Adsorption Measurements during the Synthesis of Methanol at Lower Pressures*

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Various mechanisms of the methanol synthesis reaction have been proposed by many workers.$^{1-6)}$ In deducing these mechanisms, however, the adsorption during the reaction has indirectly been estimated on the basis of either a Langmuir-Hinshelwood or a Temkin-Pyzhev-type mechanism. The importance of the adsorption measurements during surface catalysis has recently been emphasized by Tamaru.$^{7)}$ In his method, the adsorption on the catalyst surface, as well as its reaction rate, can be directly measured; such reactions as the decomposition of formic acid on metal catalysts$^{8)}$ and the synthesis and decomposition of ammonia$^{9,10)}$ have already been studied by means of this new approach.

In order to obtain further information on the mechanism of the methanol synthesis reaction, the present authors used the new

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1) G. Natta, P. Pino, G. Mazzanti and I. Pasquon, *Chimica e Industria*, **35**, 705 (1953).

2) G. Natta and G. Pastonesi, ibid., **19**, 313 (1937), **20**, 587 (1938).

3) A. Ozaki and T. Saita, *Shokubai* (*Tokyo*), 3, 158 (1961).

4) V. M. Cheredinichenko and M. I. Temkin, *Zhur. Fiz. Khim.*, **31**, 1072 (1957).

5) H. Uchida and Y. Ogino, This Bulletin, **31**, 45 (1958).

6) I. Pasquon, *Chemica e Industria*, **42**, 352 (1960).

7) K. Tamaru, This Bulletin, **31**, 666 (1958).

8) K. Tamaru, *Trans. Faraday Soc.*, **55**, 824, 1191 (1959).

9) K. Tamaru, ibid., **57**, 1410 (1961).

10) K. Tamaru, "Actes du deuxième Congr. Catalyse," Edition Technip Paris (1961), p. 325.

method to measure the adsorption during the reaction.

Experimental

The apparatus employed in these experiments was a closed circulating system, as Fig. 1 shows. A is a cylindrical reaction vessel 85 mm. long and 25 mm. in internal diameter. Passing through the central tube of the vessel, the circulating gas was pre-heated before reaching the catalyst bed, which was 45 mm. thick. B is an electric heater, regulated within ± 2°C, and D is a thermocouple. K is a circulating pump; a piece of iron sealed in a glass piston, M, was driven reciprocally by means of an electromagnet, L. During the course of the reaction, the stop-cocks, I, J, P, Q, R, S, Y, were closed. The synthesis reaction usually proceeded in such a way that the methanol produced was collected in a trap, F, maintained at the temperature of liquid nitrogen. The volume of the circulating system corresponded to about 433 ml. at a reaction temperature of 250°C.

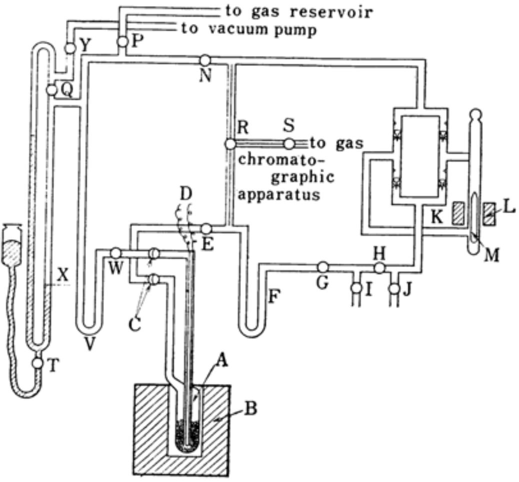

Fig. 1. Apparatus.

