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Adsorption Behavior of Hydrogen and Carbon Monoxide over Zinc Oxide in the Mixed Gas Adsorption and during the Methanol Decomposition Reaction*[1]

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Adsorption of hydrogen and carbon monoxide at the different situations has been investigated with zinc oxide which is the principal component of ordinary methanol synthesis catalysts. In the simultaneous adsorption of hydrogen and carbon monoxide the mutual interaction was also observed. The results were explained as the displacement effect as well as the enhancement took place in a certain region of the partial pressures. Adsorption measurements during the decomposition reaction suggest that in initial state the adsorbed species are mostly the adsorbed methanol and that the step of the decomposition of it is the rate-determining step of the overall reaction. The mechanism of methanol synthesis over zinc oxide is suggested to proceed in the similar way as on the three component catalyst previously used.

In the previous papers,[1-4] adsorption behaviors of hydrogen and carbon monoxide in the mixed gas adsorption and during the methanol synthesis and decomposition reaction over three component methanol synthesis catalyst have been investigated in the relation to the mechanism of the methanol synthesis. The rate-determining step of the synthesis of methanol was suggested to be the process of the Eley-Rideal type hydrogenation of the surface complex. The mutual influence of the chemisorption of hydrogen and carbon monoxide has been observed, and the facts suggest that the adsorption behavior both in the mixed gas adsorption and that during the reaction can not be estimated from the single gas adsorption.

In this work, the similar investigations as previously[1-4] reported, have been carried out with zinc oxide in order to obtain further informations on the mechanism of the methanol synthesis and decomposition, because zinc oxide is the principal component of the three component methanol synthesis catalyst previously[1-4] used.

Experimental

The apparatus employed and method were the same as was previously reported.[1-4] Known amounts of the reactants were introduced into the system, the extent of the reaction was followed by pressure measurement. The amount of gas adsorbed on the catalyst surface was estimated by material balance of reactants introduced and the partial pressure and composition of the circulating gas. The composition of the circulating mixture was determined by gas chromatography. Due allowance was made for the analytical samples removed from the apparatus. The amount of gas adsorbed on the catalyst, including the surface complex, was obtained in terms of either the adsorbed hydrogen or the carbon monoxide.

The zinc oxide catalyst (13.7 g) employed was obtained by calcining zinc hydroxide at 300°C, which was precipitated from zinc nitrate solution by ammonium hydroxide. Before each run, the catalyst was evacuated for 10 hr at 400°C. The experimental results were satisfactorily reproducible.

Results and Discussion

Simultaneous Adsorption. Typical results of simultaneous chemisorption of hydrogen and carbon monoxide on the zinc oxide catalyst are shown in Figs. 1 and 2. Pure hydrogen was first introduced into the reaction system. A marked acceleration of hydrogen chemisorption at the addition of carbon monoxide was thus observed, as shown in Fig. 1. An enhanced adsorption of carbon monoxide by the presence of hydrogen was also observed when hydrogen was added to carbon monoxide as shown in Fig. 2, where pure carbon monoxide was first introduced and then hydrogen was admitted. In both cases of hydrogen and carbon monoxide, the enhanced adsorption of the pre-admitted gas by the addition of the other gas were also observed over zinc oxide, as well as over the three component methanol synthesis catalyst.[2] The mutual enhancement of the

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*[1] This paper was presented at the Annual Meeting of the Catalysis Society of Japan, Osaka, October, 1964.

[1] S. Tsuchiya and T. Shiba, This Bulletin, **38**, 1726 (1965).

[2] S. Tsuchiya and T. Shiba, *J. Catalysis*, **4**, 116 (1965).

[3] S. Tsuchiya and T. Shiba, *ibid.*, **6**, 270 (1966).

[4] S. Tsuchiya and T. Shiba, This Bulletin, **40**, 1086 (1967).

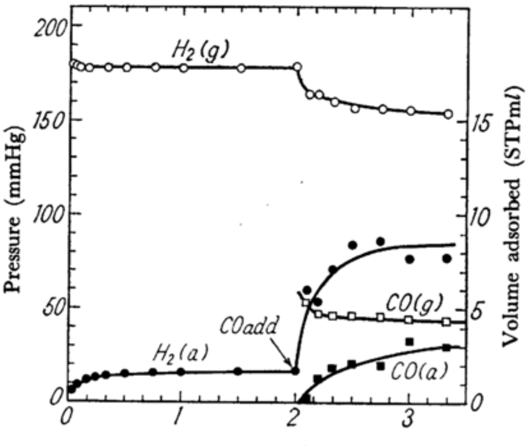

Fig. 1. Effect of carbon monoxide addition on the adsorption of hydrogen at 250°C.

