The Behaviour of Chemisorbed Species under the Reaction Conditions and the Mechanism of the Water-gas Shift Reaction on ZnO and MgO

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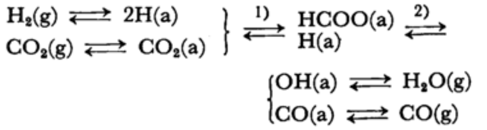
The importance of adsorption measurements during surface catalysis has previously been emphasized by one of the present authors.[1] The mechanism of the water-gas shift reaction on ZnO and MgO was studied by means of infrared techniques during the course of the reaction. It was found that a surface formate is formed on both of the catalysts as the reaction intermediate. The rate-determining step of this reaction was the decomposition of the surface formate.

When carbon dioxide and hydrogen were conducted onto ZnO at 150°C, the surface formate could be observed by infrared spectroscopy. The isotope shift of the C–H (and C–D) stretching vibration band was observed by employing deuterium gas. It was, however, difficult to find the surface formate in a mixture of carbon monoxide and water vapour on ZnO, though the surface OH group and CO(a) were found to be formed at a considerable rate. The dependence of the optical density of the infrared spectrum of the surface formate upon its coverage was obtained from a comparison of the spectroscopic and volmetric measurements on the adsorption of formic acid. The coverage of the surface formate during the overall reaction was obtained from the optical density.

The rate of the decomposition of the surface formate (v) was examined by means of infrared spectroscopy at the reaction temperature (230°C), forming the surface formate by introducing a known amount of formic acid vapour. Then the rate of the dehydration decomposition (v') was oatained by the following equation; $v'=v\times s$, where s is the selectivity, ($[CO]/[CO]+[CO_2]$), of the decomposition of the surface formate. It was then compared with the rate of the overall reaction ($H_2+CO_2 \rightarrow CO+H_2O$), v'', as measured by gas chromatographic analysis for the carbon monoxide produced. The two rates were in reasonable agreement within the limits of experimental error, provided the coverage was the same, which leads us to the conclusion that the surface formate is the reaction intermediate of the water-gas shift reaction and that its dehydration decomposition, step (2) in the following scheme, is the rate-determining step.

Run	Rate of overall reaction (v'') cc/g·hr	Rate of dehydration (v') cc/g·hr	Coverage
1	0.023	0.022	0.35
2	0.028	0.025	0.35
3	0.030	0.029	0.41



$$\left.\begin{array}{l} H_2(g) \rightleftarrows 2H(a) \\ CO_2(g) \rightleftarrows CO_2(a) \end{array}\right\} \overset{1)}{\rightleftarrows} \begin{array}{l} HCOO(a) \\ H(a) \end{array} \overset{2)}{\rightleftarrows} \left\{\begin{array}{l} OH(a) \rightleftarrows H_2O(g) \\ CO(a) \rightleftarrows CO(g) \end{array}\right.$$

When a mixture of carbon monoxide and water vapour was introduced over MgO, we confirmed the formation of a surface formate on the catalyst by means of infrared spectroscopy in a manner similar to that used in ZnO, as has been found by Scholten.[2] However, it was found that the surface formate could not be easily observed from a mixture of carbon dioxide and hydrogen on MgO.

We measured the rate of the dehydrogenation decomposition of the surface formate by infrared spectroscopy at 280°C in order to compare it with the overall reaction rate, as measured by gas-chromatographic analysis, for the carbon dioxide produced. As was the case over ZnO, the two rates were in reasonable agreement within the limits of experimental error if the adsorption of surface formate was the reaction intermediate of the reaction on MgO; the rate-determining step was the step of the dehydrogenation decomposition of the surface formate, step (1).

In the water-gas shift reaction over both ZnO and MgO, the change in the adsorptions of water, carbon dioxide, carbon monoxide, and hydrogen did not considerably influence the rate of the decomposition of surface formate under the reaction conditions employed.

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[1] K. Tamaru, "Adv. Catalysis", Vol. 15 Academic Press, Inc., New York (1964) p. 65; *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.),* **87**, 1007 (1966).

[2] J. J. F. Scholten, P. Mars, P. G. Menon and R. van Hardeveld, Proc. 3rd. Int. Congr. Catalysis, Amsterdam, 881 (1964).