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The Concentrations and the Reactivity of the Adsorbed Species during Surface Catalysis on a Ternary-component Methanol Synthesis Catalyst

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The relative reactivity of the adsorbed species during a catalytic methanol synthesis reaction on a ternary-component catalyst was investigated. Abrupt changes in the ambient pressure of a component in the gas phase, at a nearly equilibrium condition, were correlated with the corresponding changes in the amounts of the adsorption and in the total ambient pressure. The data collected from such dynamical treatments indicate that the species adsorbed on the catalyst surface, in a nearly equilibrated system of the simultaneous adsorption of hydrogen and carbon monoxide, is mostly the surface intermediate complex formed from both of them. Furthermore, the results obtained suggest an order for the reaction speed of each elementary step in the methanol synthesis reaction.

The importance of adsorption measurements on the catalyst in its working state has been emphasized by Tamaru.¹⁾ In all cases the catalytic reaction proceeds through a certain number of elementary steps, and the reactivity and the identification of the chemisorbed species are important. The concentrations of the adsorbed species during the methanol synthesis reaction catalyzed by a ternary component have been previously reported.²⁾

In this study, the authors investigated the relative reactivity of individual adsorbed species during surface catalysis by employing a dynamical technique for the adsorption measurements; thus they

obtained further information on the mechanisms of the methanol synthesis and decomposition.

Experimental

The apparatus employed was a closed circulating system, schematically illustrated in a previous paper.²⁾ Known amounts of the reactants were introduced into the system, and the extent of the reaction was followed by pressure measurements until an equilibrium state was reached. The amount of gas adsorbed on the catalyst surface was estimated by studying the material balance of the 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 carbon monoxide.

The ternary-component methanol synthesis catalyst

*¹ Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) K. Tamaru, Catalysis Meeting, Tokyo, April, 1957; K. Tamaru, *This Bulletin*, **31**, 666 (1958); *Advances in Catalysis*, **15**, 65 (1964).

2) S. Tsuchiya and T. Shiba, *This Bulletin*, **38**, 1726 (1965).

employed was of the type previously reported by the authors.²⁾ The technique for the purification of the reactants was also the same as that described before.²⁾

In order to treat the system dynamically, a certain amount of hydrogen and/or carbon monoxide was removed from, or added to, the system. Such removal or addition was carried out by first evacuating a part of the system and by then admitting a suitable amount of hydrogen and/or carbon monoxide, taking into account the volume of the system and the composition of the circulating-gas mixture. In each experiment, the initial state chosen for the dynamical treatment was a nearly equilibrium state of the reaction.

Results

Mixtures of $2\text{H}_2 : 1\text{CO}$ were first introduced into the system. After the system reached a nearly equilibrium state, and additional amount of carbon monoxide was admitted, causing an increase in the amount of the adsorption of carbon monoxide,

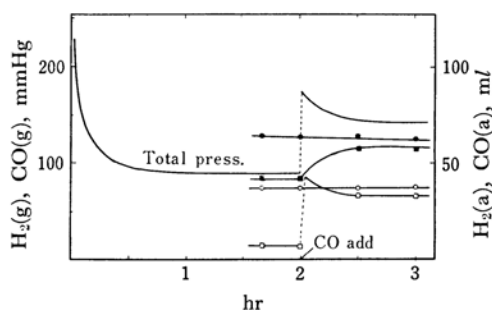


Fig. 1. Effect of carbon monoxide addition to an adsorption equilibrium system of hydrogen and carbon monoxide at 250°C .

- $\text{H}_2(\text{g})$ Ambient pressure of hydrogen
- $\text{H}_2(\text{a})$ Amounts of hydrogen adsorbed (s.t.p.)
- $\text{CO}(\text{g})$ Ambient pressure of carbon monoxide
- $\text{CO}(\text{a})$ Amounts of carbon monoxide adsorbed (s. t. p.)

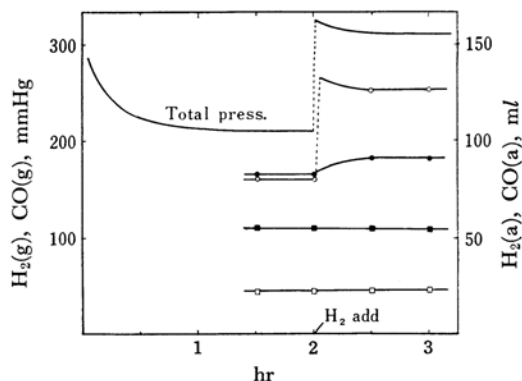


Fig. 2. Effect of hydrogen addition on the simultaneous adsorption equilibrium at 250°C .

The symbols are the same as shown in Fig. 1.

