

# Preparation of supported gold catalysts from gold complexes and their catalytic activities for CO oxidation

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A phosphine-stabilized mononuclear gold complex  $\text{Au}(\text{PPh}_3)(\text{NO}_3)$  (1) and a phosphine-stabilized gold cluster  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (2) were used as precursors for preparation of supported gold catalysts. Both complexes 1 and 2 supported on inorganic oxides such as  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$  were inactive for CO oxidation, whereas the 1 or 2/oxides treated under air or CO or 5%  $\text{H}_2/\text{Ar}$  atmosphere were found to be active for CO oxidation. The catalytic activity depended on not only the treatment conditions but also the kinds of the precursor and the supports used. The catalysts derived from 1 showed higher activity than those derived from 2.  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{TiO}_2$  were much more efficient supports than  $\text{SiO}_2$  for the gold particles which were characterized by XRD and EXAFS.

**Keywords:** supported gold catalysts; CO oxidation; gold monomer and cluster; EXAFS

## 1. Introduction

Catalysis of small Au particles supported on inorganic oxides has been intensively studied in the literature [1–11]. It has been known for a long time that gold surfaces are capable of catalyzing the oxidation of carbon monoxide to carbon dioxide [3] and also that the nature of the support has a decisive influence on the catalytic activity of gold [4]; magnesia- and alumina-supported gold were more active by more than one order of magnitude for oxygen transfer between CO and  $\text{CO}_2$  than silica-supported gold. Cant and Fredrickson studies the reactions of CO with  $\text{O}_2$  and NO over gold and silver sponges [5]. On gold, the oxidation of CO by oxygen was about 40 times faster than that by nitric oxide. Small Au particles could adsorb CO and also increased the amount of oxygen adsorbed on the supporting oxide. Vannice and co-workers studied [6] CO oxidation over differently pretreated Au/ $\text{TiO}_2$  and Au/ $\text{SiO}_2$  catalysts. After a high-temperature reduction at 773 K, Au/ $\text{TiO}_2$  became very active for the oxidation at 313 K as compared to Au/ $\text{SiO}_2$ . The high activity of the Au/ $\text{TiO}_2$  catalyst was attributed to synergistic interaction between gold and titania.

Nevertheless, it is very difficult to obtain the gold particles in a state of dispersion as high as those of platinum and palladium because the melting point of Au particles with a diameter of 2 nm is lowered to 573 K due to the quantum size effect [7]. This is mainly because the melt-

ing point of gold at 1336 K is much lower than those of Pt (2042 K) and Pd (1823 K). Haruta et al. prepared highly dispersed gold particles on various metal oxides by coprecipitation or deposition [8–10]. They found that gold supported on  $\text{TiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , NiO,  $\text{Be}(\text{OH})_2$ , and  $\text{Mg}(\text{OH})_2$  was very active for low-temperature CO oxidation. For Au/ $\text{TiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$ , the turnover frequencies for CO oxidation were almost independent of the kind of supporting oxides and increased sharply with a decrease in diameter of the gold particles below 4 nm. Recently, Hug et al. [11] studied Au/ $\text{ZrO}_2$  prepared by coprecipitation and observed significant deactivation in long-term tests for CO oxidation although the catalyst was highly active at the beginning of the reaction.

However, there is no report hitherto on catalysis of supported gold complexes or cluster compounds, although the preparation and characterization of supported homonuclear naked gold clusters ( $\text{Au}_x$ ) by a molecular beam technique have been reviewed [12]. We attempted to obtain supported gold catalysts by using well-characterized gold complexes as precursors by extending the knowledge of the nature of gold cluster compounds [13] and surface organometallic chemistry [14,15], and the way of preparation of highly dispersed metal catalysts by using metal complexes and clusters [16]. Here we report the preparation and characterization of gold catalysts derived from a mononuclear gold complex  $\text{Au}(\text{PPh}_3)(\text{NO}_3)$  (1) and an enneanuclear gold cluster compound  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (2) supported on  $\text{TiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , and the catalytic performance of these samples in CO oxidation.

