

The Effect of CO₂ and H₂O in the Methanol Synthesis Reaction on Cu-Zn-O

Harold H. Kung, George Liu, and Dave Willcox

Chemical Engineering Department, Northwestern University, Evanston IL 60201

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/CO₂ ratio (1). They observed a sharp maximum at a CO/CO₂ of about 28/2. Later, they also reported the effect of H₂O in the feed. Again, an optimum H₂O 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 CO₂ 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 H₂/N₂, and then preconditioned by a mixture of CO₂, CO, H₂ and CH₃OH, 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.

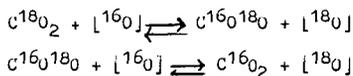
T°C	Initial Gas Composition (%)				CH ₃ OH rate	H ₂ O rate
	H ₂	CO	CO ₂	H ₂ O	10 ⁻⁵ moles/min-g	10 ⁻⁵ moles/min-g
228	70.05	27.74	2.21	0	1.27	1.30
	70.25	20.95	8.80	0	1.50	3.30
	70.02	16.22	13.76	0	1.70	4.57
	69.73	12.24	18.03	0	2.00	9.88
	69.99	0	30.01	0	2.49	11.24
220	71.13	26.3	1.66	0.90	0.118	-
	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 CO₂/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 CO₂/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 CO₂, 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 CO₂ may indicate that the hydrogenation of CO₂ is faster than that of CO, or that the hydrogenation of CO is enhanced by coadsorption of CO₂ which may facilitate the formation of some unstable intermediates.

To investigate the rate of hydrogenation of CO₂ in the feed mixture, C¹⁸O₂ was used. Using conditions similar to those used in Table 1 with a CO/CO₂ ratio of about 4/1, it was found that the initial rate of production of CH₃OH-¹⁶O was about as fast as the rate of production of CH₃OH-¹⁸O. The results indicated clearly the importance of the hydrogenation of CO₂ in methanol production.

Another interesting result is on the rate of the isotope exchange reaction of CO₂:



This exchange reaction proceeds at a reasonable rate in a mixture of CO₂ and He, and CO₂ and CO. The rate is greatly enhanced in a mixture of H₂, CO, and CO₂ with the rapid production of C¹⁸O. This result can be explained by the rapid reversible water gas shift reaction, which scrambles the oxygen in CO and CO₂, 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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