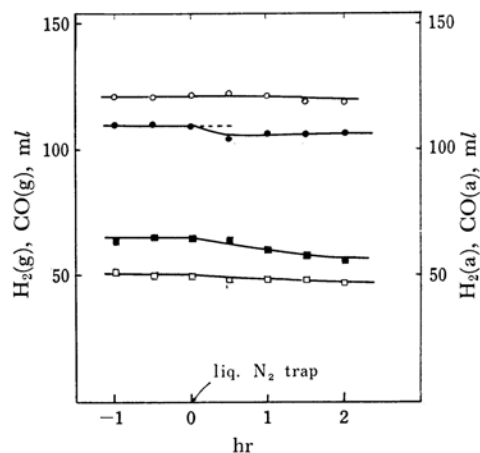


Fig. 3. Effect of elimination of methanol with a liquid nitrogen trap at the simultaneous adsorption equilibrium.

The symbols are the same as shown in Fig. 1.

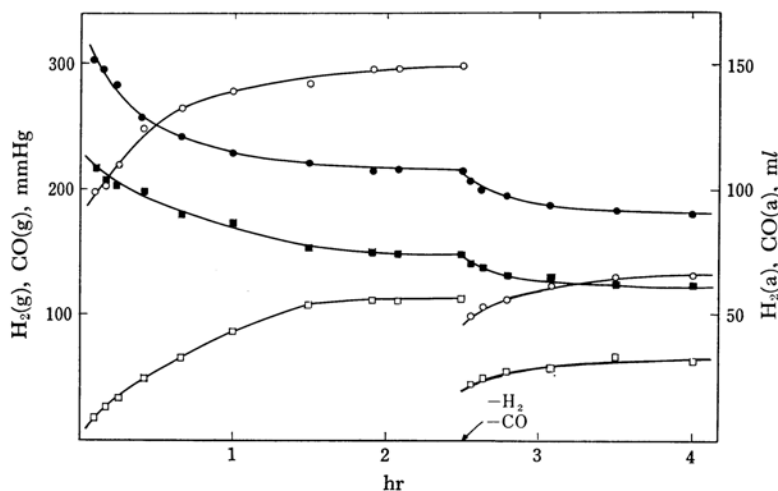


Fig. 4. Effect of elimination both of hydrogen and of carbon monoxide from the equilibrium system. The symbols are the same as shown in Fig. 1.

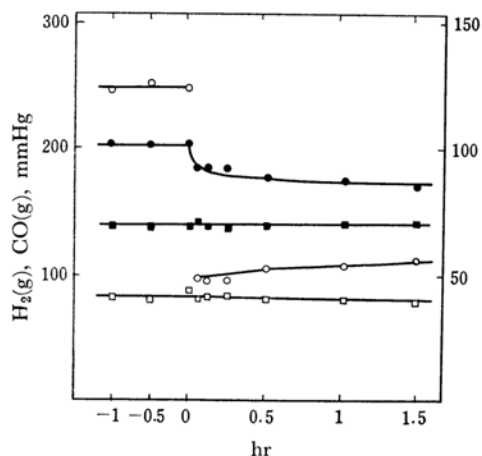


Fig. 5. Effect of elimination of hydrogen.

The symbols are the same as shown in Fig. 1.

while that of hydrogen was not affected as is shown in Fig. 1. When carbon monoxide was replaced with hydrogen, similar results were observed, as Fig. 2 shows.

When the trap in the reaction system which had been in the adsorption equilibrium was cooled with liquid nitrogen, while maintaining the circulation of gases (*i. e.*, the synthesis reaction proceeded), a slight decrease in the adsorption of both hydrogen and carbon monoxide was noticed, as is shown in Fig. 3. The adsorption also decreased with simultaneous decreases in the ambient pressure of both gases, as is shown in Fig. 4.

When the ambient pressure of hydrogen was abruptly changed, while that of carbon monoxide was kept constant, the amount of the adsorption of hydrogen decreased, but neither the adsorption nor the pressure of carbon monoxide was affected, as Fig. 5 shows.

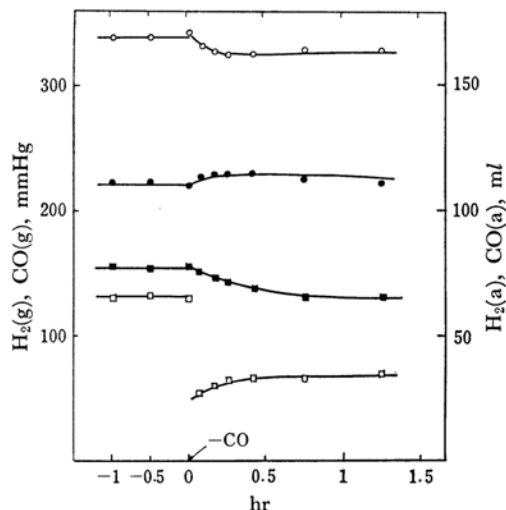


Fig. 6. Effect of elimination of carbon monoxide.

The symbols are the same as shown in Fig. 1.

When only the ambient pressure of carbon monoxide was decreased it had the effect of decreasing the amount of the adsorption of carbon monoxide, while slightly increasing that of hydrogen; there was also a decrease in the ambient pressure, as Fig. 6 shows.

As is shown in Fig. 7, the desorption of both hydrogen and carbon monoxide from the catalyst surface was observed after a few minutes' evacuation of the hydrogen and carbon monoxide present in the gas phase from the adsorption equilibrium system.