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## 2. Experimental

### 2.1. Synthesis of $Au(PPh_3)(NO_3)$ (1) and $[Au_9(PPh_3)_8](NO_3)_3$ (2)

Gold complexes **1** and **2** were synthesized according to the literature [17]. The total yields (based on Au) for **1** and **2** were above 80% and about 40%, respectively. The white crystal of **1** was light- and temperature-sensitive, and showed IR bands (KBr) for  $\nu(NO_3)$  at 1495 and 1268  $cm^{-1}$ . UV–visible spectroscopy of **2** exhibited  $\lambda_{max}$  (EtOH) at 442, 374 (sh), 351 (sh), and 313 nm, which coincides with that in the literature [13].

### 2.2. Preparation of $TiO_2$ -, $SiO_2$ -, and $\alpha-Fe_2O_3$ -supported **1** and **2**

$TiO_2$  (Aerosil P25, surface area 50  $m^2/g$ ) and  $SiO_2$  (Aerosil 300, surface area 300  $m^2/g$ ) were pretreated at 673 K under vacuum for 1 h before use as supports.  $\alpha-Fe_2O_3$  was obtained by precipitation of  $Fe(NO_3)_3$  with  $Na_2CO_3$  in aqueous solution, followed by washing, drying under vacuum at room temperature overnight, and finally calcination at 673 K for 2 h. These inorganic oxides were evacuated at room temperature in situ before supporting the Au complexes. The supports were impregnated with a  $CH_2Cl_2$  solution of the Au complex while vigorously stirring, followed by evacuation of the solvent at room temperature for 5 h. The  $CH_2Cl_2$  solvent was carefully dried over 5A molecular sieve for at least 12 h. The supported Au samples were then stored in sealed glass ampoules (under vacuum) at room temperature. The loading of Au was always 3.0 wt%.

### 2.3. Characterization of the Au catalysts

The supported Au catalysts were characterized by X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS). XRD patterns were measured on a Rigaku powder X-ray diffractometer with  $Cu K_\alpha$  radiation over the  $2\theta$ -range of 20 to 80°. The mean particle size of the gold crystallites was estimated by using the Scherrer equation and the half-widths of selected diffraction lines of Au(111) at  $2\theta = 38.2^\circ$  for Au/ $SiO_2$  and

Au/ $\alpha-Fe_2O_3$ , and of Au(200) at  $2\theta = 44.4^\circ$  for Au/ $TiO_2$ .

Au L<sub>3</sub>-edge EXAFS spectra of the samples were measured at room temperature in a transmission mode at beamline 10B of the Photon Factory in the National Laboratory for High Energy Physics (KEK) (Proposal No.: 95G200). Cluster **2** was used as a reference compound in analyzing the EXAFS data of the samples **2**/ $TiO_2$  and **2**/ $SiO_2$ . The parameters extracted from the EXAFS data for Au foil and the cluster **2** are summarized in table 1.

### 2.4. Catalytic CO oxidation

Catalysts were pretreated under several conditions before catalytic runs. **1** and **2**/ $Fe_2O_3$  and **1** and **2**/ $SiO_2$  were calcined at 673 K under an  $O_2$  flow. For the  $TiO_2$  support, several pretreatments including heating at 673 K under  $CO$  or  $O_2$  and reduction at 773 K under  $H_2$  were examined. Kinetic measurements were carried out in a fixed-bed flow reactor with a computer-controlled auto-sampling system by using 200 mg of catalyst powder. The reaction gas consisting of 1.0%  $CO$  balanced with air through a molecular sieve column was passed through the catalyst bed at a flow rate of 34 ml/min ( $SV = 10\,000\ h^{-1}$ ). The reaction products were analyzed by a gas chromatograph using a column of Unibeads C for  $CO_2$  and a column of 5A molecular sieve for  $CO$  and  $O_2$ . The material balance in the catalytic reactions was checked from the concentrations of  $CO_2$  and  $CO$ , both being in good coincidence with each other under all the conditions tested. Since temperature increase and pressure change at the surface are estimated to be 0.15 K and 0.01 mbar for 100% conversions, respectively, there seem to be no heat and mass transfer limitations.

