/hr of hydrogen (Table I(A)), only 50% of the methyldiethylamine would be produced by reaction 2). The remaining 50% was produced by the secondary reaction in which diethylamine and methanol would undergo condensation probably via a formaldehyde intermediate.

If all the diethylamine injected (14.5 mmol/2.45 g cat/hr) during the methylation of diethylamine with synthesis gas was converted to N,N-diethylformamide intermediate, only 5.8 mmol/2.45 g cat/hr of methyldiethylamine would be produced by the direct hydrogenation path (Eqn. 2)). The remainder would be converted back to the reactants, diethylamine and methanol. During the methylation of diethylamine with synthesis gas, 11.2 mmol/2.45 g cat/hr of methyldiethylamine was produced. Hence, the rate of hydrogenation of N,N-diethylformamide does not account for the rate of the overall synthesis of methyldiethylamine by synthesis gas and diethylamine. The flow rate dependence study showed that at most, 50% of the methyldiethylamine would arise by the reaction of diethylamine with surface formate, followed by the reaction sequence given by Eqns. 9), 10). The evidence against such a participation can be summarized in the following manner. It has been shown before that surface formate was a common intermediate for both methanol synthesis and the water gas shift (WGS) reaction (7). If surface formate underwent amination, one would expect the rate of the WGS reaction to be lowered as compared with the WGS reaction rates in the absence of amine but with an equivalent amount of water. Vedage et al. (7) showed that the WGS reaction rates were unaffected by the methylation of diethylamine with synthesis gas. Therefore, the C<sub>1</sub> intermediate undergoing amination is not formate or a precursor of formate but an intermediate formed subsequent to the surface formate in methanol synthesis. This intermediate can be deduced as an aldehydic type intermediate by the process of elimination. This intermediate which can take the form formyl, formaldehyde or hydroxycarbene is therefore a kinetically significant intermediate in methanol synthesis.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- (1) P. Sabatier and J. B. Senderens, *Ann. Chim. Phys.* **4**, 418 (1905); P. Sabatier and A. Mailhe, *C.R.* **146**, 1376 (1908).
- (2) J. C. Lavalley, J. Saussey and T. Rais, *J. Mol. Catal.* **17**, 289 (1982).
- (3) J. Saussey, J. C. Lavalley, J. Lamotte and T. Rais, *J. Chem. Soc. Chem. Commun.*, 278 (1982).

- (4) A. Ueno, T. Onishi and K. Tamaru, *Trans. Faraday Soc.* **67**, 3585 (1971).
- (5) A. Deluzarche, R. Kieffer and A. Muth, *Tetrahedron Lett.* **38**, 3357 (1977).
- (6) M. Bowker, H. Houghton and K. C. Waugh, *J. Chem. Soc., Faraday Trans. 1*, **77**, 3023 (1981).
- (7) G. A. Vedage, R. Pitchai, R. G. Herman and K. Klier, 8th Intern. Congr. Catal., Berlin (1984).
- (8) K. Klier, V. Chatikavanij, R. G. Herman and G. W. Simmons, *J. Catal.* **74**, 343 (1982).
- (9) I. L. Finar, "Organic Chemistry - The Fundamental Principles," Longman Group Limited, London, 1973.
- (10) H. Adkins and B. Wojcik, *J. Am. Chem. Soc.* **56**, 247 (1934).
- (11) R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, J. B. Bulko and T. P. Kobylinski, *J. Catal.* **56**, 407 (1979).
- (12) J. B. Bulko, R. G. Herman, K. Klier and G. W. Simmons, *J. Phys. Chem.* **83**, 3118 (1979).