- A Reaction vessel
- B Electric heater
- D Thermocouple
- F Trap cooled with liquid nitrogen
- K Circulation pump

Known amounts of the reactants, pure hydrogen and carbon monoxide, in a synthesis reaction, and methanol in a decomposition reaction, were introduced into the system; the reaction followed, the pressure and composition of the circulating gas being measured at suitable time intervals. The amounts of products condensed in the trap, F, were determined at the end of each run. Gas chromatography as described by Murakami[11] was used for the analyses of gases and condensed products. In this method, the amounts of hydrogen, carbon monoxide, methane, and carbon dioxide were simultaneously determined, using two columns, one (80 cm. long) packed with silica gel as an adsorbent, and the other (2 m. long) packed with 13x Molecular Sieves, successively at room temperature, where herium was employed as a carrier gas. In the analyses of methanol and water, on the other hand, the amounts of carbon monoxide co-existing in the trap, F, were first estimated, and then the ratios of the amounts of the methanol and water to that of carbon monoxide were determined, using successively two columns (1 m. long), packed with polyethylene glycol on celite 545 and with 5A Molecular Sieves, at 60°C, where the carrier gas was hydrogen.

The amounts of the gases adsorbed on the catalyst were obtained as either hydrogen or carbon monoxide from the amounts of reactants introduced into the system, the pressure and the composition of the circulating gas, and the amounts of products trapped. Due allowance was made for the analytical samples removed from the apparatus.

Carbon monoxide was prepared by decomposing sodium formate with sulfuric acid, and it was purified by repeated fractional distillation at the temperature of liquid nitrogen after having passed through a soda-lime column. Hydrogen was obtained from a commercial cylinder, and purified over palladium asbestos at 350°C. Methanol was purified by repeated distillation after having been dried over calcium oxide.

The catalyst employed had the composition Zn : Cr : Cu = 1.0 : 0.49 : 0.16, and it was reduced at 280°C under atmospheric pressure, initially in a hydrogen stream for 60 hr. and then in a hydrogen stream saturated with methanol vapor at room temperature for 50 hr. Before each run, the catalyst was evacuated for 3 hr. at 400°C. Thus the experimental results were satisfactorily reproducible.

Results and Discussion

The measurements of the adsorption and of the reaction rate were carried out at 250°C. A typical result during the methanol synthesis reaction is shown in Fig. 2. The amounts of the adsorption of hydrogen and carbon monoxide during the reaction were greater than those separately adsorbed, which are represented by solid symbols, when the corresponding amounts of gases were introduced. This fact can be explained as indicating a marked mutual influence on the adsorption of hydrogen and carbon monoxide in the presence of the other gas. It was thus suggested that the adsorption behavior during the reaction can not be estimated from the results observed in the absence of the other gas. A similar effect was reported during the ammonia synthesis reaction.[10] The amounts of methanol formed were far less than those calculated from the equilibrium constant and from the circulating rate. The circulating rate was occasionally measured by means of a soap film meter, connected with the system through the stop-cocks I and J, precautions being taken to prevent the

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[11] Y. Murakami, This Bulletin, **32**, 316 (1959).

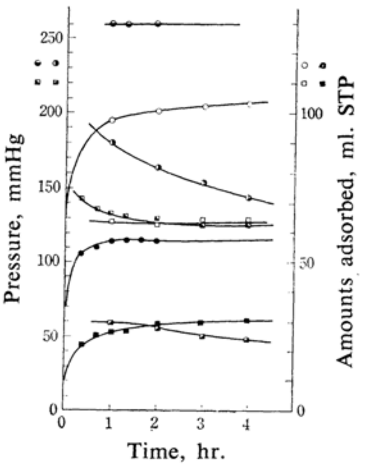

Fig. 2. Adsorption measurements during methanol synthesis at 250°C.
Amounts introduced: H_2, 183.3 ml.; CO, 92.0 ml., (STP)
○ H_2 adsorbed
□ CO adsorbed
◑ Ambient H_2 pressure
◪ Ambient CO pressure
● H_2 adsorption in the absence of CO
■ CO adsorption in the absence of H_2
◒ H_2 pressure in the absence of CO
◩ CO pressure in the absence of H_2

water vapor from contaminating the catalyst. The observed products of the reaction were usually identified as methanol and carbon dioxide and, depending on the reaction conditions, small amounts of water and a trace of methane.

