

# Characteristic behavior of chemisorbed oxygen on silver in the reaction with carbon monoxide

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## Abstract

When chemisorbed oxygen on silver at full coverage was exposed to carbon monoxide at 273 K, a small amount of the chemisorbed oxygen reacted readily with carbon monoxide, but the rest of the oxygen remained inert. However, when some oxygen gas was added to the ambient carbon monoxide, the reaction to form carbon dioxide proceeded at a remarkable rate. The rate of the reaction in the presence of both oxygen and carbon monoxide in the ambient gas was first order with respect to carbon monoxide, and zero order with respect to oxygen gas. Such behavior suggests that the reaction between oxygen and carbon monoxide takes place in a very limited part of the silver surface, all the rest part remaining unreactive, and both active and unreactive regions being fully covered by oxygen during the reaction. A method to identify the limited number of active sites on the surface is suggested using scanning tunneling microscopy (STM) at nanoscale resolution. It is in conjunction with the isotope jump method at condition where all the surface species are immobile except those on the limited active part of the surface during the reaction. © 2000 Published by Elsevier Science B.V.

*Keywords:* Characteristic behavior; Carbon monoxide; Chemisorbed oxygen

## 1. Introduction

When oxygen is chemisorbed on the silver (110) surface, the chemisorbed oxygen forms one-dimensional linear chains along the (001) direction, which may be considered as “pseudomolecules”. These chains repulse each other and separate to form the  $(n \times 1)$  arrangement where the value of  $n$  changes sequentially depending upon the amount of chemisorbed oxygen on the surface. Let us assume that a considerable part of the silver surface employed in this study behaves in a manner similar to that on the silver (110). Consider starting at full coverage of chemisorbed oxygen and introducing hydrogen gas to react with such linear “pseudomolecules”. If the reaction takes place at both ends of such linear structure, the reac-

tion would be initially zero order with respect to the amount of chemisorbed oxygen, because the number of the reaction sites would stay unchanged at the beginning. The linear structure would just get shorter by consuming both ends of the pseudomolecules. However, the rate of the reaction was actually first order with respect to the amount of chemisorbed oxygen from the beginning, which suggests that hydrogen molecules attack the pseudomolecules not at the ends of the molecules but at the middle part of the molecules for hydrogen molecules to dissociatively react with the linear structure [1]. Consequently, all the chemisorbed oxygen seemingly behaves uniformly and hydrogen molecules attack the chemisorbed oxygen, although no chemisorption of hydrogen could be observed during the course of the reaction.

When oxygen is chemisorbed on copper (110) surface, the linear pseudomolecules coalesce with each other to form island structure. When such island structures react with hydrogen, the reaction seemingly takes place at the peripheral part of the islands of chemisorbed oxygen, reacting with dissociatively adsorbed hydrogen. It is because the rate of the reaction is approximately proportional to the number of peripheral atoms of the oxygen islands and to the square root of hydrogen pressure.

In the silver and copper cases above the rate of the reaction is dependent upon the structure of chemisorbed oxygen. A further interesting problem is to consider how carbon monoxide, instead of hydrogen, reacts with chemisorbed oxygen on a silver surface. Since silver is a famous catalyst for the partial oxidation of olefins, the behavior of the chemisorbed oxygen on silver surface is an interesting subject to study, although many people, such as, for instance, Campbell, Madix, Sachtler, Van Santen, and Vannice, have studied the system [2–8]. In this study, a silver with very large surface area was employed to study in detail the behavior of chemisorbed oxygen. It was found that the behavior of chemisorbed oxygen with carbon monoxide is remarkably different from that with hydrogen.

## 2. Experimental

The reaction between chemisorbed oxygen and carbon monoxide was studied in a closed circulation system with a bellows-type recirculation pump, as reported in a previous paper [1]. Unsupported fine particles of silver were prepared by an evaporation technique. Approximately 100 g sample was employed, corresponding to a surface area of 200 m<sup>2</sup>. In this system, since the surface area of the sample was so large, the behavior of chemisorbed oxygen could be followed quantitatively.

The silver sample was first heated to 420 K in vacuum until all the carbonate in the surface was decomposed and subsequently treated by hydrogen at 343 K for a few hours until all the oxygen on the surface was removed. Oxygen was introduced onto the clean surface at 273 K for a quarter of an hour to saturate the surface with chemisorbed oxygen.

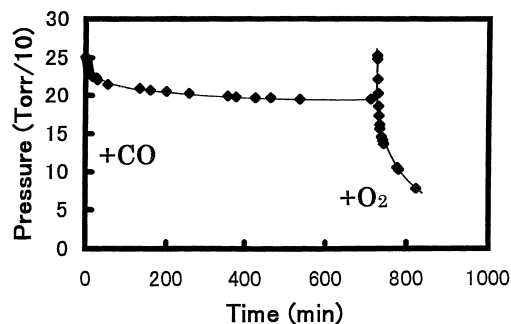


Fig. 1. Reaction between carbon monoxide and oxygen chemisorbed on silver at 350 K. Oxygen gas was subsequently added.