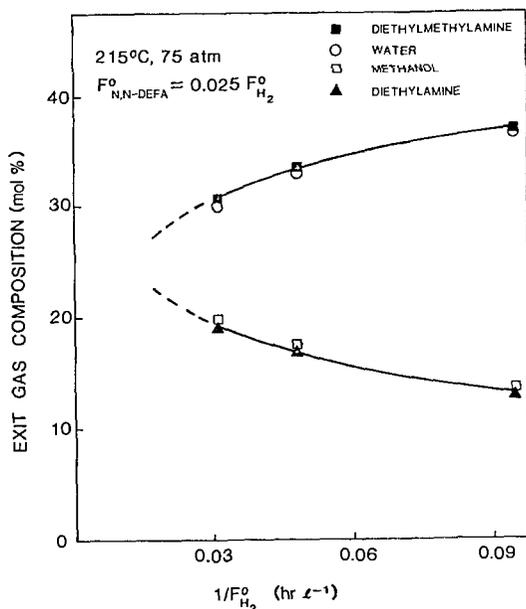


Figure 1. Diethylmethylemine, diethylamine, methanol and water produced by Eqns. 2) and 3) as a function of the reciprocal flow rate of hydrogen at 215°C, 75 atm and over 2.45 g Cu/g<sub>no</sub> (30/70) catalyst.

Periodic Dosing of Methanol Synthesis Over a Copper Zinc  
Mixed Oxide Catalyst

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INTRODUCTION

Transient operations of reactor systems have been used for many years in kinetic studies as a means of elucidating kinetic mechanisms. In the last two decades, however, interest has grown in using intentional transient operation as a means of improving the performance of chemical reactors. The requirement of maintaining a uniform level of production at unsteady state can be achieved through cyclic operations in which one of the variables in the reaction system is periodically shifted between two values. When viewed on a larger time scale than that of the periodic shifts, the system exhibits uniform production. Figure 1 illustrates how periodic operation may be performed. In the LHS of the diagram the normal steady state operation is shown. A feed of fixed composition is fed to the reactor and once steady state has been achieved, one expects a constant stream of product to flow from this unit, as illustrated in the upper LHS. In the cyclic mode, however, the partial pressure or concentration of both the reactants making up the feed are changed periodically between two levels (in the simplest case). Before a new steady state is achieved after this switch, a second switch is made back to the original levels. The operation is characterized by a period  $t$ . It can be seen from the diagram that it is not necessary for the length of time at the two different concentrations to be the same. This can be changed as well so that the system may be exposed to a short period in which there is a high concentration of one component and a much longer period in which that same component is at a much lower level. This introduces a new variable referred to as the cycle split. Additional variables are, of course, the amplitudes of the individual changes. The result of periodic changes in composition, as illustrated in the diagram, is a constantly varying product composition at the exit of the reactor. This variation occurs around a mean value which we will refer to hereafter as the time-average product concentration, and from this value we can obtain a time-average reaction rate.

There is a growing body of literature suggesting that this mode of operation can cause substantial improvements in catalyst activity (Unni et al., 1973; Asfour et al., 1983; Jain et al., 1982; Jain et al., 1980; Wilson and Rinker, 1981; Kenny and Cutlip, 1976; Lynch, 1982). For CO oxidation of platinum, the system most extensively explored, Lynch (1982) suggests that periodic operation is exploiting the existence of multiple steady states at low CO<sub>2</sub>/oxygen ratios in the feed.

Apart from those reactions which exhibit multiple steady states, the explanation frequently advanced for the improvement found with cyclic operation is that redox reactions are involved in which periodic operation involves changes in the coordination of metal atoms in the surface oxide structures which can interact with the bulk of the system through diffusional processes. This gives rise to a storage phenomena in the bulk of the catalyst that is not attainable in steady state operation. The stored reactant becomes available through pulsing.

Methanol synthesis over the copper zinc oxide system appears as an interesting candidate for this new mode of reactor operation because it probably proceeds via a redox mechanism. The use of cyclic operation can be implemented in two ways. The first of these is to periodically change the hydrogen to carbon monoxide ratio in the feed just as has been done in most of the other studies given above. The use of carbon dioxide dosing of this system suggests an alternate mode which might be explored. It has been found with the copper-zinc oxide-alumina system, which forms the basis for many of the commercial methanol synthesis catalysts, that the catalyst undergoes slow deactivation unless a low concentration of carbon dioxide is maintained in the feed. In place of maintaining  $\text{CO}_2$  at a constant level, it can be pulsed in the feed.