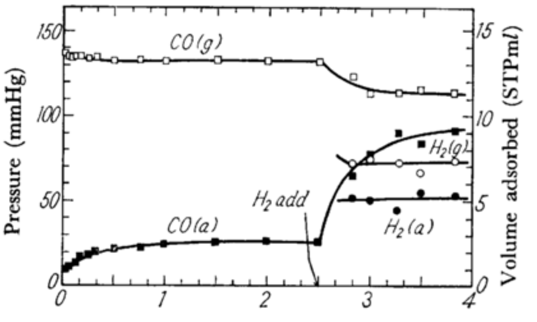

Fig. 2. Effect of hydrogen addition on the adsorption of carbon monoxide at 250°C.

adsorption was complicatedly varied by the added gas and the ratio of hydrogen to carbon monoxide.

The mutual interaction of the adsorption of hydrogen and carbon monoxide is shown more quantitatively in Fig. 3. The amounts of adsorption of hydrogen pre-admitted increased by the addition of the carbon monoxide, but the amounts of the increments rather decreased, when the pressure of carbon monoxide added increased. These results suggest that a part of the hydrogen adsorbed was displaced by carbon monoxide added. The similar results were observed when the same was done replacing carbon monoxide with hydrogen. It is consequently suggested that the mutual enhancement as well as displacement of the chemisorption of hydrogen and carbon monoxide take place on zinc oxide. The mutual enhancement effect might be due to the creation of additional sites as was suggested by Nagarjunan, Sastri and Kuriacose⁵⁾ and the displacement would

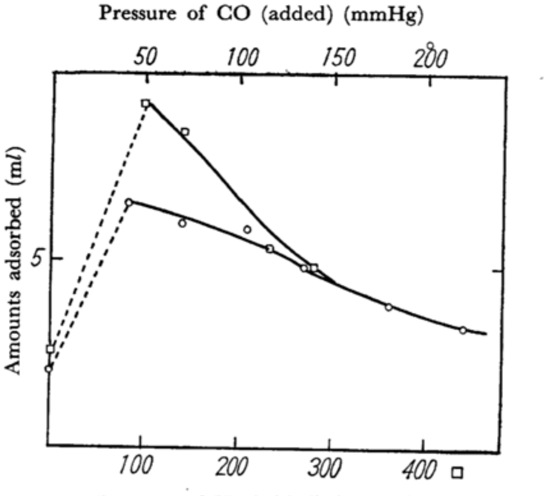

Fig. 3. Mutual interaction in the adsorption of hydrogen and carbon monoxide.

occur when the amounts of gas were in excess of the total sites.

The adsorption isotherms of hydrogen and carbon monoxide, are shown in Figs. 4 and 5, respectively. The mixed adsorption isotherms were obtained by introducing the mixtures of the $2H_2$: $1CO$ gases. The adsorption was more enhanced at 250°C than at 300°C.

Using the BET method for nitrogen adsorption at −190°C, the surface area and volume of gas which gives a complete monolayer v_m of the catalyst were estimated to be 6.7×10^5 cm² and 15 m*l*, respectively. As Figs. 4 and 5 show, in some

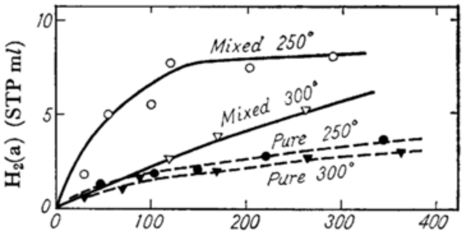

Fig. 4. Adsorption isotherms of hydrogen.

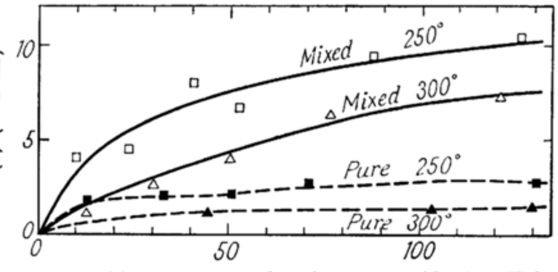

Fig. 5. Adsorption isotherms of carbon monoxide.

