ceeds on normal surface-gold sites. The slow and activated adsorption observed is in accordance with the suggestion that oxygen adsorption is the rate-determining step in carbon monoxide oxidation.

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Chemisorption of Carbon Monoxide on Ferric Oxide

A Test for the Active Site on the Transition Metal Oxides

It has been shown that the transition metal oxides such as Co_3O_4, NiO, Cr_2O_3 are active catalysts for the isotopic mixing in hydrogen (*1*) and ethylene (*2*), and the hydrogenation of ethylene (*3*). The twin peak pattern of the activity change (*1*) introduced by Dowden, Mackenzie, and Trapnell is well known, and a crystal field interpretation of this pattern has been proposed (*4*). On the other hand, it has been shown that the catalytic activities of these oxides for the isotopic mixing in ethylene is developed by dehydration of the oxide surface brought about by evacuation at higher temperatures above 200°C (*2*). The active sites thus formed on the oxide surface are admittedly oxygen vacant because of the removal of a water molecule from the hydroxylated surface. Accordingly, it seems that the oxygen vacancy is an essential condition for the active oxide catalyst.

As previously reported (*2*), the active sites on these oxides are effectively blocked by carbon monoxide and also by water. The fatal amounts of carbon monoxide that prevent the isotopic mixing in ethylene are generally small as follows: Co_3O_4:2.4, NiO:0.4, Cr_2O_3: <0.3 10^{14} molecules/cm^2, where oxides were pre-evacuated at 500°C. These figures give the approximate number of active sites. Thus one can estimate the number of active sites by the chemisorption of carbon monoxide at low pressure on these oxides.

In this respect it is interesting to study the chemisorption of carbon monoxide on ferric oxide which is known to be inactive for the isotopic mixing (*1–2*). However no data relevant to this problem is available. Thus it was decided to study the nature of the active site by the chemisorption of carbon monoxide on ferric oxide at low pressure.

EXPERIMENTAL

The ferric oxide sample was prepared by decomposition (550°C, 6 hr, in air) of ferric hydroxide, which was prepared by precipitation from ferric nitrate with ammonia. BET area of the sample was 20 m^2/g. Adsorption measurements were carried out at room temperature following pressure change by means of a rotating McLeod gauge. The dead space in the adsorption system was 915 ml. The initial pressure was around 7×10^{-2} mm Hg.

Results and Discussion

There was an initial rapid decrease in the pressure followed by a slow but steady decrease. The rate of decrease in the later period was rather independent of the evacuation temperature and seemed to be a slow oxidation of carbon monoxide by the ferric oxide. Thus the initial rapid adsorption was estimated by extrapolation of the later steady decrease to the time zero. The amounts of the initial adsorption thus obtained are plotted against the preevacuation temperature as shown in Fig. 1.

It is clear that the oxide is activated for the initial rapid adsorption of carbon monoxide by the preevacuation above 200°C and that the amount of adsorption increases with the preevacuation temperature. The number of adsorption sites estimated from this result reaches about $1 \times 10^{14}/cm^2$ after evacuation at 470°C.

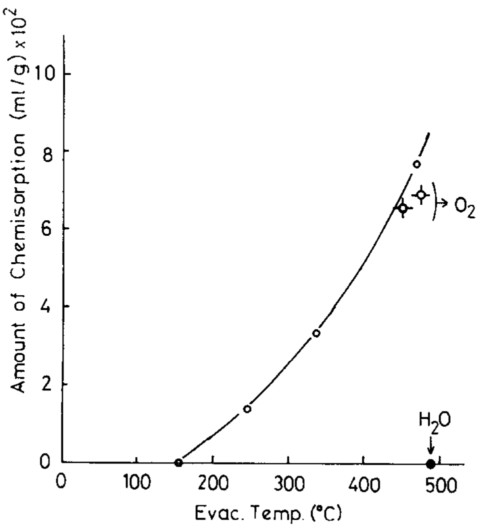

Fig. 1. Adsorption of carbon monoxide on ferric oxide at room temperature as a function of evacuation temperature: ⌖ cooled in O_2 and reevacuated at 165°C, and ● cooled in H_2O vapor and reevacuated at 170°C.

In order to examine the cause of the activation, a small amount of oxygen was introduced over the oxide after the preevacuation at 450°C. Thus the oxide was cooled in the oxygen atmosphere down to room temperature and again evacuated at 165°C for 3 hr. The adsorption measurement made on this sample proved no effect of oxygen as shown in Fig. 1. But when the oxide was cooled in water vapor after evacuation at 490°C, and evacuated again at 170°C for 3 hr, this sample gave no adsorption of carbon monoxide as shown in Fig. 1. This result clearly shows that ferric oxide is activated for the carbon monoxide adsorption by dehydration from the surface. This means that there are exposed metal ions on the ferric oxide surface after the evacuation at high temperature. The mode of activation as shown is quite similar to that observed with nickel oxide or cobalt oxide. Accordingly, it may be concluded that the inactiveness of ferric oxide is due, not to lack of the site, but to inability of the exposed metal ion itself.

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