In an earlier paper (Nappi et al., 1984) we examined the performance of a reactor operating under cyclic variations of the hydrogen-to-CO ratio in the feed. Even though nonlinear transient behaviour was observed, periodic forcing of this system failed to improve the yield to methanol. Indeed, the main effect was to roughly double the production rate of methane in the system. We speculated that the surprising lack of improvement was due to rather small changes in the reducing power of the feed gas in switching from hydrogen-rich to carbon-rich mixtures. When maximum amplitude experiments were carried out in which the feed varied between pure carbon monoxide and pure hydrogen, performance was significantly better, but still failed to attain the levels possible with steady-state operation. Thus, in this paper, we examine periodic forcing with carbon dioxide.

#### EXPERIMENTAL

The question addressed in our experimental program was whether periodic pulsing of the reaction system with carbon dioxide could increase the production rate of methanol to a greater extent than maintaining a small bleed of the same gas into the system. Only exploratory experiments were carried out. These employed the stoichiometric hydrogen-carbon monoxide mixture for methanol synthesis of 2:1. In one of the source gases, carbon dioxide was added to a level of 2% by volume. The experiments were then carried out by periodically switching the feed from the source containing carbon dioxide to the source free of  $\text{CO}_2$ . Referring to Figure 1, the variables explored were period and the length of exposure to the gas containing carbon dioxide, referred to earlier as the cycle split. All experiments were carried out at a pressure of 2.52 MPa and 250°C. The catalyst used was a commercial low temperature water gas shift catalyst with the following formulation: Cu/Zn/Al = 29/47/24. BET surface area of this catalyst was 80.0  $\text{m}^2/\text{g}$  and its pore volume was measured as 0.470 mL/g. Thus, the mean pore diameter was 240 Å. Auger spectroscopy showed the presence of copper as  $\text{Cu}^+$  on the surface. Transmission electron microscopy indicated the catalyst was a finely dispersed mixture of various phases.

Measurements were carried out using a Berty reactor. This reactor behaves as totally backmixed which simplifies experimentation, as well as interpretation of the results. It has the disadvantage, however, that the reactor contains a significant dead volume which limits the switching frequency in cyclic operation. If this frequency is too high, the well stirred dead volume smooths out the concentration pulse so that the catalyst phase sees no change in composition with time. The arrangement of the experimental equipment is shown schematically in Figure 2. Details of the experimental equipment are available elsewhere (Jain et al., 1983; Nappi et al., 1984). The only change made from the reactor described in these publication is that the interior has been electroplated with copper in an attempt to reduce the methanation activity.

Blank runs were performed to check methanation activity. It was found that a very small amount of methane was produced; however, it is not certain whether this methane was produced on the reactor walls or in the low temperature, catalytic oxygen scavenging unit located upstream from the reactor. Methane found in the blank runs, in any case, was well below the methane contained in the source cylinders feeding the reactor. Corrections were made for both methane sources.

Analyses were performed by gas chromatography using a 3-m Porapak Q column and a hot wire detector in series with a flame ionization detector.

It was found experimentally that a cyclic stationary state was achieved after about two cycles between the CO<sub>2</sub> containing and CO<sub>2</sub> free synthesis gas mixtures. In most cases the experiment was carried out over a time frame of many hours so that up to 20 complete cycles were run. Sampling was done intermittently, but sufficient measurements were made to characterize completely the time-varying methanol and methane yields.

#### EXPERIMENTAL RESULTS

Table 1 summarizes the experimental results for methanol production. Of the two variables that were explored in these measurements, the period was only examined at 12 and 30 minutes. Decreasing the period effected a small improvement. Reactor dead space and mixing rendered experiments much below 12 minutes unproductive. As the cycle split is decreased, however, the effect is the opposite, the rate of methanol production decreases. This is, of course, expected because it has been demonstrated that at low levels of carbon dioxide in the feed, methanol production becomes proportional to the concentration of this component. Thus, as the cycle split is decreased, the quantity of carbon

Table 1  
Time-Average Rate of Methanol Production as a Function of  
Period and Cycle-Split With CO<sub>2</sub> Dosing

