Importance of Metal-oxide Interfaces for Low Temperature CO Oxidation over Supported Au and FeO\textsubscript{x} Promoted Pt Catalysts

Atsuko Tomita, Koji Tajiri, and Yutaka Tai

Inorganic Functional Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, JAPAN

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Low-temperature CO oxidation mechanisms were investigated for size-selected Au nanoparticle catalyst and water-treated Pt/FeO\textsubscript{x}Al\textsubscript{2}O\textsubscript{3} catalyst. Both catalysts had high CO oxidation activity even below room temperature. Interestingly, CO oxidations over these catalysts involved important contributions from the metal-oxide interface. For the Au catalyst system, the effects of heat-treatment in air and H\textsubscript{2}/Ar were investigated on Au/titania-coated silica aerogel catalysts prepared through adsorption of size-selected thiol-capped Au nanoparticles (AuNPs). Change in the form of sulfuric compound lead to a step-wise change in catalytic activity without affecting activation energy, which was observed for both active (<D>\textsubscript{Au} = 2 nm) and inactive (<D>\textsubscript{Au} = 4.9 nm) catalysts. These observations strongly indicate that the Au-titania interfaces function as reaction sites in low temperature CO oxidation over a wide Au size range. For the Pt catalyst system, Pt/Fe-containing alumina cata-
lysts treated with water could catalyze CO oxidation with a very low activation barrier (9.2 kJ/mol). Pt nanoparticles and iron oxides formed efficient contacts in the catalysts, probably because of the enhanced mobility of Pt species induced by water treatment. Active oxygen is probably generated at the Pt-FeO\textsubscript{x} boundary, synchronized with the Fe redox reaction.

Keywords
Carbon monoxide oxidation, Supported gold catalyst, Supported platinum catalyst, Metal-oxide interface, Water treatment

1. Introduction

Low temperature oxidation of CO using heterogeneous catalysts has been intensively investigated to establish methods to preferentially oxidize CO in H\textsubscript{2}-rich gas\textsuperscript{1}, clean air, and lower automotive emissions\textsuperscript{2}. Conventional Pt catalysts generally require temperatures above 100 °C to oxidize CO, whereas Au nanoparticle catalysts with appropriate supports can catalyze CO oxidation at low temperatures even below 0 °C\textsuperscript{3}.

The mechanism of CO oxidation reaction is among the central problems remaining to be solved regarding supported Au catalysts. Many reaction mechanisms have been proposed for CO oxidation on the Au catalysts. Au-support interactions are believed to be important: for example, reactions at the perimeters of Au nanoparticles (AuNPs)\textsuperscript{4–8}, strain induced at Au-support interfaces\textsuperscript{9,10}, and charging of AuNPs via electron transfer from defects on surfaces\textsuperscript{11}. On the other hand, gold-only mechanisms have also been suggested: for example, effects of low-coordination sites\textsuperscript{12–15} and thickness of Au islands on support surfaces\textsuperscript{16,17}. The second section of this review summarizes our approach to the clarification of CO oxidation mechanisms based on the preparation and structural analysis of size-selected Au nanoparticle catalysts\textsuperscript{18–21}.

Generally, conventional Pt catalysts require temperatures above 100 °C to catalyze CO oxidation, but various additives have been proposed for Pt catalysts\textsuperscript{22–25} to realize CO oxidation at lower temperatures, of which iron is one of the most common additives\textsuperscript{26–30}. Promotional effects in iron-doped supported Pt cata-
lysts have been attributed to either activation of oxygen atoms on Fe sites (bimetallic effect)\textsuperscript{31,32} or lower adsorption energy of CO over Pt surfaces\textsuperscript{27,29}. A recent report by Fu et al. revealed that at coordinatively unsaturated ferrous (CUF) sites formed at boundaries between FeO\textsubscript{x} and the Pt(111) surface, O\textsubscript{2} molecules adsorb and then cleave into oxygen atoms with a very low activation barrier\textsuperscript{33}.

