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Generation of Oxygen Vacancies at a Au/TiO_2 Perimeter Interface during CO Oxidation Detected by in Situ Electrical Conductance Measurement

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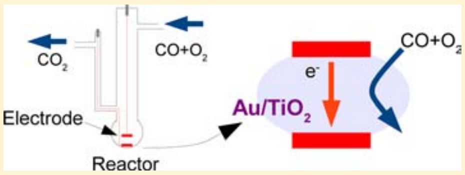
S *Supporting Information*

ABSTRACT: Although the importance of a Au/oxide perimeter interface has been recognized in the field of gold catalysis, the experimental evidence on the reaction occurring at the perimeter is still limited. In this research, we applied in situ electrical conductance measurement (in situ ECM) to measure the CO oxidation with O_2 over Au/TiO_2 catalyst powder and found that the oxygen vacancies are generated at the Au/TiO_2 perimeter interface during the CO oxidation. The present result supports the reaction model in which oxygen molecules are activated on such oxygen vacancies.



1. INTRODUCTION

In order to clarify the mechanism of a catalytic reaction, the observation of reduction and oxidation of the catalyst under the reaction conditions affords important information about the interaction between the catalyst and the molecules in the gas phase. X-ray photoelectron spectroscopy (XPS) is well-known to give information about the oxidation state of surface elements. However, it is not suitable for in situ measurement under reaction conditions because it requires an ultrahigh vacuum environment. Infrared spectroscopy is effective for the in situ measurement. For example, frequency shifts of adsorbed CO molecules provide the information on the electrical charge transfer between CO and the catalyst. However, it is not applicable to support oxides such as TiO_2 that do not adsorb CO molecules chemically.

In situ electrical conductance measurement (in situ ECM) is the technique which measures the electrical conductance of the catalyst simultaneously with the kinetics of the catalytic reaction.[1−9] It allows us to investigate oxygen vacancies produced on the surface of catalysts under the reaction conditions. The method is highly sensitive for detecting the oxygen vacancies, because they usually release conduction electrons in semiconducting metal oxides. For example, Onish determined the amount of oxygen vacancies to be 0.2% of the surface lattice oxygen of TiO_2 in the steady state of CO oxidation.[2] In situ ECM technique was frequently used in the study of the catalytic oxidation of CO on metal oxide catalysts, such as TiO_2, MoO_3, CeO_2, and SnO_2, in the 1970s−1980s. Currently, however, few research groups employ the in situ ECM technique.

The tremendous catalytic activity for the low-temperature CO oxidation of Au nanoparticles (NPs) deposited on a series of reducible semiconductor metal oxides such as TiO_2, Fe_2O_3, and Co_3O_4 was first discovered by Haruta et al. and reported in 1987.[10] Concerning the mechanism of the generation of the catalytic activity, they pointed out the importance of the Au/oxide perimeter interface[11] and proposed that oxygen molecules are activated at the perimeter interface, assuming the generation of oxygen vacancies.[12] Recently, Whidmann et al. found that surface lattice oxygen at the Au/TiO_2 perimeter interface is easily removed in a CO atmosphere.[13] However, the generation of oxygen vacancies during the catalytic CO oxidation has not been verified. We consider that the detection of oxygen vacancies under the reaction conditions is very important in order to clarify the mechanism of the activation of oxygen molecules as well as that of the generation of the catalytic activity of the Au/metal oxide systems.

In this study, we applied the in situ ECM to Au/TiO_2 catalysts under the catalytic CO oxidation with O_2. The electrical conductance of the Au/TiO_2 catalyst was observed to increase sharply as soon as the reaction mixture of CO and O_2 was introduced. Since TiO_2 is an n-type semiconductor, the increase indicates that the oxygen vacancies were generated during the CO oxidation. The amount of easily removable oxygen in the CO atmosphere was estimated to correspond to 41% of surface lattice oxygen around the perimeter interface between Au NPs and TiO_2. These results support the mechanism of the activation of O_2 molecules on oxygen vacancies produced at the perimeter interface proposed by Haruta et al.