$\tau$ (min)	Cycle Split	Quasi-Steady- State Rate (10 <sup>-7</sup> mol/g cat*s)	Transient Average Rate (10 <sup>-7</sup> mol/g cat*s)	*Normalized Rate
12	0.05	7.10	8.25	1.16
12	0.10	7.38	9.34	1.27
12	0.25	8.22	9.89	1.20
12	0.50	9.61	10.1	1.05
12	0.75	11.0	11.4	1.03
30	0.50	9.61	9.97	1.04

\* The transient rate was normalized with respect to the quasi-steady-state rate.

dioxide the catalyst sees within a cycle falls. It is incorrect, therefore, to compare the measurements from the cyclic operation to the steady state measurements with CO<sub>2</sub> free synthesis gas. The proper comparison is with the steady state results at the same mean level of CO<sub>2</sub> used in a complete cycle in the

periodic forcing experiments. For example, if the cycle split were 0.5 and the two source gases contained 2% and 0% CO<sub>2</sub>, the mean level would have been 1%. Unfortunately, a complete set of steady-state experiments at different CO<sub>2</sub> levels was not made. However, it is possible to estimate these steady state rates by assuming a linear relationship between the mole % CO<sub>2</sub> in the gas and the rate of methanol formation. If this is done, and the estimated steady state value is divided into the measurements shown in Table 1, the normalized rate is obtained. These are found in the last column of the table. Normalized results reflect the improvement in methanol yield over the comparable steady state through periodic forcing.

Adding 2% CO<sub>2</sub> by volume to the stoichiometric mixture increases the steady-state methanol formation from  $6.8 \times 10^{-7}$  to  $12.4 \times 10^{-7}$  mol/g cat\*s. Evidentially, periodic forcing is capable of further increasing the methanol production rate by about 25%. Worth noting is that the measurement reported in this paper are of a screening nature and no attempt has been made to optimize the periodic dosing sequence.

Table 2 shows our methane production results. Introduction of a steady stream of CO<sub>2</sub> into the feed gas dramatically suppresses the steady-state rate of formation of methane in this reaction system from  $3.4 \times 10^{-8}$  to  $5.4 \times 10^{-9}$  g mol/g cat\*s. Although the methane formation rate for this catalyst in the absence of carbon dioxide is only about 5% of the formation rate for methanol, the introduction of CO<sub>2</sub> suppresses this rate to just 0.4% of the methanol rate. Table 2 shows that cycle period has a much stronger effect on methane than on methanol production. Unlike methanol production however, periodic pulsing with CO<sub>2</sub> reduces methane formation substantially and shortening the pulse length exerts just a small effect on the rate of formation.

Table 2

Time-Average Rate of Methane Production as a Function of Period and Cycle-Split With CO<sub>2</sub> Dosing

$\tau$ (mins)	Cycle Split	Quasi-Steady-State Rate ( $10^{-9}$ mol/g cat*s)	Transient Average Rate ( $10^{-9}$ mol/g cat*s)	*Normalized Rate
12	0.05	32.6	3.10	0.095
12	0.10	31.2	3.42	0.11
12	0.25	26.9	3.39	0.13
12	0.50	19.7	2.98	0.15
12	0.75	12.6	5.83	0.46
30	0.50	19.7	5.87	0.30

\* The transient rate was normalized with respect to the quasi-steady-state rate.

If the rate of formation of methane is proportional to the carbon dioxide concentration, the rate of formation at quasi-steady-state will be a close estimate of the steady state for CO<sub>2</sub> levels between 0 and 2 vol%. These values are appropriate for comparison with the time-average rates of methane formation under periodic pulsing. We have assumed appropriateness and the last

column in Table 2 compares the time-average cyclic rates with the assumed steady-state ones. These results indicate the large influence of dosing time on methane formation.

Periodic sampling through the gas chromatograph permits a reconstruction of the change of rate with time inside a dosing cycle. These reconstructions are shown in Figures 3 and 4 for two quite different cycling conditions: the first is for a short pulse of CO<sub>2</sub> containing feed while the second figure considered a relatively long pulse. Immediately upon introduction of the CO<sub>2</sub>-containing gas, methane production falls to a level which cannot be detected with our analytical equipment. In Figure 4, when the CO<sub>2</sub>-free gas stream is introduced, the methane concentration builds up to about one. The measurements have been normalized with exit concentration measured at steady state with the CO<sub>2</sub>-containing gas. If a short CO<sub>2</sub> pulse is used, Figure 3 shows the normalized concentration rising to about 2.4. In both cases, these values are well below the steady state values expected for a CO<sub>2</sub>-free synthesis.