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5) T. S. Nagarjunan, M. V. C. Sastri and J. C. Kuriacose, *J. Catalysis*, **2**, 223 (1963).

cases the sum of the amounts of hydrogen and carbon monoxide adsorbed exceeded v_m to some extent, which suggests the formation of surface complex from hydrogen and carbon monoxide, coupling with the fact that zinc oxide has the catalytic activity for methanol synthesis from hydrogen and carbon monoxide.

Decomposition Reaction. Typical result of the decomposition of methanol is shown in Fig. 6. As the decomposition proceeded, the partial pressure of methanol decreased with time, and those of hydrogen and carbon monoxide increased, while the ratio of adsorption of hydrogen to carbon monoxide changed.

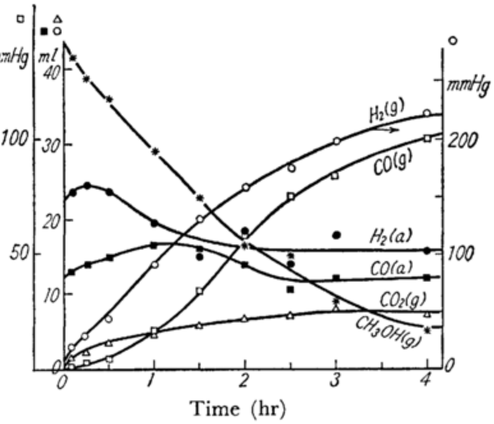


Fig. 6. Adsorption measurements during the methanol decomposition at 250°C.

At the initial stage, the ratio of the sum of the amounts of hydrogen adsorbed to that of carbon monoxide adsorbed, which include those in the surface complex formed from them, was nearly two. The adsorbed species on the zinc oxide is probably suggested to be CH_3OH at the initial stage of the reaction as was previously[3)] concluded over the three component methanol synthesis catalyst. The results that the change of the ratio of hydrogen to carbon monoxide adsorbed during the course of the methanol decomposition, is explained in terms of the existence of "free hydrogen" and "free carbon monoxide" which was suggested previously,[4)] as well as the surface complex.

If the decomposition of methanol over a zinc oxide and over a three component methanol synthesis catalyst proceeds in the same way as proposed previously,[3)] the mechanism of the reaction would be as given by Scheme A.

The authors previously[3,4)] expressed hydrogen adsorbed as $H_2(a)$, which include both atomic and molecular ones.

However, the hydrogen adsorbed might be atomic becaurse the hydrogen and deuterium equilibration reaction took place over a zinc oxide.[6)]

The amounts of adsorption during the decomposition of methanol were always greater than those in the adsorption from the mixture $2H_2 : 1CO$; the amounts of the adsorption both of hydrogen and of carbon monoxide from the mixture were less than 10 m*l* even at 200 mmHg pressure. The results suggest that not all of the species adsorbed on the catalyst—hydrogen, carbon monoxide, and any intermediate complex formed from hydrogen and carbon monoxide—were in equilibrium with hydrogen and carbon monoxide in the gas phase, and that the process of the adsorption of methanol (process 1) can not be the rate-determining step of the reaction.

As shown in Fig. 7, the ambient pressure of hydrogen did not decrease when methanol was abruptly removed from the system during the reaction, and the amount of methanol in the trap stayed constant during the trapping. The facts suggest that the major part of the adsorbed species, hydrogen, carbon monoxide, and the complex formed from them, on the catalyst is not in equilibrium with the methanol in the gas phase; otherwise,

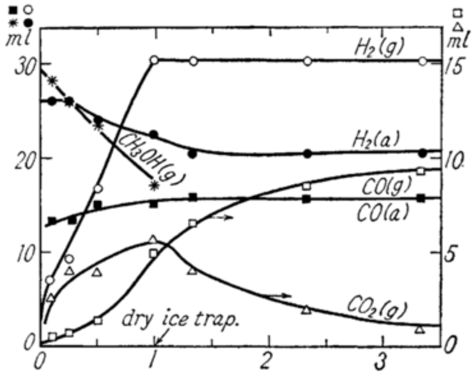
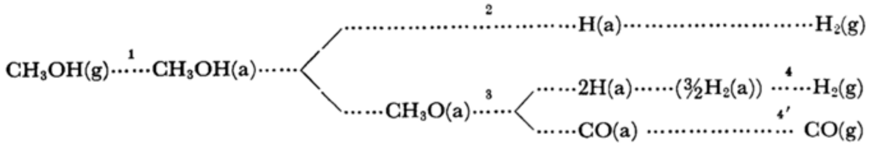


Fig. 7. The effect of methanol elimination during the decomposition reaction.



