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Mutual Influence of Adsorption of Hydrogen and Carbon Monoxide on a Methanol Synthesis Catalyst*

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The mutual influence of the chemisorption of hydrogen and carbon monoxide on a three-component methanol synthesis catalyst has been studied. The rate as well as the equilibrium amounts of the chemisorption of hydrogen and carbon monoxide are mutually enhanced by the presence of the other gas. The mutual enhancement of the adsorption is explained in terms of the complex formation. It is also suggested that the complex formed is the intermediate of the methanol synthesis reaction, and that the rate-determining step of the over-all reaction is the reaction between hydrogen gas and the surface complex.

INTRODUCTION

Extensive studies have been carried out so far on the methanol synthesis, which lead to a variety of mechanisms for the reaction. A termolecular reaction scheme was proposed by Natta, Mazzanti, and Pasquon (*1*). They concluded from their experimental results that the adsorption and the desorption proceed at much higher rates than the surface reaction, and that the rate-determining step is the reaction between two adsorbed hydrogen molecules and an adsorbed carbon monoxide. On the other hand, a bimolecular reaction scheme was also proposed that proceeds as follows: In the first step, an adsorbed hydrogen molecule reacts with an adsorbed carbon monoxide to form formaldehyde, which is followed by its hydrogenation to give methanol. The former process was originally considered to be rate-determining by Natta and Pastonesi (*2*), while the latter step was favored by Ozaki and Saita (*3*). Pasquon (*4*) recently suggested that both processes can proceed at comparable rates. Uchida and Ogino (*5*), on the other hand, suggested that the desorption of methanol from the surface is the rate-determining step. Cheredmichenko and Temkin (*6*) discussed the mechanism in the kinetic and internal diffusion regions and, according to their conclusion, the Knudsen diffusion of methanol in the catalyst pores was ascribed to be the rate-determining step.

Recently the importance of the adsorption measurements during surface catalysis has been emphasized by Tamaru (*7*), and such reactions as the decomposition of formic acid on metal catalysts (*8*) and the synthesis and decomposition of ammonia (*9*), have been studied with this new approach.

By means of Tamaru's method, the present authors reported in a previous paper (*10*) that the rate of reaction of the methanol synthesis is expressed by Eq. (1), or by Uchida-Ogino's equation (2),

$$r = kP_{H_2}A_{CO} \tag{1}$$

$$r = k(P_{H_2}P_{CO})^{\alpha} \tag{2}$$

where A_{CO} is the amount of carbon monoxide adsorbed in any forms of surface complexes with or without hydrogen, P_{H_2} and P_{CO}, the ambient pressures of hydrogen and carbon monoxide, respectively, and α, a constant, which is nearly 0.7. During the reaction, it was also observed that the ad-

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sorption of both hydrogen and carbon monoxide are enhanced by the presence of the other gas, and that the stoichiometric formula of the adsorbed species is CH_3O and not CH_2O. It is accordingly concluded that the reaction between hydrogen gas and the adsorbed CH_3O is the rate-determining step of the reaction (*10*), the Eley-Rideal type reaction taking place.

Mutual enhancement in the adsorption of gases has been reported by several authors, e.g. adsorption of hydrogen and carbon monoxide on a Fischer-Tropsch synthesis catalyst (*11*), and the adsorption of hydrogen and nitrogen on an ammonia synthesis catalyst (*8*b, *12*).

The present authors studied the mutual enhancement in the adsorption of hydrogen and carbon monoxide more extensively to secure further information on the mechanism of methanol synthesis.