In both figures, methanol production changes very little. Although it is shown in the figures, the CO<sub>2</sub> detected in the stream leaving the reactor changed very little within the dosing cycle.

#### DISCUSSION

The failure of the methanol production rate to follow the changes in the CO<sub>2</sub> content of the gas coupled with the dramatic 20 to 25% improvement in production rate with respect to steady state strongly suggests that the introduction of CO<sub>2</sub> causes a restructuring of the surface and/or reoxidation of the sites in the system. These sites, or surfaces, however, are not corrected immediately back to their starting condition when CO<sub>2</sub> is removed. Restructuring or reductions appears to be very slow. A long-term decay of the copper/zinc oxide catalyst activity in the absence of CO<sub>2</sub> in the feed gas is observed, of course, in steady state operation. If a massive reoxidation of copper in the catalyst were occurring on the introduction of CO<sub>2</sub>, methanol production would have changed much more sharply than what can be seen in the data shown in Figures 3 or 4.

A sharp change in production rate does appear, however, for methane. It seems likely that the explanation for this is a wholesale destruction of the sites responsible for methane production by the introduction of CO<sub>2</sub>. Evidentially, these sites must be quite different from those for methanol formation judging from the sharply different behaviour when CO<sub>2</sub> is either introduced or removed from the system. Substantial adsorption of CO<sub>2</sub> accounts for the lack of change in CO<sub>2</sub> levels in the exit stream. The presence of CO<sub>2</sub> when the feed is CO<sub>2</sub>-free seems to result from methane formation. Methane formation is favoured thermodynamically at the operating conditions employed so that CO<sub>2</sub> suppression cannot occur through an equilibrium interaction because the reaction system operates so far away from equilibrium.

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#### REFERENCES

- Jain, A.K., P.L. Silveston, and R.R. Hudgins, "Forced Composition Cycling Experiments in a Fixed Bed Ammonia Synthesis Reactor", Proc. Seventh Internat. Sympos. Chem. Reaction Engg., Boston, Mass., ACS Sympos., Ser. 196, 97-107 (1982).
- Jain, A.K., P.L. Silveston, and R.R. Hudgins, "Influence of Forced-Feed Composition Cycling on the Rate of Ammonia Synthesis Over an Industrial Iron Catalyst: Part I - Effect of Cycling Parameters and Mean Composition", Can. J. Chem. Eng., 61, 824-831 (1983).
- Unni, M.P., R.R. Hudgins and P.L. Silveston, "Influence of Cycling of the Rate of Oxidation of SO<sub>2</sub> over a V<sub>2</sub>O<sub>5</sub> Catalyst," Can. J. Chem. Eng. 31, 623-9 (1973).
- Asfour, H., P.L. Silveston, and R.R. Hudgins, "Effect of Forced Concentration Cycling of the Claus Reaction", Paper presented at the 66th Can. Chem. Conf., Calgary, Canada (1982).
- Cutlip, M.B. and Kenny, C.N., Paper presented at the 15th Int. Symp. on Chemical Reaction Engineering, Houston, Texas, March (1978).
- Lynch, D.T., Can. J. Chem. Eng. 61, 183, 1983.
- Nappi, A., R.R. Hudgins, and P.L. Silveston, "Influence of Forced Feed Composition Cycling on Catalytic Methanol Synthesis", Preprints, 9th ISCRE Meeting, Edinborough, U.K. (1984).
- Wilson, H.D. and Rinker, "Concentration Forcing in Ammonia Synthesis - I Controlled Cyclic Operation", Chem. Eng. Sci., 37, 343-355 (1982).