## 3. Results and discussion

### 3.1. EXAFS and XRD measurements

Fig. 1 shows the EXAFS spectra for **2**/ $TiO_2$  before treatment. Figs. 1a, 1b and 1c present the EXAFS oscillation, its associated Fourier transform, and curve fit-

Table 1  
Crystallographic data and curve-fitting results for Au L<sub>3</sub>-edge EXAFS data of **2** and Au foil<sup>a</sup>

Sample	Crystallographic			EXAFS				
	shell	N	r (Å)	N	r (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E$ (eV)	$R_f$ (%)
Au foil [Au <sub>9</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>3+</sup>	Au–Au	12	2.88	12.0	2.88	0.0000	0.7	0.04
	Au–Au	4.4	2.78	4.4	2.79	0.0004	2.9	0.35
	Au–P	0.9	2.30	0.9	2.31	0.0000	1.9	0.35

<sup>a</sup> N: coordination number, r: interatomic distance,  $\sigma$ : Debye–Waller factor,  $\Delta E$ : difference in the origin of photoelectron energy between reference and sample,  $R_f$ : residual factor in the curve fitting.  $\Delta k$ : 3.00–14.56 Å<sup>−1</sup> (Au foil), 3.43–13.50 Å<sup>−1</sup> (Au–Au and Au–P for **2**);  $\Delta r$ : 1.95–3.18 Å (Au foil), 1.55–3.00 Å (Au–Au and Au–P for **2**).