EXPERIMENTAL

The apparatus employed in these experiments was a closed circulating system as is shown in Fig. 1. The composition of the catalyst employed was Zn:Cr:Cu = 1:0.49 :0.16 (*10*). The catalyst (19.7 g) was reduced at 280°C for 280 hr in a hydrogen stream, saturated with methanol vapor at room temperature, under atmospheric pressure in the same apparatus shown in Fig. 1. Before each experiment the catalyst was evacuated for 3 hr at 400°C. Being treated as such, the results of the experiments were reproducible. The purification of hydrogen, carbon monoxide, and methanol were carried out as previously described (*10*). The adsorption measurements were carried out volumetrically in the usual manner. In the simultaneous adsorption, the ambient gas was circulated to maintain a uniform composition throughout the system. The composition of the circulating gas was analyzed by means of gas chromatography as described by Murakami (*13*). Due allowance was made for the gas sample which was removed from the system.

RESULTS

Typical results of simultaneous chemisorption of hydrogen and carbon monoxide on a methanol synthesis catalyst are shown in Figs. 2 and 3. Pure hydrogen (148 ml, STP) was first introduced into the reaction system. A marked acceleration of hydrogen

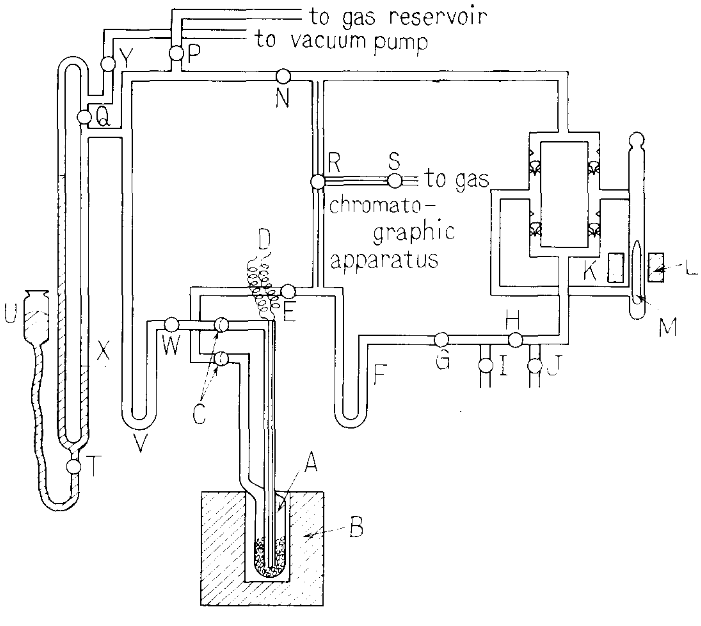

FIG. 1. Apparatus. A: reaction vessel. B: electric heater. D: thermocouple. F: trap cooled with liquid nitrogen. K: circulation pump.

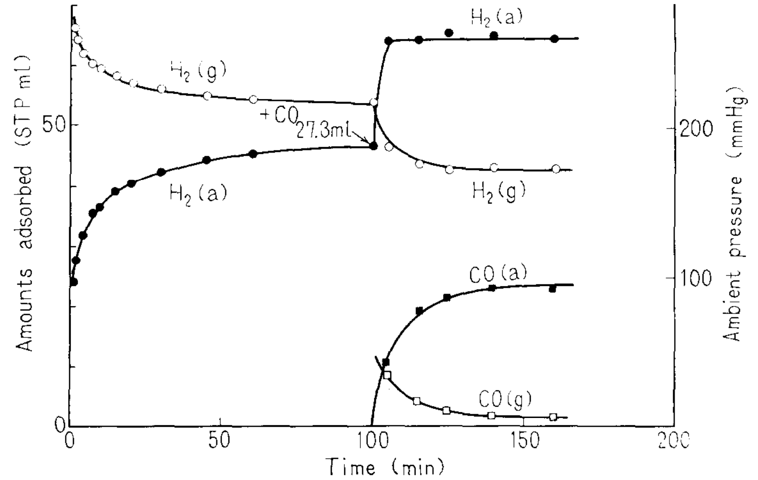

FIG. 2. Effect of carbon monoxide addition on hydrogen chemisorption at 250°C.

chemisorption at the addition of carbon monoxide was thus observed; as shown in Fig. 2. 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. 3, where pure carbon monoxide (160 ml, STP) was first introduced and then hydrogen was admitted. During the simultaneous adsorption, the methanol formed was neglected, because its amount was very small (less than 0.1% of the total gases) even if the synthesis reaction would reach an equilibrium.