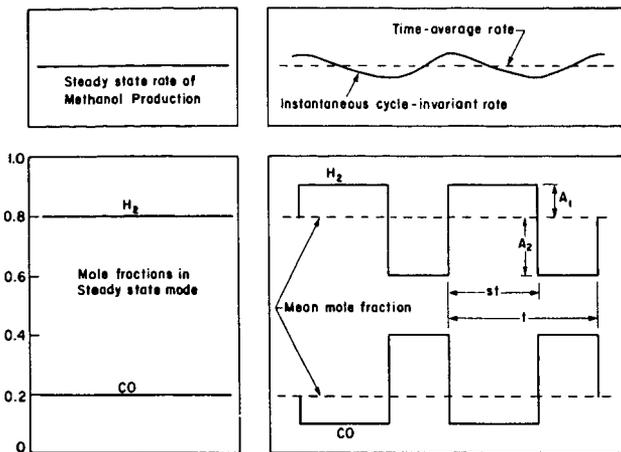


Figure 1 Schematic of the Periodic Operation of a Catalytic Reactor.

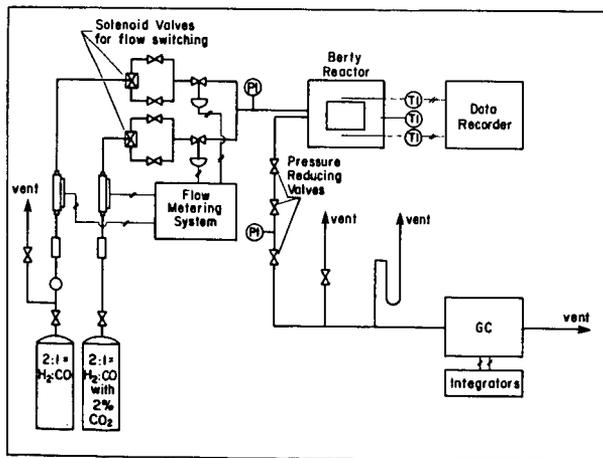


Figure 2 Schematic of the Experimental Apparatus (PI = pressure gauge, TI = thermocouple, GC = gas chromatograph)

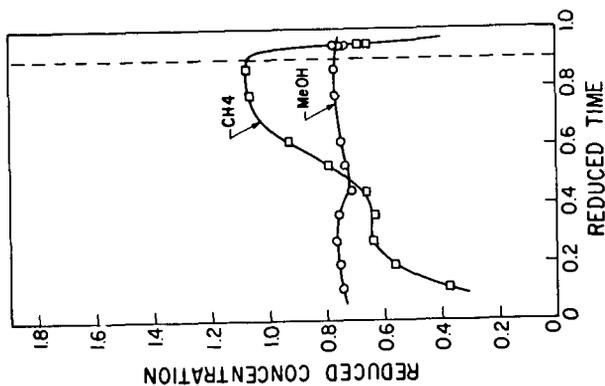


Figure 3 Time Variation of Product Concentrations Under Periodic Dosing with 2 vol. % CO<sub>2</sub> for  $\tau=12$  Minutes,  $*s=0.10$  (Concentrations Normalized With Steady State Product Concentration Using 2 vol.% CO<sub>2</sub> in Feed, 250°C 2.513 MPA).

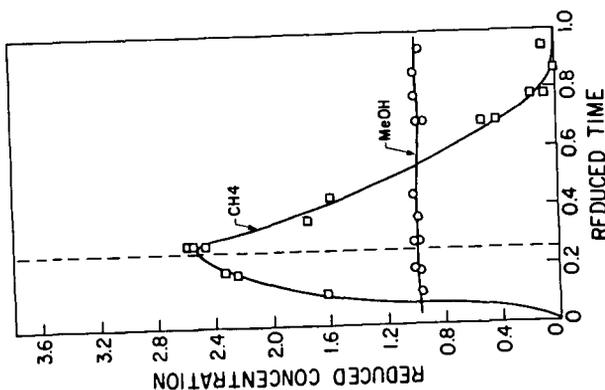


Figure 4 Time Variation of Product Concentrations Under Periodic Dosing with 2 vol. % CO<sub>2</sub> for  $\tau=12$  Minutes,  $*s=0.75$  (Concentrations Normalized With Steady State Product Concentration Using 2 vol.% CO<sub>2</sub> in Feed, 250°C 2.513 MPA).

$*s$ , defined as the ratio of the CO<sub>2</sub>-rich portion of the cycle to the cycle period.