The surface area of the catalyst was estimated to be 1.0×10^7 cm^2 by using the B. E. T. method for nitrogen adsorption at -196°C after the catalyst had been reduced.

The ratios of adsorbed hydrogen to carbon monoxide during the synthesis and the decomposition reaction of methanol are plotted against the ratios of their ambient pressures in Fig. 3. The compositions of the adsorbed phase did not depend on those of the gas phase, in spite of the wide change (about eight thousand-fold) of the partial pressure ratio. The composition of the adsorbed phase would reasonably depend on their partial pressure ratios if the two gases were separately adsorbed. The marked constancy of the composition of the adsorbed species suggests, accordingly, that most of the adsorbed hydrogen and carbon monoxide (more than 80% of the hydrogen and 75% of the carbon monoxide) form a complex, and the average value, 1.5, suggests that the stoichiometric formula of the complex is CH_3O.

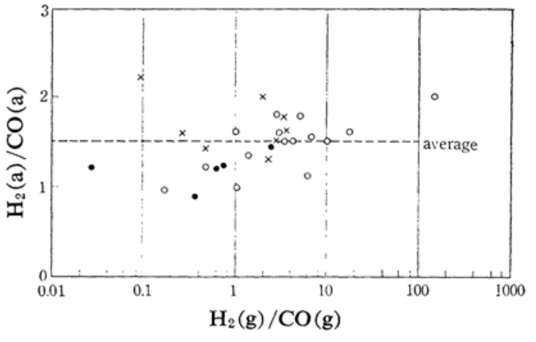

Fig. 3. Relationship between $H_2(g)/CO(g)$ and $H_2(a)/CO(a)$.
○ Synthesis with liquid nitrogen trap
● Synthesis without liquid nitrogen trap
× Decomposition

Figures 4 and 5 give two examples of the plots of the average synthesis rate against the ambient pressure, as well as the amounts of adsorption of hydrogen and carbon monoxide. The rates of methanol synthesis reaction were represented by the cumulative amounts of methanol synthesized over a four-hour period, the rates being too slow to determine with time. The ambient pressure and the amounts of the adsorption of hydrogen and carbon monoxide were represented by their average value over the four-hour period. As is shown in Fig. 4, the synthesis rate of methanol can be expressed by Eq. 1:

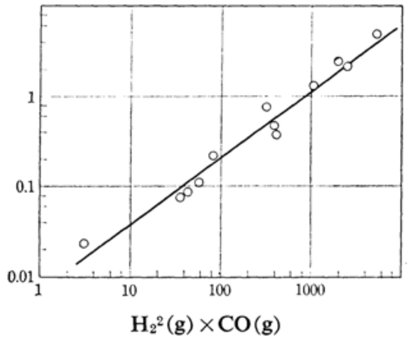

Fig. 4. Synthesis rate vs. $H_2^2(g)\times CO(g)$.

$$r=k(P_{H_2}{}^2P_{CO})^n \qquad (1)$$

where P_{H_2} and P_{CO} are the ambient pressures of hydrogen and carbon monoxide respectively; k, the rate constant, and n, a constant, which is 0.75. Uchida and Ogino[5)] previously reported Eq. 2:

$$r=k(P_{H_2}{}^2P_{CO})^{1-\alpha} \qquad (2)$$

where α is a constant equal to 0.3. These equations are in good agreement in spite of the different conditions of the experiments (at 300—360°C, under 90—150 kg./cm^2 by Uchida and Ogino, but at 250°C, under 100—760

TABLE I. ADSORPTION OF HYDROGEN AND CARBON MONOXIDE DURING THE METHANOL SYNTHESIS AT VARIOUS CONDITIONS (250°C)