## 3. Results and discussion

The surface thus prepared was exposed to carbon monoxide, and the carbon dioxide formed was collected by a liquid nitrogen trap in the recirculation system while the total pressure was measured as a function of time. The results are given in Figs. 1 and 2. It is very interesting to observe that the reaction proceeded only to a small extent at the beginning, and that the rate of the reaction soon dropped down to very low value, even though most of the silver surface was still covered by chemisorbed oxygen under carbon monoxide gas. In the case of hydrogen, instead of carbon monoxide, the chemisorbed oxygen behaved in a uniform manner from the beginning, as shown in the previous paper [1]. The rate of the reaction at 273 K between carbon monoxide and chemisorbed oxygen on the surface is plotted against the coverage

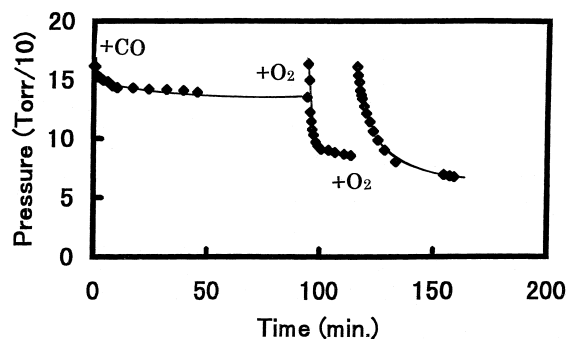


Fig. 2. Reaction between carbon monoxide and oxygen chemisorbed on silver at 273 K. A small amount of oxygen was first added and then more oxygen was added later.

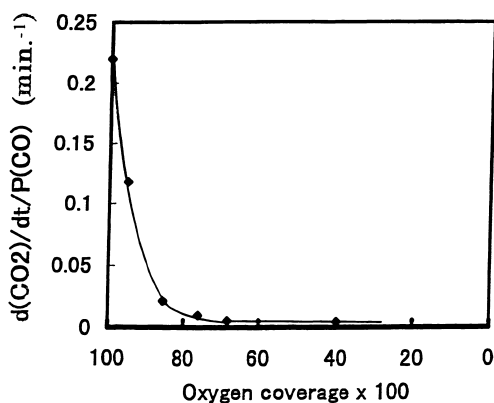


Fig. 3. Rate of reaction between carbon monoxide and chemisorbed oxygen on silver at 273 K as a function of oxygen coverage.

of the chemisorbed oxygen in Fig. 3. The rate shows a sharp drop with coverage, indicating that only a small number of sites on the surface is active. At higher temperatures the drop of the rate with coverage decreased considerably as shown in Fig. 4. The figure suggests that the reaction actually takes place over a wider range of sites, perhaps by the diffusion of reactive species around the active sites. It is accordingly suggested that at temperatures much lower than 273 K the drop of the rate with coverage will become much sharper and actual active sites will be much more limited in number on the catalyst surface.

A more exciting observation was recorded when oxygen gas was added to the ambient carbon monoxide gas. The reaction took place at a remarkable rate

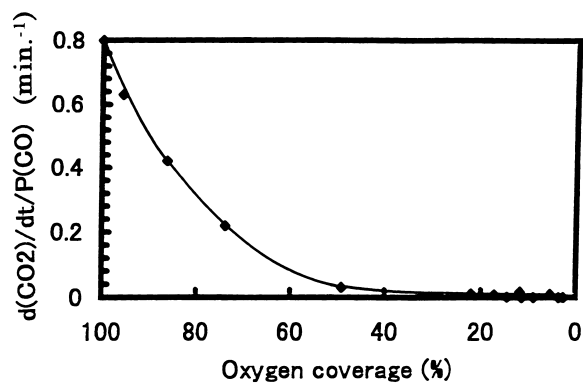


Fig. 4. Rate of reaction between carbon monoxide and chemisorbed oxygen on silver at 347 K as a function of oxygen coverage.

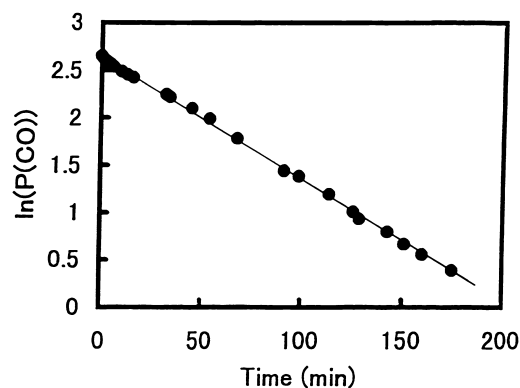


Fig. 5. Logarithms of carbon monoxide pressure are plotted against reaction time in the reaction between carbon monoxide and oxygen gas.

on oxygen addition as given in Fig. 2. The rate is given by the slope of pressure versus time curves and was calculated to increase by approximately two-orders of magnitude on addition of the oxygen. The kinetics of the latter reaction in the presence of both oxygen and carbon monoxide in the ambient gas was studied by changing the partial pressure of reacting gases during the course of the reaction. The rate of the reaction was first order with respect to carbon monoxide, as given in Fig. 5, whereas zero order with respect to oxygen pressure. Such behavior can be fully explained if the reaction between carbon monoxide and oxygen proceeds on a very limited part of the surface which is fully covered by chemisorbed oxygen during the course of the reaction. The rest of the surface stays inert towards carbon monoxide, although it is also fully covered by chemisorbed oxygen. The zero-order kinetics with respect to oxygen excludes the possibility of “adsorption-assisted processes” for oxygen molecules to activate the inert chemisorbed oxygen and other surface species.

