Characteristic Behavior of Chemisorbed Oxygen towards CO on Ag Surface

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When oxygen reacts with CO on Ag surface, the silver surface is fully coveed by oxygen, but only a limited part of the chemisorbed oxygen participates in the reaction. Such characteristic behavior was discussed on the basis of STM observation.

Oxygen is chemisorbed on silver (110) surface, growing one-demensional linear chain along the (001) direction. These chains repulse each other and separate to form the (nx1) arrangement where the value of n changes sequentially depending upon the amount of chemisorbed oxygen. The behavior of chemisorbed oxygen towards hydrogen was studied on a silver surface in a previous paper[1]. If the hydrogen attacks the terminal parts of the chains at full coverage, the reaction should be zero order with respect to the amount of chemisorbed oxygen, because the number of the reaction sites will stay unchanged at the beginning of the reaction. However, the reaction between the chemisorbed oxygen at full coverage and hydrogen gas proceeded as first order with respect to the pressure of hydrogen and also to the amount of chemisorbed oxygen from the beginning. It was thus suggested that the reaction between the chemisorbed oxygen and molecular hydrogen gas would take place not at the ends of the linearly chemisorbed oxygen chains, but at the middle part of the chains, all the chemisorbed oxygen, uniformly participating in the reaction. It is, accordingly, very interesting to study the behavior of the chemisorbed oxygen towards carbon monoxide to form carbon dioxide on the same silver surface, because silver is a unique catalyst for the partial oxidation of olefins

The behavior of chemisorbed oxygen on a ultrafine particles of silver was studied in a closed system with bellow-type circulation pump, as reported in a previous paper[1]. Approximately 100 gr. of the silver ultrafine particles were employed. The average size of the particles was estimated to be 20~30 nm in diameter from the surface area measurements. At first the silver sample was heated to 420 K until all the carbon dioxide decomposed was collected in a liquid nitrogen trap. The sample was subsequently treated by hydrogen at 343 K for a few hours until all the oxygen on the surface was removed. The sample was exposed to oxygen at 273 K for a quarter of an hour to saturate the surface. When carbon monoxide was introduced onto the silver surface fully covered by chemisorbed oxygen, carbon dioxide was collected in a liquid nitrogen trap in the circulating system and the total pressure decreased as shown in Figure 1. The reaction proceeded to some extent at the beginning, but soon became very slow, although the major part of the chemisorbed oxygen remains on the surface under CO gas.

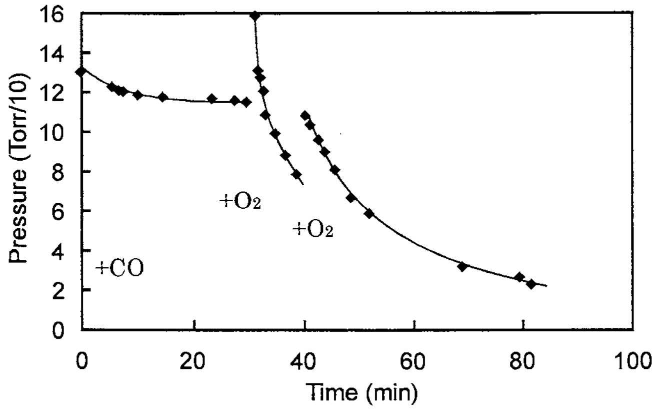

Figure 1. The reaction between CO and oxygen on a ultrafine particles of silver at 350 K in a closed circulating system. The effect of addition of oxygen gas to CO gas.

When oxygen gas was added to carbon monoxide in the gas phase, the reaction between carbon monoxide and oxygen to form carbon dioxide proceeded at a remarkable rate as given in Figure. 1, a negligible amount of chemisorbed oxygen increased on the oxygen addition. The reaction was zero order with respect to oxygen pressure, whereas first order to carbon monoxide. The rate of the reaction between chemisorbed oxygen and the ambient carbon monoxide in the absence of oxygen gas was plotted against the coverage of oxygen on the silver surface in Figure 2, which demonstrates that only a limited part of the chemisorbed oxygen is reactive towards carbon monoxide, major part of the chemisorbed oxygen remaining inert towards carbon monoxide.

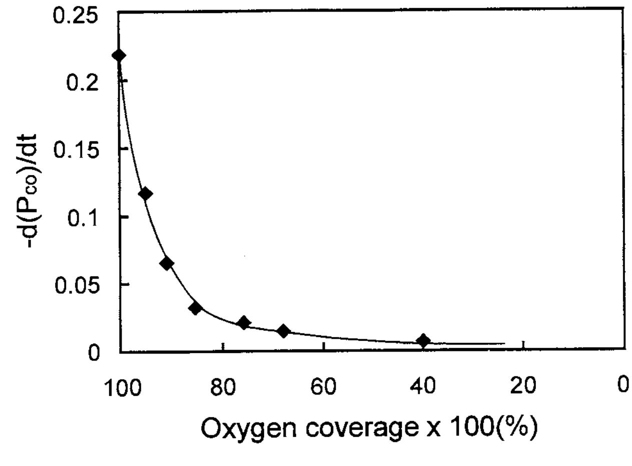

Figure 2 . The dependence of the rate of reaction between CO and chemisorbed oxygen upon the amount of chemisorbed oxygen at 273 K.

As mentioned above, the oxygen chemisorbed on a silver surface reacted with hydrogen as first order with respect to not only hydrogen pressure, but also to the amount of chemisorbed oxygen, all the oxygen on the silver surface uniformly participating in the reaction. However, in the case of the reaction with carbon monoxide, only its small part reacts with carbon monoxide, major part of the chemisorbed oxygen remaining inactive. It is, accordingly, of great interest to find out that carbon monoxide reacts with the chemisorbed oxygen in quite a different manner from hydrogen on silver surface. Why all the chemisorbed oxygen uniformly does react with hydrogen, whereas only its limited part only reacts with carbon monoxide ?

The limited active part of the silver surface is seemingly saturated with chemisorbed oxygen during the course of the reaction (because it is zero order with respect to oxygen pressure) and the reaction takes place between such strongly chemisorbed oxygen in the limited part of the surface and incident carbon monoxide molecules.

The formation of carbonate on introduction of carbon dioxide onto oxygen precovered silver surface was studied by various people such as, for instance, Madix, Sachtler and Campbell[2] and more recently, in particular, by Stensgaard and Tanaka[3] by means of STM techniques. It is very interesting to note that the oxygen fully covered the silver surface forms carbonate when carbon dioxide is introduced onto the surface, being supplied from the upper edge of the step site. The amount of carbonate formation on the surface becomes less as more oxygen is chemisorbed, because the carbonate formed on the surface is considerably bulky, the rest part of the chemisorbed oxygen on the surface is so tightly pushed to change from, for instance, (3x1)(-Ag-O-) to (2x1)(-Ag-O-), consequently becoming inert to form carbonate due to steric effects. The only exception looks to be the chemisorbed oxygen near the step edge of Ag(110), where CO_2 can form carbonate. This observation by STM is well correlated with the dynamic behavior of chemisorbed oxygen on silver surface, supporting the non-uniform behavior of chemisorbed oxygen.

References

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