When either carbon monoxide or hydrogen was added to the system if the other gas was present beforehand in adsorption equilibrium, the gas preadsorbed was further adsorbed in amounts corresponding to the amount of gas added afterwards. At this temperature (250°C), the apparent adsorption equilibrium of the added gas was seem-

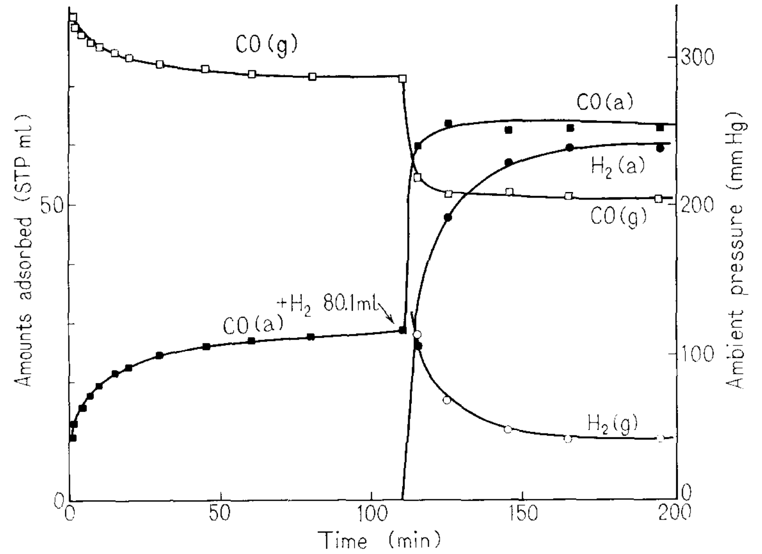

FIG. 3. Effect of hydrogen addition on the adsorption of carbon monoxide at 250°C.

ingly realized in 2 hr or so, while that of the preadmitted gas attained equilibrium much more rapidly. The results are shown in Fig. 4(a) and (b), where the amounts of preadmitted gas chemisorbed are plotted against the amounts of gas added. These results suggest that the mutual enhancement of adsorption has a certain saturation. When the amounts of gas introduced were less than those at knick points, the preadmitted gases were present in excess amounts. When the ratios of the amounts of hydrogen introduced to the amounts of carbon monoxide introduced were less than about 1, the situations corresponded to the "in excess" state of carbon monoxide, and when the ratios were more than about 2, the situations corresponded to the "in excess" state of hydrogen.

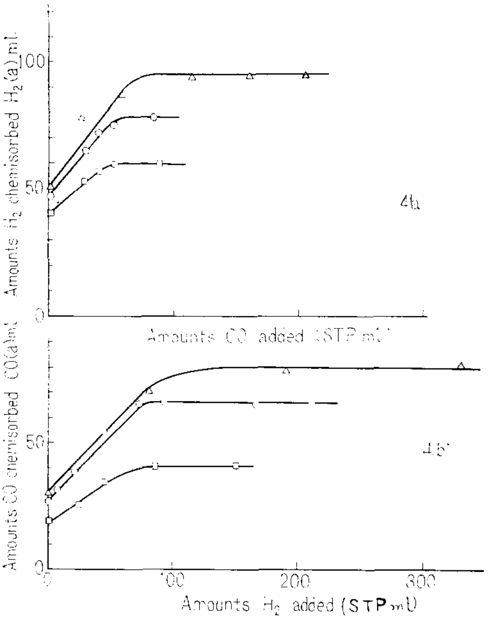

FIG. 4(a) and (b). The amounts of hydrogen [4(a)] or carbon monoxide [4(b)] chemisorbed at 250°C in adsorption equilibrium are plotted against those of the other gas admitted.