We have recently reported that Pt nanoparticles (PtNPs) form efficient contacts with iron oxides, leading to high CO oxidation activity in Pt/Fe-containing Al\textsubscript{2}O\textsubscript{3} catalysts which were prepared and treated with...
water under moderate conditions. Catalysts loaded with 1 wt% Pt prepared with this method could catalyze CO oxidation at low temperatures, even below 0 °C, with conversions above 90%. The third section of this review discusses the preparation and CO oxidation mechanism over the water-treated Pt/FeOx-Al2O3 catalyst.

2. CO Oxidation over Size-selected Au Nanoparticle Catalyst

2.1. Catalyst Preparation and Treatment

Supported Au catalysts are conventionally prepared using the deposition precipitation (DP) method, in which gold hydroxides are deposited on powdered oxides such as TiO2 by adjusting the pH of the preparation solution, and then the product composite is dried and calcined in air. Another approach is the use of preformed NPs. We reported previously that thiol-capped AuNPs are adsorbed efficiently onto the surfaces of oxide gels in nonpolar solvents. The deposition of preformed NPs onto supports is advantageous for controlling the size and structure of the NPs in catalysts. Highly selective as well as durable catalysts have been prepared by such NP deposition methods.

Gold catalysts prepared through the deposition of preformed AuNPs must be treated at high temperature to remove the capping molecules on the Au cores. Removal of thiols from thiol-capped AuNPs has been achieved via heat treatment in oxidative or reductive atmospheres. Under oxidative conditions, the thiol molecules undergo combustion to form CO2, H2O, and SOx. These gases might affect the structure and activity of the catalyst; for example, treatment in SO2 can deactivate Au/TiO2. In contrast, under reductive or inert conditions, the thiol molecules desorb from the surfaces of the AuNPs. However, active catalysts have been obtained under both oxidative and reductive conditions.

We have applied heat treatment at various temperatures and gas conditions to dodecanethiol (DDT)-capped AuNPs [mean Au diameters (<D>mean) of 2.0 nm and 4.9 nm]titania-coated silica aerogel (Ti-Si AG) catalysts and investigated the correlations between the catalyst structures and CO oxidation activity. To incorporate AuNPs in the support, the powdered gels in a size range from 106 to 212 μm were immersed in a toluene solution of DDT-capped AuNPs in a screw-capped vial and gently shaken using a rotary mixer, so that the NPs were homogeneously adsorbed on the gels. After adsorption of the NPs on the gels was completed, confirmed through decoloration of the solution, the composite gels incorporating the AuNPs were dried in air and then heat-treated under various conditions. Au loading was fixed at 5 wt%. Details of the preparation of AuNPs and Ti-Si AG are described elsewhere.

2.2. Growth of AuNPs and Catalytic Activity

Figures 1 and 2 compare the size distributions of AuNPs in samples treated at various calcination temperatures. The mean diameters of AuNPs did not differ from those prior to calcination (2.0 nm) if the calcination temperature was below 500 °C. Further heat-treatment under H2/Ar at 400 °C or 450 °C did not affect the size distribution of the AuNPs. On the other hand, calcination at temperatures above 600 °C led to sintering of the AuNPs: the mean Au diameters of the catalysts calcined at 600 °C and 700 °C were 3.2 nm and 4.7 nm, respectively.
although its function is not well understood\(^5\). Samples calcined at temperatures below 150 °C under air did not have catalytic activity. Samples calcined at temperatures in the range from 200 to 500 °C in air had very similar catalytic activities. This finding is consistent with the fact that no sintering of the AuNPs occurred below 500 °C (Fig. 2). Samples calcined at 600 °C and treated at 400 °C in H\(_2/\)Ar after calcination at 400 °C exhibited much higher TOFs.