2. EXPERIMENTAL SECTION

As a support, TiO_2 powder (rutile type, purity 99.99%, surface area 2.65 m^2/g) was purchased from Kojundo Chemical Laboratory Co., Ltd. By using $HAuCl_4$ as a starting material, Au NPs were deposited on the TiO_2 powder by the deposition precipitation method.[11] The loading amount of Au measured by ICP analysis was 0.34 wt %, and the average diameter of the Au NPs was determined to be 3.2 nm from TEM images (see Figure S1 in the Supporting Information [SI]).

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We refer to reference 4 for the apparatus and procedure of in situ ECM. The closed recirculation reaction system equipped with the in situ ECM reactor (Figure 1) was made of Pyrex glass, and the base pressure was below 1.33×10^{-3} Pa. The CO oxidation was carried out using a reaction mixture with a stoichiometric composition of CO/O_2 = 2/1. During the CO oxidation, the product CO_2 was condensed in the trap cooled by liquid nitrogen. The reaction rate was determined from the rate of the decrease of total pressure measured by a capacitance-type pressure gauge (MKS Instruments Inc., Baratron 627B).

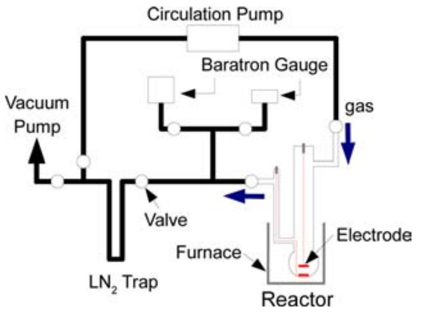

Figure 1. Schematic diagram of the closed recirculation reaction system with a reactor for in situ ECM.

A pair of gold disk electrodes with 1 cm diameter was mounted into the reactor. A 500-mg powder catalyst of Au/TiO_2 was introduced between two electrodes. The electrical conductance of the catalyst was measured in the following manner. The catalyst powder between the electrodes was weighted by a glass rod of 33.9 g to obtain a steady and reproducible value of the electrical conductance. Direct current voltage of 10 V was applied between the electrodes, and electric current was measured by a picoammeter (TAKEDA RIKEN TR8641). The detection limit of the current was approximately 1×10^{-10} A. In this case, the electrical conductivity is calculated to be 1×10^{-10} S/m, assuming that the interelectrode distance was 1 mm. This value is small enough compared with the conductivity of semiconductor (typically ~1 S/m).

Prior to each experiment, the sample was degassed at 673 K for 30–60 min, which caused a remarkable increase of the electrical conductance of the catalyst. It was probably caused by dehydration from surface hydroxyl groups accompanying the production of H_2O molecules and oxygen vacancies as well as conduction electrons. The electrical conductance of the catalyst decreased instantaneously by the introduction of O_2 at 6.65 kPa. The oxidizing treatment was continued for 30 min. After this pretreatment the electrical conductance was not detected when the sample was heated below 623 K in vacuum, indicating that the sample was fully oxidized (see Figure S2 in SI).

3. RESULTS AND DISCUSSION

Figure 2 shows time dependencies of the pressure of the reaction mixture and the electrical conductance simultaneously obtained during the CO oxidation performed at 473 K on (a) Au/TiO_2 and (b) TiO_2 catalysts. For Au/TiO_2, the logarithm of the pressure of the reaction mixture decreased linearly with time, indicating that the reaction is of the first order with respect to the total pressure. The electrical conductance immediately increased from 1×10^{-11} to 5×10^{-9} S just after the introduction of the reaction mixture, and then it gradually increased to reach to 1.1×10^{-8} S. In the case of TiO_2, the pressure of the reaction mixture decreased very little with time, and the electrical conductance remained less than 2×10^{-11} S during the exposure to the reaction mixture. The facts that (1) the activity of Au/TiO_2 was much larger than that of TiO_2 and (2) the electrical conductance immediately increased after the introduction of the reaction mixture indicate that the electrical conductance clearly correlates with the activity and the mechanism of CO oxidation on Au/TiO_2 catalysts.