The mutual enhancement of the adsorption of these gases is shown more quantitatively in Figs. 5 and 6. In these two figures,

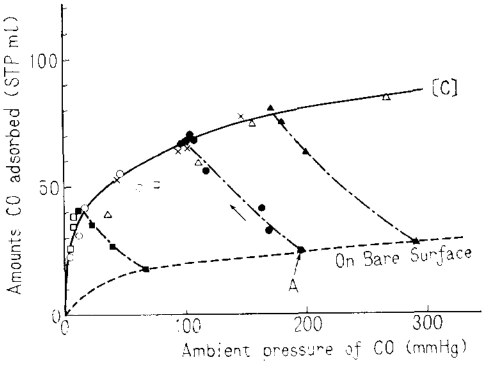

FIG. 5. The influence of hydrogen addition on the adsorption of carbon monoxide and the adsorption of carbon monoxide on a hydrogen-covered surface at 250°C.

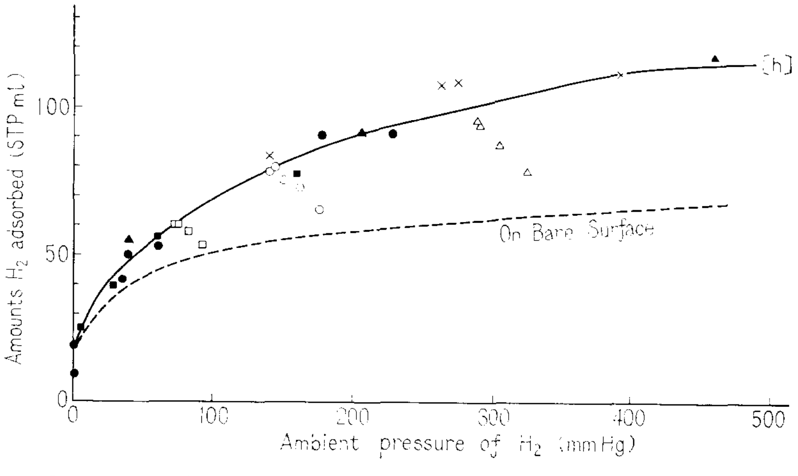

FIG. 6. The influence of carbon monoxide addition on the adsorption of hydrogen and the adsorption of hydrogen on the catalyst surface covered by carbon monoxide at 250°C.

the same symbols are employed for a series of runs. The dotted lines represent the adsorption isotherms on bare surface, and all the points which do not fall on the dotted lines represent the results of the enhanced adsorption of carbon monoxide or hydrogen by the presence of the other gas. The point A in Fig. 5 represents, for instance, an adsorption equilibrium of pure carbon monoxide. When a certain amount of hydrogen was added, the adsorption of carbon monoxide represented by solid circles changed in such a manner as indicated by an arrow, corresponding to the amount of hydrogen admitted, and when hydrogen is present in excess amount, the adsorption of carbon monoxide is expressed by the solid curve (c). Similar results were also obtained when the amounts of preadsorbed carbon monoxide were varied. The adsorption of hydrogen, in this case, is represented by solid symbols which fall on curve (h) shown in Fig. 6, excess carbon monoxide being present for the amounts of hydrogen.

When carbon monoxide was added to the system in adsorption equilibrium of hydrogen, the adsorption of hydrogen changed in a similar way as shown in Fig. 6 by open symbols. The curve (c) in Fig. 5 gives the adsorption of carbon monoxide when hydrogen was present in excess amounts.

The points x in Figs. 5 and 6, are the results obtained from the simultaneous adsorption of premixed gas whose composition was 1 CO:2 H_2 and they fall well on curve (c) or (h). A similar enhancement was also observed at 300°C, as shown by solid symbols in Fig. 7. The amounts of adsorption at 250°C were greater than those at 300°C.