Figure 3(b) shows the relative TOF values at \(-63 °C (1/T = 4.76 \times 10^3 K^{-1})\) for the samples plotted versus the calcination temperature. The TOF values were normalized to that of the sample calcined at 200 °C in air. The TOFs of the samples calcined at 600 °C in air and at 400 °C in H\(_2/\)Ar after treatment at 400 °C in air were about 3-5 times greater than those of samples calcined at temperatures below 500 °C in air, although the mean AuNP diameter had increased from 2 to 3.2 nm in the former sample. The TOFs of the present catalysts are reportedly similar if the AuNP diameters are 2-4 nm\(^{20}\). Therefore, the drastic change in TOF was not due to the size effect. The catalyst treated at 700 °C in air had lower activity than that treated at 600 °C, presumably because some of the NPs grew larger than 5 nm, as indicated in Fig. 2. The apparent activation energies were similar (20-25 kJ mol\(^{-1}\)) for all of the samples.

Similarly, the TOF of the catalyst incorporating AuNPs with \(<D>_{Au}\) of 4.9 nm increased sharply if treated at 600 °C in air. Figure 4(a) displays the change of \(<D>_{Au}\) versus calcination temperature. The mean diameter did not change up to but sharply increased above 600 °C. Figure 4(b) displays the relationship of the TOF at 0 °C to Au diameter for catalysts treated at various temperatures. Treatment at 600 °C raised the TOF by a factor of 2.5 without changing Au diameter. Higher calcination temperature led to greater Au diameter, but did not affect the TOF value or activation energy. Note these TOF values are about 20 times higher than that of the catalyst treated at 600 °C in air in in Fig. 3(a) extrapolated to 0 °C because of the AuNP size. These findings indicate that, regardless of the original CO oxidation activity, high temperature (\(>600 °C\)) treatment or sequential O\(_2/\)H\(_2\) treatment drastically enhances the CO oxidation activity of the catalysts.

### 2.3. Catalyst Structure and CO Oxidation Mechanism

The effects of calcination on the combustion of thiols were investigated using IR, thermogravimetry-differential thermal analysis (TG/DTA) and X-ray fluorescence (XRF) measurements of the sample with original \(<D>_{Au}\) of 2.0 nm\(^{21,56}\). Table 1 summarizes the state of sulfur after heat-treatment under various conditions de-
rived from the results. Removal of thiols from the AuNP surfaces was consistent with the emergence of the catalytic activity at 200 °C [Fig. 3(b)]. The disappearance of sulfates on calcination at 600 °C and H2/Ar treatment at 400 °C following calcination at 400 °C coincided with drastic enhancement of the catalytic activity [Fig. 3(b)].

To investigate the charged states of Au in the catalysts, diffuse reflectance infrared fourier transform (DRIFT) spectra of the adsorbed CO were obtained (Fig. 5). No peak was detected in the spectrum for the uncalcined sample [spectrum (a)]. CO stretching bands were detected in the spectra of samples calcined at 400 °C in air [spectrum (b)] and further heat-treated under H2/Ar at 400 °C [spectrum (c)]. The intensity of the CO stretching band in spectrum (b) was very similar to that in spectrum (c), indicating similar numbers of adsorption sites in both samples. The peaks of the bands occurred at 2125 cm–1 and 2114 cm–1 in spectra (b) and (c), respectively. Bands at ca. 2110 cm–1 assigned to CO adsorbed on Au(0) are often reported for Au/TiO2 catalysts prepared using both the DP and colloid deposition processes48),49),57)ʙ59). CO molecules on isolated Au cations, which often exhibit stretching bands above 2150 cm–1 57),59), were not detected in Fig. 5. Bands at 2120-2140 cm–1 have been ascribed to CO on positively charged AuNPs57),60),61) and two-dimensional small Au clusters62),63). In our present study, small clusters with D <1 nm were not detected by TEM and laser desorption-mass spectrometry (LDMS) of the preformed AuNPs. Therefore, our results in Fig. 5 imply that the AuNPs were more cationic without H2/Ar treatment.