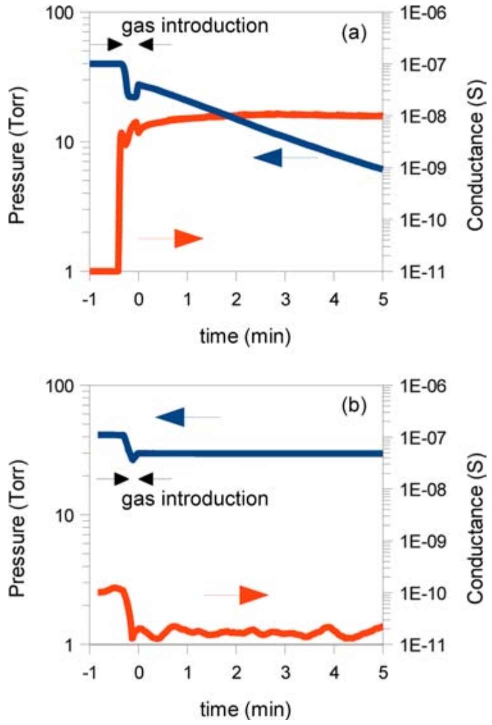

Figure 2. Time-dependencies of pressure and electrical conductance simultaneously obtained during CO oxidation performed at 473 K on (a) Au/TiO_2 and (b) TiO_2. The axes of pressure and conductance are represented in logarithmic scale.

Figure 3 shows Arrhenius plots of (a) the reaction rate constant of the CO oxidation (k_{CO_2}) and (b) the electrical conductance, measured on Au/TiO_2 and TiO_2. The values of k_{CO_2} of Au/TiO_2 were about 400 times larger than those of TiO_2 at 473 K. The remarkable increase of the catalytic activity is clearly due to Au NPs deposited on the surface of TiO_2.

The plot of k_{CO_2} of Au/TiO_2 breaks at 353 K; the apparent activation energies in the temperature ranges above and below 353 K were estimated to be 0.04 and 0.20 eV, respectively. Both are smaller than that of TiO_2 (0.33 eV). Haruta et al.[14] and Fujitani et al.[15] have also reported the similar breaks in the Arrhenius plots of the rate of CO oxidation on Au/TiO_2.

Regarding the electrical conductance, the apparent activation energy in the case of TiO_2 was estimated to be 0.73 eV. This value is comparable to the energy difference between the oxygen vacancy state and the conduction band bottom in TiO_2 (~0.7 eV, corresponding to the ionization energy of the oxygen vacancy),[16−18] suggesting that oxygen vacancies were generated on the surface of TiO_2 during the CO oxidation. The electrical conductance of Au/TiO_2 during the CO oxidation is much larger than that of TiO_2. The activation energy in the case of Au/TiO_2 (0.51 eV) was smaller than that of TiO_2. We consider that many more oxygen vacancies were produced on the surface of Au/TiO_2 by the influence of Au NPs deposited on it.

In the probable mechanism of CO oxidation, the surface lattice oxygen is removed by the CO molecules adsorbed on the Au NPs, and the resulting oxygen vacancies activate the oxygen molecules in the gas phase. In order to examine the reduction process of Au/TiO_2 in the mechanism, the Au/TiO_2

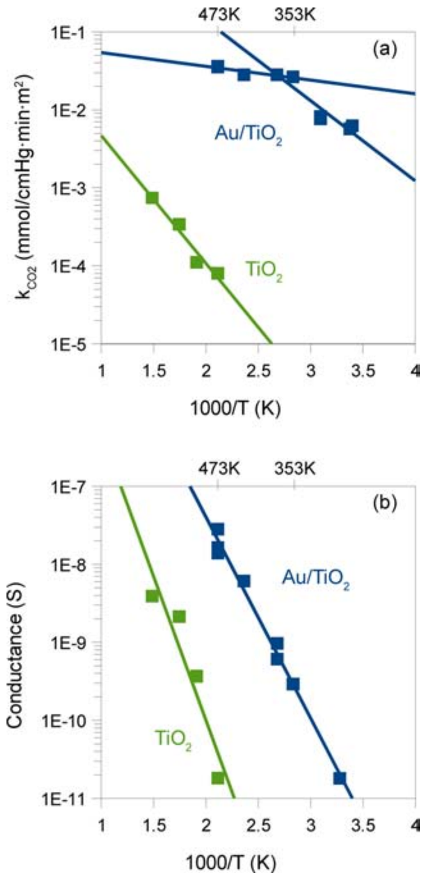

Figure 3. Arrhenius plots of (a) reaction rate constant of CO oxidation (k_{CO_2}) and (b) electrical conductance measured on Au/TiO$_2$ and TiO$_2$.