A typical result of the adsorption measurements during the methanol decomposition reaction is shown in Fig. 8. The amounts of hydrogen and carbon monoxide adsorbed during the course of the reaction are greater than those in their adsorption equilibria. During the course of the reaction, the amount of methanol in the gas phase could be neglected, because it fell to less than 2% in a few minutes and less than 0.1% in the equilibrium. The relations between adsorption and ambient pressure of hydrogen and carbon monoxide after the decomposition are represented with open symbols in Fig. 7, which fall well on curve (c) or (h).

The surface area of the catalyst was estimated to be 7.0×10^6 cm^2 using the BET method with nitrogen adsorption at −196°C.

DISCUSSION

Mutual enhancement in adsorption has been explained by some workers (*11*b, *12*, *14*) in terms of the surface potential effect

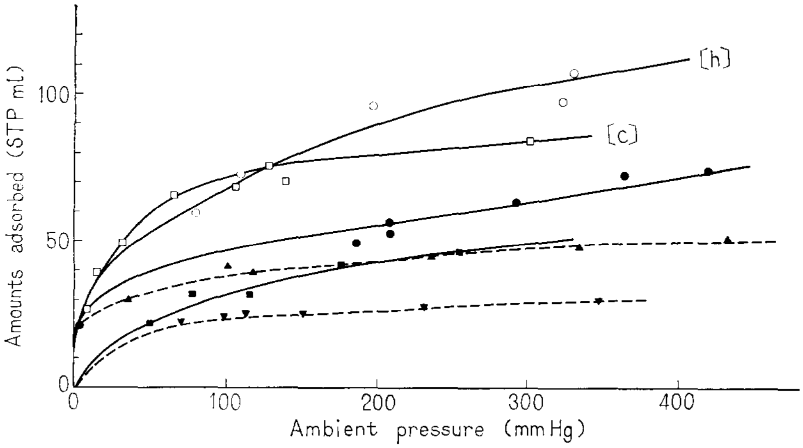

FIG. 7. The mixed adsorption of hydrogen (solid circles) and carbon monoxide (solid squares) at 300°C and the relation between partial pressure and adsorption of them after methanol decomposition reaction. The dotted lines represent the adsorption isotherms of hydrogen (solid delta) and carbon monoxide (solid atled) on bare surface at 300°C.

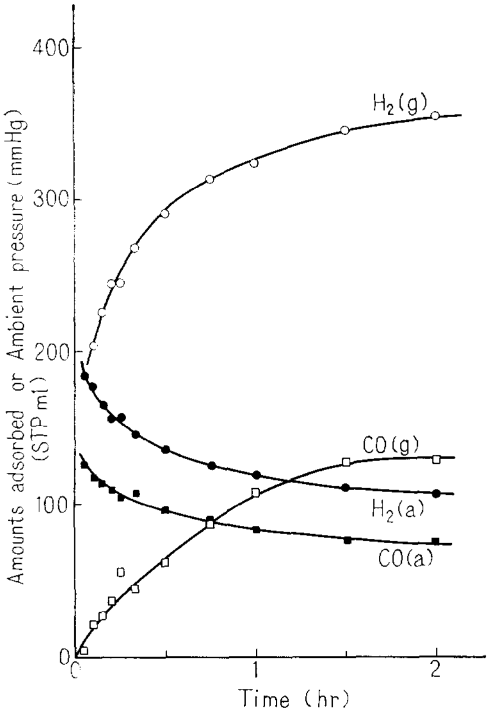

FIG. 8. Adsorption during decomposition of methanol at 250°C.

and/or the complex formation. As shown in Figs. 2 and 3, a marked increase in its equilibrium amount of adsorption of preadmitted gases was observed when the other gas was admitted. It is also shown in Figs. 5, 6, and 7 that the amounts of adsorbed gases in the mixed adsorption were greater than those separately adsorbed. These results might be due to the creation of additional sites, as was suggested recently by Nagarjunan, Sastri, and Kuriacose (*14*). In the process of additional creation of sites, according to them, the chemisorption of hydrogen would create additional donor levels in the catalyst and reduce the surface charge barrier, sharing its electron to form, for instance, a Zn–H bond. The situation created in such a way would be favorable for carbon monoxide adsorption. Carbon monoxide, on the other hand, by sharing the electrons of the catalyst, might facilitate the formation of Zn–H, where the hydrogen donates its electron. These gases would thus enhance their adsorption with each other.