Figure 3(b) reveals that the TOF changed drastically after calcination at 200 °C (TOF: 0 \rightarrow 1) and at 600 °C (TOF: 1.5 \rightarrow 5). The latter increase also occurred after

Table 1 Form of Sulfur after Heat-treatment under Various Conditions

<table>
<thead>
<tr>
<th>Temp. [°C]</th>
<th>Ambience</th>
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<tbody>
<tr>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>150</td>
<td>Thiol</td>
</tr>
<tr>
<td>200</td>
<td>Sulfate</td>
</tr>
<tr>
<td>300</td>
<td>Sulfate</td>
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<tr>
<td>400</td>
<td>Sulfate</td>
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<tr>
<td>500</td>
<td>Sulfate</td>
</tr>
<tr>
<td>600</td>
<td>No</td>
</tr>
<tr>
<td>700</td>
<td>No</td>
</tr>
</tbody>
</table>

N.A.: not assessed.

All spectra were recorded 20 min after onset of a 1 vol% CO/He flow.

Fig. 5 DRIFT Spectra for the Samples (a) without Heat-treatment, (b) Calcined at 400 °C for 4 h, and (c) Heat-treated at 400 °C in H2/Ar after Calcination at 400 °C for 4 h.
heat-treatment in H2/Ar at 400 °C after calcination at 400 °C. This behavior is well correlated with the changes in the forms of the sulfuric compounds in the catalysts. Table 1 shows that the onset of the catalytic activity was due to removal of the thiols on the AuNPs, which occurred at temperatures above 200 °C. The oxidized thiols reacted with titania and remained on the surfaces as sulfates64. The latter change in the catalytic activity, caused by calcination at 600 °C or reduction by H2/Ar at 400 °C, was correlated with the removal of these sulfates.

The shift of the CO stretching bands to lower wave-numbers after H2 treatment (Fig. 5) suggests that the AuNPs were more cationic prior to H2/Ar treatment, consistent with the presence of electronegative sulfates in close proximity to the AuNPs. AuNPs on TiO2(110) surfaces have extraordinary ability to absorb and disassociate SO2 under vacuum conditions65. Density-functional calculations showed that the stable adsorption geometries of SO2 on Au (atom)/TiO2(110) incorporated a SO2 molecule bridge between Au and TiO265. These results may explain the interactions between AuNPs and sulfated titania in our present experiments.

The intensity of CO stretching bands (Fig. 5) and the activation energy of the reaction [Fig. 3(a)] did not change appreciably after H2 treatment. These results suggest that neither the number of CO adsorption sites nor the reaction mechanism was affected by the removal of sulfates. Thus, the drastic change in the TOF after removal of the sulfates was probably due to an increase in the number of reaction sites.

The key to understanding the reaction mechanism is the character of the sites at which O2 molecules are adsorbed and activated. Many theoretical and experimental investigations have proposed that low-coordination sites on AuNPs(22−15), interfaces between AuNPs and supports6−8,13, and defects on the support4 are possible O2 adsorption sites. The mechanism of O2 adsorption may also differ according to the reducibility of the supports31,66. For the Au/TiO2 system, density functional theory (DFT) simulations have suggested that O2 molecules can be adsorbed on support sites adjacent to the AuNPs through cooperative charge donation to O2 from both vacancies on the support and the AuNPs through the support31. The adsorbed O2 molecules may orient toward the AuNPs and react with the adsorbed CO. A model proposed by Bond and Thompson is based on a similar activation process of O2 molecules, although the formation of Au-OH via transfer of OH from the support was assumed to result in the generation of vacancies66.

A study of an Au/TiO2(110) model catalyst showed that (i) at temperatures less than 47 °C, moisture is essential for the CO oxidation reaction, and (ii) the TOF for the CO oxidation reaction is proportional to the number of gold atoms at perimeter interfaces67. Our experiments have clearly shown that by partially blocking the Au-titania interfaces by sulfates, CO oxidation is prohibited simply because of the decrease in the number of the reaction sites. Moreover, the TOF increase resulting from the removal of sulfates was similarly detected in active (<D>2Au = 2 nm) and inactive (<D>2Au = 4.9 nm) catalysts. These observations strongly support the hypothesis that the Au-titania interfaces function as reaction sites for low temperature CO oxidation over a wide range of Au sizes67. However, the differences in the activation energies and TOF values in active and inactive catalysts cannot be explained simply by the perimeter length.