It is of great interest to note that the behavior of chemisorbed oxygen towards the reducing gases, hydrogen and carbon monoxide, is quite different. In the former case all the chemisorbed oxygen behaved uniformly, whereas in the latter case only very limited part of the adsorbed oxygen on the silver surface is active.

The reaction between carbon dioxide and chemisorbed oxygen on Ag(1 1 0) has been previously studied [9] and the formation of carbonate was reported, which takes a parallel conformation to the Ag(1 1 0)

surface and compresses the remaining oxygen into a structure giving a  $(2 \times 1)$  LEED pattern. This interesting behavior was studied in more detail by means of the STM technique [10,11]. It was demonstrated by STM that the  $(-\text{Ag}-\text{O}-)$  strings were compressed into the  $(2 \times 1)$  structure as the coverage of carbonate species increased, and the reactivity of the  $(-\text{Ag}-\text{O}-)$  strings towards carbon dioxide was markedly suppressed when the  $(-\text{Ag}-\text{O}-)$  strings were compressed into the  $(2 \times 1)$  arrangement. For instance, when a  $(-\text{Ag}-\text{O}-)/\text{Ag}(110)\text{p}(3 \times 1)$  was exposed to carbon dioxide, bulky carbonate species are formed and the remaining  $(-\text{Ag}-\text{O}-)$  strings over the  $\text{Ag}(110)$  surface are compressed into the  $(2 \times 1)$  structure, the reactivity consequently being much suppressed by the compression. On the other hand, the STM images showed that the reaction of  $(-\text{Ag}-\text{O}-)$  strings with carbon dioxide proceeded from the step edges, but the surface steps did not move during the reaction.

It is of great interest to note that the behavior of the chemisorbed oxygen towards carbon monoxide on the silver surface observed by the volumetric method reasonably conforms to that observed by the STM method. Taking the behavior observed by STM into consideration, it is very probable that the limited number of active sites in the Ag surface corresponds to position near the step structure.

Generally speaking, during the course of a catalytic reaction most of the chemisorbed species are diffusing around on the catalyst surface. Although the solid surface generally contains various structures such as, for instance, different crystal planes, steps, kinks, and defects, which have different electronic properties with different catalytic activity, the reaction at these different sites are generally averaged out. However, the characteristic feature of the reaction system between carbon monoxide and oxygen with chemisorbed oxygen on the silver surface may be interpreted as follows. During the course of the reaction all the silver surface is completely covered by chemisorbed oxygen containing some carbonate species, and all the chemisorbed species are immobile except in the limited part near the steps on the surface on which the reaction is actively taking place. It is consequently suggested that if the isotope jump method which the author proposed previously [12] would be applied to the reaction system, the number of the limited active sites may be estimated. In other words, during the course

of the reaction between oxygen and carbon monoxide in the ambient gas, if carbon monoxide is replaced with its oxygen isotope labeled counterpart during the steady state of the reaction, the carbonate (or oxygen) at the active sites can only be replaced by its oxygen isotope as the result of reaction. All the other chemisorbed species will stay unchanged during the reaction, while the reaction product, carbon dioxide, will contain the isotopic label in large proportion after the isotope jump. The quantity of the isotope fixed on the catalyst surface should reveal the number of the active sites involved in the reaction. However, as Figs. 3 and 4 indicated, as the temperature is raised this number will be increased as the sites near the real active sites will be involved by surface diffusion processes.

Recently the vibrational spectroscopy of single molecule adsorbed on solid surface has been studied by the STM technique [13]. By means of this technique the determination of the isotopic abundance of each of the adsorbed species may be possible. In the case of the reaction between oxygen and carbon monoxide on a silver surface, for instance, by applying the isotope jump technique: (1) most of the carbonate species on the surface may be confirmed not to be reaction intermediates, staying unchanged after the isotope jump; (2) whereas only those at the special active sites will be replaced by the labeled species. The labeled species should not move around on the surface after the isotope exchange and such experiments should be carried out at lower temperatures such as liquid nitrogen or dry ice temperatures so that only the species on the active sites may undergo isotopic exchange. Measurement of the vibrational spectra of each of the surface species at liquid helium temperature can then be undertaken to examine the isotopic abundance. In this manner the real active sites may be identified at a nanoscale level. If such experiment would actually be realized it would become the first example of directly identifying the active sites on the catalyst surface at an atomic level.

Recently characteristic behavior of step (or defect) sites has been studied by Yates and coworkers [14] and King and coworkers [15].

At least a direct method to identify the real active sites may be carried out by combining isotope jump method and single molecule vibrational observation during the course of reaction under the conditions that all the chemisorbed species are not mobile.

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