As is shown in Fig. 7, the results obtained after the methanol decomposition reaction agree with those of mixed adsorption. In addition, a very small amount of methanol (less than 0.2% of the total gases) was detected in the gas phase in equilibrium. It is therefore conceivable that these curves represent equilibrium states between hydrogen, carbon monoxide, and methanol.

The formation of surface complex during the reaction was previously suggested (*10*) on the basis of the fact that the composition of the adsorbed phase hardly depends on that of ambient gas. Siddiqi and Tompkins (*15*) considered a complex formation on an evaporated Ni film at low temperature, −195°C, on the basis of the results of surface potential measurements. Eischens and Pliskin (*16*) did not find any evidence of complex formation with their spectroscopical measurements.

In the present experiment, the catalyst employed was a typical three-component methanol synthesis catalyst and quite different from their catalysts, and in addition, the temperature was different. Consequently, in the mixed adsorption, therefore, the formation of surface complex is highly probable. A constant composition of adsorbed species has been reported quite recently by Nagarjunan, Sastri, and Kuriacose (*14*), suggesting a complex formation on a methanol decomposition catalyst which is similar to the present results, although the temperature and catalyst employed were different from the present experiments.

In some cases of the present experiments, the sum of the adsorbed amounts of hydrogen and carbon monoxide exceeded 152 ml, v_m in the BET equation, to some extent, which does not contradict a complex formation on the catalyst.

Under a certain condition, the adsorption of both hydrogen and carbon monoxide fell on the curves (h) and (c) in Figs. 5 and 6, respectively. The ratio of the adsorbed hydrogen to carbon monoxide in these cases is nearly 1.5. This result agrees with those previously observed during the reaction (*10*).

The saturations in the adsorption increase, indicated in Fig. 4, suggest the excess adsorption of either hydrogen or carbon monoxide, which does not form a complex. Their amounts, however, would be small, as the ratio of the adsorbed hydrogen and carbon monoxide did not change widely by changing their partial pressures (*10*).

As to the amounts of adsorption during the present experiments, about 85% of the catalyst surface is covered by the species, presumably CH_3O, of which the cross-sectional area is estimated to be 25 Å^2. It is, however, necessary to determine the part of the adsorption which participates in the reaction, because the adsorption observed during the reaction, by means of Tamaru's method, may include an ineffective adsorption in the reaction. It was previously reported that the rate of methanol synthesis could be expressed by Eq. (1) (*10*). It is consequently suggested that at least a major part of the adsorbed species is the intermediate of the reaction.

After a methanol decomposition reaction reached an equilibrium, hydrogen and carbon monoxide in the gas phase were quickly pumped off in a minute or so, hydrogen alone was then admitted, and circulated again. In this way methanol was found in the circulating gas, from hydrogen and the intermediate surface complex. This fact also suggests that the surface complex is a reaction intermediate of the over-all reaction.

As for the hydrogen, on the other hand, the exponent of P_{H_2} in Eq. (1) is unity. This fact suggests that hydrogen molecules react with the surface complex at the rate-determining step, because the exponent of P_{H_2} should be 0.5 if hydrogen atoms react with the surface complex.

In relation to the mechanism of methanol synthesis, it is concluded that the reaction between adsorbed complex on the catalyst surface and hydrogen is the rate-determining step of the reaction, coupling with the previous results (*10*).

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