catalyst was reduced with CO (typically 6.7−27 Pa) at 473 K (Figure S3 in SI). The pressure of CO decreased rapidly in the initial few minutes and then decreased more slowly, and the electrical conductance increased at first rapidly and then slowly, corresponding to the change of the pressure of CO. On the other hand, in the case of TiO$_2$, the CO pressure and the electrical conductance retained almost their initial values during the exposure to CO performed at the same temperature. It is clear that Au NPs deposited on TiO$_2$ promote the creation of the oxygen vacancies on the surface.

The amount of oxygen vacancies on the Au/TiO$_2$ catalyst was estimated from the amount of consumed CO during the initial 5 min. The amount of surface lattice oxygen at the perimeter interface between Au NPs and TiO$_2$ was calculated from the loading of gold (0.34 wt %) and the average diameter of Au NPs (3.2 nm), assuming that each Au NP made contact with the supporting TiO$_2$ surface with hemispherical shape. Comparing the obtained values, the amount of oxygen vacancies produced (2.5×10^{-7} mol) corresponds to 41% of the "perimeter oxygen" (6.1×10^{-7} mol) and only 0.6% of the surface lattice oxygen (3.8×10^{-5} mol). This can be understood if we consider that the oxygen vacancies are created mainly at the perimeter interface. This finding is consistent with Whidmann's recent result that the oxygen vacancies were generated at the Au/TiO$_2$ perimeter interface.[13]

The electrical conductance of Au/TiO$_2$ reached 3×10^{-5} S after CO exposure for 5 min. This value is larger by 2700 times compared to that observed during the CO oxidation. If we assume that electrical conductance is proportional to the amount of oxygen vacancies, the amount of oxygen vacancies during the CO oxidation is calculated to be 0.01% of surface lattice oxygen at the perimeter interface. Although the calculated value is probably underestimated, this shows that the concentration of oxygen vacancies around the perimeter interface is extremely low during the course of the CO oxidation. From another viewpoint, the uptake rate of oxygen to the oxygen vacancy produced at the perimeter interface is so fast that the perimeter interface is almost saturated with active oxygen. This result is consistent with the low kinetic order for oxygen in CO oxidation on Au/TiO$_2$, previously reported to be 0.07−0.46.[19]

The Arrhenius plot of the electrical conductance of Au/TiO$_2$ shown in Figure 3b does not show any break, indicating that the mechanisms of the generation of the oxygen vacancies and the conduction of the electrons were not changed in the temperature range investigated. On the other hand, the plot of k_{CO_2} in Figure 3a shows the break at 353 K. Fujitani explained that oxygen molecules are activated at the perimeter interface in the low-temperature range, whereas the activation of oxygen molecules mainly takes place on the gold surface in the higher-temperature range.[15] Therefore, we consider that the oxygen vacancies were generated at the perimeter interface in the whole temperature range; with respect to the CO oxidation reaction, they played a much more important role in the low-temperature range but not in the higher-temperature range.

4. CONCLUSION

In spite of the importance of oxygen vacancy in the Au/oxide catalysts, oxygen vacancies under reaction conditions have not been confirmed. By using the in situ ECM, we successfully confirmed the generation of the oxygen vacancies at the Au/TiO$_2$ perimeter interface in CO oxidation. Although several controversial issues still remain, e.g. the quantum size effect, the influence of moisture, and the temperature dependency, the obtained evidence on the oxygen vacancy supports Haruta's reaction model, in which oxygen molecules are activated on the oxygen vacancies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A TEM image, detailed kinetic and electrical conductance data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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