3. CO Oxidation over Water-treated Pt/FeO–Al2O3 Catalyst

3.1. Catalyst Preparation and Treatment

Catalytic reactions over supported Pt catalysts can be promoted by adding various oxide materials. Probably the most important example is the three-way catalyst (TWC) for purification of automotive exhaust emissions22). The presence of ceria or ceria_zirconia in the TWC promotes oxidation of hydrocarbons and CO by supplying oxygen onto the PGMs under fuel-rich conditions. Various other additives also promote low temperature CO oxidation over Pt catalysts. CeO2–ZrO2–Bi2O3 (CZB) supported on γ-alumina can supply reactive oxygen at temperatures even below 100 °C69. Potassium-doped Pt catalysts show high catalytic activity for the preferential oxidation of CO (PROx) and the water gas shift (WGS) reactions68,70.

Iron oxide is a commonly used promoter and is still studied intensively. A recent report demonstrated that co-impregnation of Pt and Fe on TiO2 is quite effective for CO oxidation71. We aimed at formation of efficient contacts between Pt nanoparticles (PtNPs) and iron oxides in Pt/Fe-containing supports. Our strategy is based on the observation that water enhances the mobility of Pt species on support surfaces. Slow desorption of water from the catalyst leads to suppression and fast desorption to the enhancement of the mobility of Pt species, which has allowed control of the dispersion of PtNPs in Y-type zeolite by adjusting the desorption rate of water72. Fe atoms prefer binding to Pt rather than silica35 and alumina32, so we suspected that the enhanced mobility of Pt species during the catalyst preparation process may well lead to closer contacts between PtNPs and FeO on alumina.

Catalysts were prepared based on the impregnation of Pt(NH3)2(NO3)2 into Fe-containing alumina (JRC-ALO-5, Fe content 0.45 wt%) or the co-impregnation of Pt(NH3)2(NO3)2 and Fe(NO3)3⋅9H2O into pure γ-alumina34. Composite after impregnation was (I) calcined at around 200 °C in a flow of dry air and then
(II) reduced at the same temperature in a flow of H2/Ar (1/1). Prior to measurement of CO conversion, the catalyst was (III) wetted with deionized water and (IV) heat-treated under a flow of H2. Here, the treatments [(III) + (IV)] are called “water-treatment,” and treatment without wetting the catalyst is called “dry-treatment”34). The notation of the prepared catalysts follows the system PtX/ALO-5 (2-2-W2), where X denotes the Pt loading in wt%; and the symbols in parentheses designate the history of the catalyst treatment: in this example, the catalyst was calcined at 200°C, reduced at 200°C, wetted with water (represented by W), and heat-treated in H2 at 200°C.

3. 2. Catalyst Structure and CO Oxidation Activity

Catalyst structure was analyzed using electron microscopy and X-ray absorption fine structure (XAFS) spectroscopy. Figure 6 shows the high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images of the catalyst before and after water-treatment. Pt particles grew from mean 0.8 to 1.3 nm with treatment. Interestingly, PtNPs grew further if the catalyst without Fe was treated with water repeatedly. However, the diameter of PtNPs remained at 1.3 nm in catalysts containing Fe34). These observations indicate that the mobility of PtNPs is enhanced by water-treatment and the particle size increases. However, PtNPs seem to be pinned at the Fe sites and the growth is terminated if the catalyst contains Fe. Pt LIII-edge XAFS measurement suggested that PtNPs did not contain Fe atoms if the Fe loading was less than ca. 1 wt%, and bimetallic Pt–Fe particles were formed above this Fe loading (Pt loading was fixed at 2.5 wt%)37).