Scheme A.

[6)] E. Molinari and G. Parravano, *J. Am. Chem. Soc.*, **75**, 5233 (1953).

the major part of them would rapidly be desorbed to be caught by the trap. Neither of the processes of the desorption of hydrogen nor carbon monoxide (processes 3, 4, and 4′) are accordingly suggested to be the rate-determining step of the reaction. Consequently, the rate-determining step is suggested to be the process of the dissociation of adsorbed complex (process 2). The suggestion conforms to the conclusion previously[1-4] reported in the case of the reaction over the three component methanol synthesis catalyst.

The results for decomposition of various amounts of methanol are shown in Fig. 8, where the pressure of methanol is plotted against time. The pressures at time zero were, however, estimated from the amounts of methanol introduced and the volume of the reaction system. The initial decreases in the methanol pressure represented by the upper dotted lines were followed by the linear part of the decreases in the pressure, represented by solid lines. The initial rate of the pressure decrease in the solid line range was almost independent of the methanol pressure; deviation from linearity, however, occured at later time.

The initial rapid decrease in the methanol pressure represented with the upper dotted lines can be considered to be due to the adsorption of methanol as menthioned above. Hence the order of methanol decomposition reaction is approximately zero and the rate of the reaction would be roughly expressed by Eq. (1), since the solid lines would show the methanol decomposition reaction.

$$r \fallingdotseq k \qquad (1)$$

The results agreed with those observed previously.[3] The apparent activation energy of the decomposition reaction was estimated to be 27.8 kcal/mol from the Arrhenius plots of k.

A curve considered to be an adsorption isotherm of methanol was obtained as shown with a solid line for 250°C in Fig. 9. The ambient pressure of methanol was obtained by extraporating the pressure-time curve in Fig. 8 to time zero (lower dotted lines), and the adsorbed amount was estimated from the mass balance between the amount of the methanol introduced and that in the gas phase at that time, because the methanol only adsorbed on the surface. It is thus shown in Figs. 8 and 9 that the nearer the amounts of methanol initially adsorbed approach v_m in BET equation (see Fig. 9), the nearer the reaction order comes to zero (see Fig. 8). At 150°C the decomposition of methanol was not observed, so the curve was obtained by means of the usual manner for the adsorption measurement.

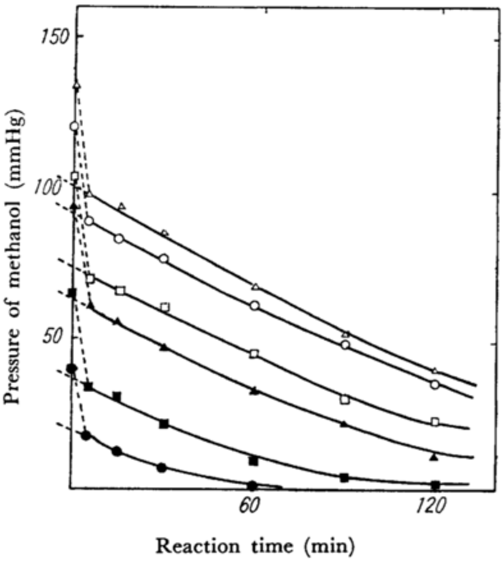


Fig. 8. The methanol decomposition at various initial pressure at 250°C.

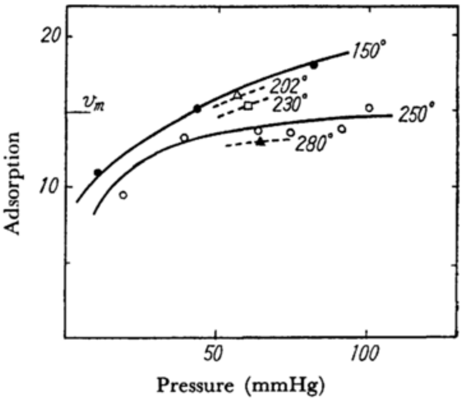


Fig. 9. Relation between adsorbed and gaseous methanol.

As for the mechanism and kinetics of the methanol decomposition, it is consequently concluded that the process of the dissociation of the adsorbed methanol into the adsorbed intermediate complex and hydrogen is the rate-determining step of the overall reaction as on the three component catalyst. The mechanism of methanol synthesis on zinc oxide is thus suggested to proceed in the similar way as on the three component catalyst.