Amounts introduced		Ratio	Gas phase volume		Amounts adsorbed		
H_2, ml. (STP)	CO, ml. (STP)	H_2/CO	H_2, ml. (STP)	CO, ml. (STP)	H_2, ml. (STP)	CO, ml. (STP)	Total, ml. (STP)
229.8	107.1	2.15	99.5	34.6	125.8	69.2	195.0
185.8	137.8	1.35	82.4	57.7	100.6	75.2	175.8
148.3	69.4	2.14	73.7	12.0	72.8	57.0	129.9
80.9	180.6	0.45	18.3	105.4	62.1	65.9	138.0
339.4	47.6	7.15	239.8	1.5	93.4	45.9	139.3
348.5	206.5	1.69	235.5	90.7	91.9	94.3	186.2
318.5	137.7	2.32	193.7	62.5	106.0	66.3	172.3
139.2	68.0	2.05	63.5	16.9	73.9	48.8	122.7
200.6	92.0	2.09	106.4	29.7	91.1	56.2	147.3
76.8	178.9	0.43	5.3	112.4	71.5	58.2	128.7
275.1	92.8	3.37	173.5	34.3	94.8	53.8	148.6
316.4	151.5	2.09	172.5	59.8	129.2	67.9	197.1

mmHg by the present authors). These equations can be interpreted as implying that the catalyst surface is partially covered with adsorbate, assuming that a Langmuir-type adsorption is valid. It is, however, found that considerable amounts of adsorption on the surface are involved, as is shown in Table I.

It thus seems inappropriate to apply the Langmuir-type adsorption. Moreover, the results reported by Uchida and Ogino[12] indicate that the rate of the reaction of methanol synthesis can not be expressed by any equation based on the Langmuir-type adsorption.

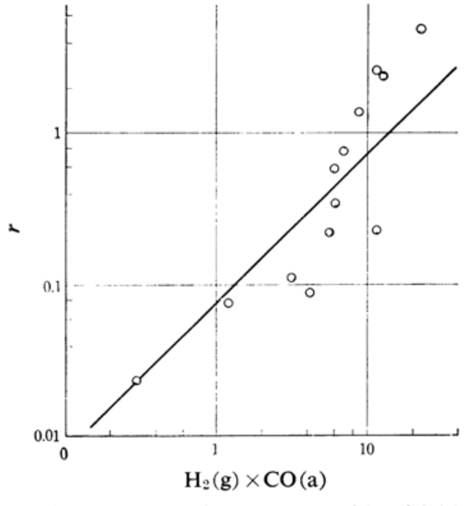

Fig. 5. Synthesis rate vs. $H_2(g)\times CO(a)$.

As Fig. 5 shows, the synthesis rate may also be expressed by Eq. 3:

$$r=kP_{H_2}A_{CO} \tag{3}$$

where A_{CO} is the amount of carbon monoxide adsorbed in any form combined or not combined with hydrogen on the surface. The adsorbed carbon monoxide mostly forms a complex, so:

$$A_{CO}\doteqdot A_X$$

where A_X is the amount of the surface complex. Taking the surface complex to have the CH_3O composition, the Eley-Rideal-type hydrogenation of the adsorbed complex would be the rate-determining step of the over-all reaction:

$$CH_3O(a)+H_2(g) \nrightarrow CH_3OH(a)+H(a)$$

The synthesis rate is thus expressed by Eq. 4:

$$r=kP_{H_2}A_{CH_3O} \tag{4}$$

It may, accordingly, be concluded that the Eley-Rideal-type hydrogenation of the surface complex is the rate-determining step of the methanol synthesis reaction.

Summary

Adsorption has been studied on a three-component methanol synthesis catalyst during the synthesis of methanol in a closed circulating system. It has been shown that the adsorption of hydrogen and carbon monoxide are both enhanced by the presence of the other. The composition of the adsorbed phase has scarcely been affected at all by the ratio of the partial pressure of hydrogen to carbon monoxide, and the formation of surface complex has been suggested. The rate-determining step of the synthesis of methanol has been suggested to be the process of the Eley-Rideal type hydrogenation of the surface complex.

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[12] H. Uchida and Y. Ogino, Annual Meeting of Catalysis Club of Japan, April, 1957.