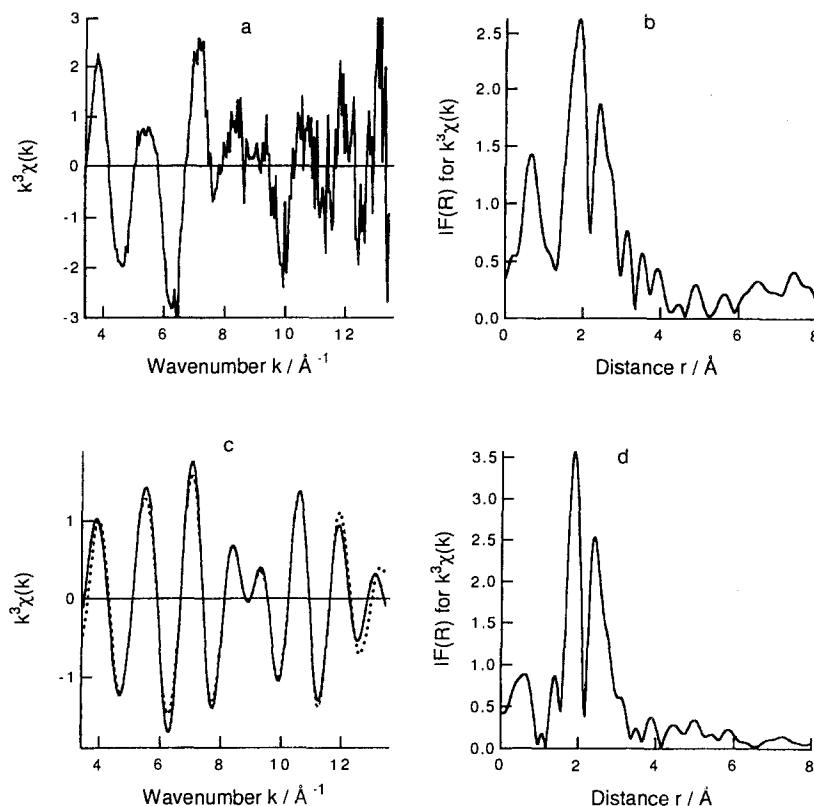


Fig. 1. The EXAFS data for 2/TiO<sub>2</sub> at Au L<sub>3</sub>-edge measured at 293 K in vacuum. (a)  $k^3$ -weighted EXAFS oscillation; (b) its associated Fourier transform; (c) curve-fitting analysis (inversely Fourier transformed) for Au–P and Au–Au: (—) observed; (···) calculated; (d) Fourier transform of the EXAFS oscillation for 2.

ting, respectively. By comparison with the EXAFS Fourier transform for 2 in fig. 1d, the peaks in fig. 1b are straightforwardly assigned to Au–P and Au–Au bonds. The best-fit results are listed in table 2. The data demonstrate that the cluster framework  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  in 2/TiO<sub>2</sub> is almost the same as that for the unsupported 2. By heating the incipient 2/TiO<sub>2</sub> to 573 K under vacuum, the EXAFS Fourier transform (fig. 2b) changed to exhibit only one peak due to the Au–Au bond. The Au–Au bond distance and the coordination number were determined to be 2.88 and 11.9 Å, respectively, by curve-fitting analysis (fig. 2c and table 2). The lack of an Au–P bond and the coordination number for the Au–Au bond suggest decomposition of the cluster framework to form metallic gold particles on TiO<sub>2</sub> surface at 573 K under vacuum.

The EXAFS analysis for the incipient 2/SiO<sub>2</sub> at 293 K is shown in table 3. The data imply that a phosphine ligand still coordinates to an Au atom but the clus-

ter framework is partially fragmented on SiO<sub>2</sub>, judging from a decrease in the coordination number of Au–Au bonds from 4.4 to 3.0. After heating the sample to 573 K under vacuum, the incipient supported clusters were decomposed to metallic Au particles, as shown in table 3.

X-ray diffraction patterns of the samples 1/TiO<sub>2</sub> and 1/SiO<sub>2</sub> before and after heat-treatments under air, 5% H<sub>2</sub>/Ar, and CO atmosphere were measured to estimate the mean particle size of the Au crystallites. The patterns indicate that after the treatments the supported gold complexes were decomposed to form metallic particles on the oxides, while the incipient supported species showed no crystalline pattern, coinciding with the results from EXAFS. Similar decomposition to Au particles was observed in case of the samples 2/TiO<sub>2</sub>, 2/SiO<sub>2</sub>, 1/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and 2/TiO<sub>2</sub> by XRD. For example, the Au particle sizes for 1/SiO<sub>2</sub> (treated at 673 K in air), 1/TiO<sub>2</sub>, 2/TiO<sub>2</sub> (both are treated at 773 K in 5% H<sub>2</sub>/Ar),

Table 2  
Curve-fitting results for the Au L<sub>3</sub>-edge EXAFS data of 2/TiO<sub>2</sub>

<i>T</i> (K)	Au–P				Au–Au				<i>R<sub>f</sub></i> (%)
	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E$ (eV)	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E$ (eV)	
293	1.0	2.33	0.0030	6.1	4.0	2.77	0.0016	3.5	3.3
573					11.9	2.88	0.0000	0.2	1.1