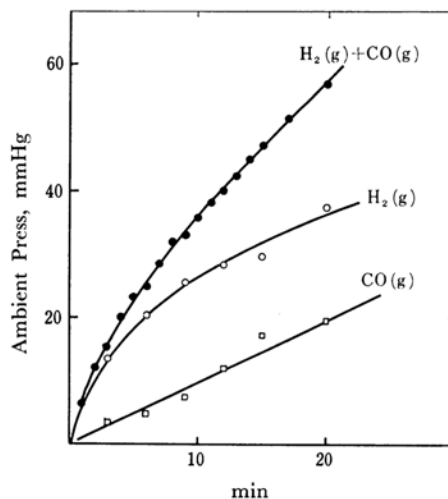


Fig. 7. Desorption measurements after a few minutes evacuation of gas phase.

○ Ambient pressure of hydrogen
□ Ambient pressure of carbon monoxide
● Total pressure of hydrogen and carbon monoxide

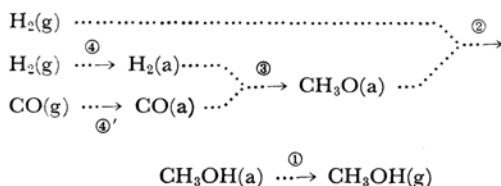
Discussion

The mutual enhancement of the chemisorption of hydrogen and carbon monoxide and its saturation has previously been reported.³⁾ As is shown in Figs. 1 and 2, when either hydrogen or carbon monoxide was admitted into the system after it reached its simultaneous adsorption equilibrium of hydrogen and carbon monoxide, the adsorption of the other gas was not affected. These results may be explained in terms of the saturation of the adsorption increment of the pre-admitted gas. The results also show that neither hydrogen nor carbon monoxide is in the form of a surface complex of the two gases, as had previously been expected.³⁾ They should rather be called "free hydrogen" or "free carbon monoxide". The findings, given in Fig. 5, that the adsorption of carbon monoxide was not affected when the

3) S. Tsuchiya and T. Shiba, *J. Catalysis*, **4**, 116 (1965).

ambient pressure of only hydrogen was abruptly decreased, seem to show the existence of "free hydrogen" on the surface. The amounts of this "free hydrogen" and "free carbon monoxide", however, would be small, since the decrease in the adsorption of hydrogen and carbon monoxide was small (about 10% of each), and the ratio of the amount of hydrogen adsorbed to that of carbon monoxide did not change widely with changes in their partial pressures.²⁾

As is shown in Fig. 3, when the gaseous methanol was abruptly removed from the pre-equilibrated system, the amount of hydrogen in the gas phase did not change, while that on the catalyst surface quickly decreased. This decrease in the amount of adsorbed hydrogen was of the same order of magnitude as that of methanol condensed in the trap. These results can be explained in terms of the desorption from the catalyst surface of adsorbed methanol. This conclusion is consistent with the mechanism previously proposed.²⁾



Consequently, it seems that the amount of hydrogen adsorbed in the form of methanol is small on the surface at the simultaneous adsorption equilibrium, since all the methanol adsorbed on the catalyst was presumably removed from the surface by the trapping. When liquid nitrogen was used for cooling the trap, both carbon dioxide and methanol were condensed, and it became very difficult to follow the behaviour of carbon.

It has been suggested that the amount of adsorbed methanol is small in the simultaneous adsorption, and that the rate-determining step of the methanol synthesis and decomposition reaction is step ②.²⁻⁴⁾ Only the surface complex, the free hydrogen,

and the free carbon monoxide can release hydrogen and carbon monoxide into the gas phase when such experiments as are shown in Figs. 4, 5, 6, and 7 are made. In the experiment shown in Fig. 7, the reactant was the surface complex; it produced hydrogen and carbon monoxide.

If the reaction of the step ④ proceeds more slowly than that of the step ③ or step ④' when the ambient pressure of hydrogen is decreased, its adsorption would not decrease without influencing carbon monoxide. However, as is shown in Fig. 5, the opposite result was obtained, suggesting that the reaction of the step ④ proceeds at the highest rate of the three. When the ambient pressure of carbon monoxide was decreased, the pressure and the adsorption of both hydrogen and carbon monoxide were affected, as Fig. 6 shows. If the reaction of the step ③ proceeded more slowly than that of the step ④', no effect on hydrogen would have been observed. This suggests that the reaction of the step ④' proceeds at the lowest rate of the three.

Consequently, the elementary steps would follow this order as far as the speed of reaction is concerned:



It may, therefore, be concluded that, in an equilibrium system of the methanol decomposition reaction, or in the simultaneous adsorption of carbon monoxide and hydrogen, the catalyst surface is mostly covered with the surface-intermediate complex, CH_3O , and that the speed of each elementary step during the decomposition reaction is $\text{④} > \text{③} > \text{④}' > \text{②}$, with ② being the rate-determining step.

The authors are grateful to Professor Yoshisada Ogino of Tohoku University for providing a catalyst sample.

4) S. Tsuchiya and T. Shiba, *ibid.*, **6**, 270 (1966).