Figure 7 displays the temperature dependence of the CO conversions over Pt/ALO-5 catalysts prepared under various conditions. The reactant gas [CO (1 %), O2 (0.5 %), N2 (98.5 %)] was passed through the catalytic bed at an HGSV of 20,000 mL/(h g-cat.). The concentrations of CO, O2, and CO2 were monitored with gas chromatography, and the carbon balance of 100 % was confirmed in all of the following CO oxidation experiments. Conversion over Pt5/ALO-5 (6-4-2), catalyst calcined at 600°C, reduced at 400°C, and dry-treated at 200°C, was very low at temperatures below room temperature, but sharply increased at temperatures above 100°C. Lowering treatment temperatures to 200°C [Pt5/ALO-5 (2-2-2)] resulted in enhancement of the CO conversion by 5-15 %, presumably because of the smaller particle sizes formed at the lower treatment temperatures. Application of water-treatment (2-2-W2) enhanced the CO oxidation activity dramatically: CO conversion over the water-treated catalyst reached greater than 99 %. This value of CO conversion is much higher than that of the dry-treated catalyst [Pt5/ALO-5 (2-2-2)], although the Pt dispersion was lower (Fig. 6). The TEM observations showed that water-treatment enhanced the mobility of Pt species and likely formed PtNPs around iron oxides. Therefore, we consider that efficient contact formation between PtNPs and iron oxides is the crucial factor for the drastic enhancement of the low-temperature CO oxidation activity. Even at Pt content of only 1 wt% [Pt1/ALO-5 (2-2-W2)], the CO conversion remained above 90 %, Pt0.25/ALO-5 (2-2-W2), which contained only 0.25 wt% Pt, still provided a remarkably high conversion of 60 % at 25°C. These catalysts exhibited higher activity at temperatures below 0°C than Au1.5/TiO2 (World Gold Council Au–Ti#02-6; Au content: 1.5 wt%) under this feed condition. Because the addition of water vapor to
the reaction gas did not affect the CO conversions, the shift reaction, \(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\), due to residual water in the catalyst, was not likely to contribute to CO oxidation. Other reactions necessitating the consumption of \(\text{H}_2\text{O}\) or surface OH groups \(^\text{22),28),73),74)\), which might be formed by the water-treatment, can be excluded for the same reasons.

The Fe loading dependence of CO oxidation activity exhibited interesting behavior (Fig. 8). Clearly, the CO oxidation activity below 100 °C was dramatically improved with a low content of Fe (0.18 wt%), but gradually dropped if the Fe content exceeded 1 wt%. In contrast, CO oxidation activity at high temperature (> 120 °C) rose almost monotonously with Fe content. Since Pt La-edge XAFS measurements showed that Pt–Fe alloy was formed at higher Fe content, alloy formation probably enhances the activity at high temperature \(^\text{37)\).}

Co and Ni also acted as promoters to the water-treated catalysts, but the catalytic performance was inferior to Fe \(^\text{37)\).}

3.3 Mechanism of Low Temperature CO Oxidation

Figure 9 shows the dependences of reaction rate on (a) temperature and (b) CO and O\(_2\) partial pressures. The apparent activation energy derived from Fig. 9(a) was 9.2 kJ/mol; this value is much lower than those of Pt/\(\gamma\)-Al\(_2\)O\(_3\) (71 kJ/mol) \(^\text{75)\) and Pt/FeO \(_x\) (30.4 kJ/mol) \(^\text{30)\). The kinetic order for the transformation of CO over Pt0.25Fe0.072/\(\gamma\)-Al\(_2\)O\(_3\) (2-2-W2) was 0.09 \(\sim\) 0.10 at 0 °C for CO, and 0.7 \(\sim\) 1.0 and 0.9 \(\sim\) 1.1 for O\(_2\) at \(-40\) °C and 0 °C, respectively [Fig. 9(b)]. CO and O\(_2\) adsorb competitively onto the Pt surfaces of Pt/alumina and Pt/silica catalysts \(^\text{75)\sim77)\). The heat of adsorption on the Pt surface is much larger for CO than for O\(_2\), so the surface is overwhelmingly covered by CO at ambient pressures. As a result, negative kinetic orders for CO and O\(_2\) were weakly positive and approximately 1, respectively. \(\text{In-situ}\) FT-IR spectra of Pt2.5/ALO-5 after water-treatment, recorded at 25 °C under a 1% CO and 1% O\(_2\) mixture in N\(_2\) flow (not shown), revealed that the Pt surfaces were covered with CO as in conventional Pt catalysts. In the absence of competition for O\(_2\) adsorption, so that the adsorption rate exceeds the rate of reaction between adsorbed CO and O\(_2\), the kinetic order for O\(_2\) can also be close to zero. Such examples are reported for CO oxidation over Au/TiO\(_2\) and Au/Fe\(_2\)O\(_3\) catalysts \(^\text{55)\) on which CO on the metal surface is considered to react with oxygen at the metal-support interface \(^\text{21),67)\). The large O\(_2\) kinetic order may result from competitive adsorption of CO and O\(_2\) at the Pt–FeO\(_x\) boundary. At boundaries between the FeO\(_x\) monolayer and the Pt(111) surface [FeO\(_x/Pt(111)\)], the adsorption energy for O\(_2\) is comparable to that for CO \(^\text{33)\).
In-situ XAFS measurements were performed to elucidate the behavior of oxygen in the reaction. Figure 10 shows the Fourier transforms (FTs) of Pt LIII-edge EXAFS for Pt2.5/ALO-5 (2-2-W2) catalyst under various gas conditions. Contribution from C backscatter was confirmed as CO flow was admitted, which is consistent with the IR results that the Pt surfaces were covered with CO. Oxygen was detected only under the He + O2 condition. Therefore, the EXAFS analysis found no indication of oxygen adsorption on the Pt surfaces, even under the reaction conditions He + CO + O2. Figure 11 shows the corresponding Fe K-edge XANES spectra. The K-edge threshold shifted to higher energy under (1 % CO + 0.5 % O2)/He, then shifted back slightly to lower energy under 1 % CO/He, and then again to higher energy under 0.5 % O2/He, and then shifted back to lower energy under 1 % CO/He. These results clearly suggest that the redox cycle, Fe2+ ↔ Fe3+, can participate in the reaction. Based on the above arguments, we propose that (i) the Pt surface is covered with CO, and O2 is adsorbed at the boundaries between Pt and FeOx in competition with CO, and (ii) CO molecules react with O species supplied from FeOx and the reaction is accompanied by the redox cycle (Fe2+ ↔ Fe3+) occurring at the boundaries of PtNP and FeOx.

4. Conclusion

The results of heat-treatment experiments using Au/titania-coated silica aerogel catalysts prepared through adsorption of size-selected thiol-capped AuNPs strongly indicate that the Au-titania interfaces function as reaction sites for low temperature CO oxidation in a wide Au size range. In the water-treated Pt/FeOx-Al2O3 catalyst, active oxygen is probably generated at the Pt-FeOx boundary, synchronized with Fe redox change. These findings indicate that the metal-oxide interface is very important in O2 activation for both types of catalyst. Water treatment enhanced the mobility of Pt species, which probably led to the formation of PtNPs at FeOx sites on alumina. This specific action of water may provide a new strategy for the preparation of supported metal catalysts.

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要  旨

担持触媒および鉄添加白金触媒の低温 CO 酸化における金属-酸化物界面の重要性

富田 章子, 田尻 耕治, 多井 豊

産業技術総合研究所 無機機能材料研究部門, 463-8560 名古屋市守山区下志段味穴ケ淵2266-98

室温以下の低温においても高い CO 酸化活性を発現する担持触媒と水酸化処理鉄添加白金触媒における CO 酸化反応メカニズムを議論する。興味深いことに、両触媒とも金属-酸化物界面が反応に重要な役割を有する。金触媒系に関しては、サイズを制御したチオール保護金ナノ粒子をチタニア被覆シリカエラゴルに吸着担持した触媒を種々の条件下で熱処理し、硫黄化合物の形態と触媒活性の相関を調べた。その結果、金-担体界面を硫酸イオンが部分的にブロックすることで、反応機構に影響を及ぼすことなく反応速度を降下させること、また広いサイズ領域において、金-担体界面が反応サイトとなることが示唆された。水酸化処理鉄添加白金触媒においては、水酸化処理時における Pt 種の移動により、効果的に白金-酸化鉄界面が形成されることが示唆された。鉄の酸化還元を伴う活性酸素の効果的な供給により、極めて低い活性障壁で CO 酸化が起こるものと考えられる。