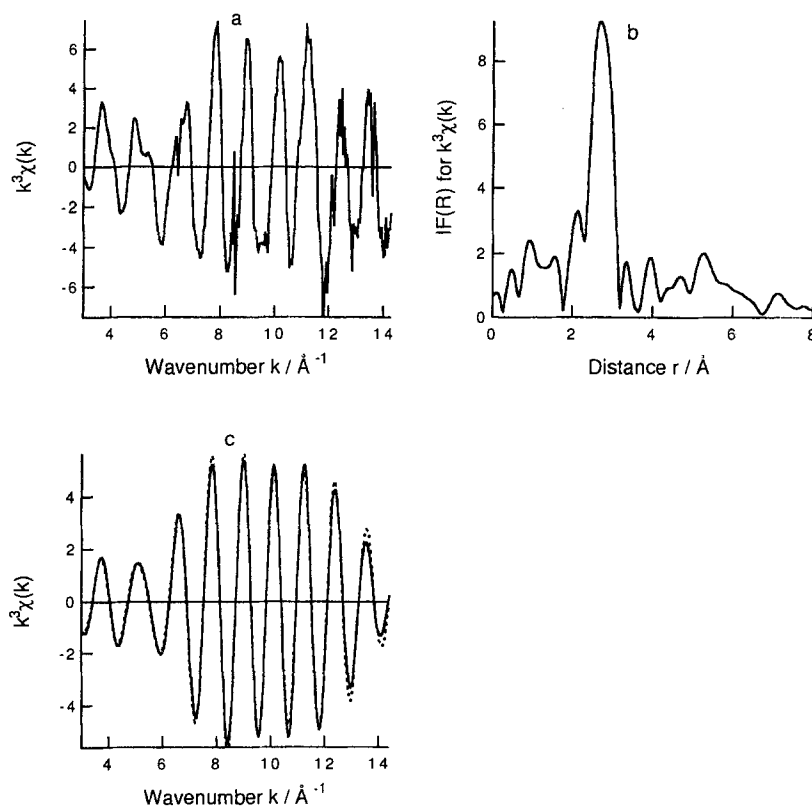


Fig. 2. The EXAFS data for 2/TiO<sub>2</sub> treated at 573 K in vacuum. (a)  $k^3$ -weighted EXAFS oscillation; (b) its associated Fourier transform; (c) curve-fitting analysis (inversely Fourier transformed) for Au-P and Au-Au: (—) observed; (···) calculated.

and 1/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (treated at 673 K in air) were estimated to be 160, 160, 180 and 120 Å as determined by XRD, respectively.

### 3.2. Catalytic activity for CO oxidation

No measurable activity of the incipient supported samples for CO oxidation at 313 K was detected. The catalytic activity was observed on the samples which were decomposed to form metallic gold particles on oxide supports except those on SiO<sub>2</sub> over which no CO<sub>2</sub> was produced at 313 K. Figs. 3, 4 and 5 depict CO conversion measured on the Au catalysts derived from 1 and 2 as a function of reaction temperature. The 1/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 1/TiO<sub>2</sub> catalysts treated at 673 or 773 K showed high CO oxidation activities in the temperature range 300–600 K, while the 1/SiO<sub>2</sub> catalyst showed the activity only above 600 K. The activity of the catalysts derived from 2 was much lower than that of the catalysts derived

from 1 as a common feature for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> supports as shown in Figs. 3, 4 and 5. Turnover frequencies (TOF) of some Au catalysts at 313 K are given in table 4. The TOF in this work is defined as the number of converted CO molecules per second divided by the total number of Au atoms included in the catalyst, because it is difficult to measure the accurate Au surface area by specific gas adsorption on XRD. The TOF of 1/TiO<sub>2</sub>, 2/TiO<sub>2</sub> (pretreated at 773 K with 5% H<sub>2</sub>/Ar) and 1/Fe<sub>2</sub>O<sub>3</sub> (pretreated at 673 K in air), at 353 K are 0.0025, 0.0004, and 0.0082 s<sup>-1</sup>, respectively, as shown in table 4. The addition of 2 to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> had a little positive effect on the oxidation activity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. 3). The activity of 1/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was higher than that of the catalyst prepared by an impregnation method using HAuCl<sub>4</sub> as precursor, but lower than that of the catalyst prepared by a coprecipitation method [8,9], possibly due to the different sizes of gold particles formed in these catalysts. The TiO<sub>2</sub>-supported Au catalyst derived from HAuCl<sub>4</sub> was

Table 3  
Curve-fitting results for the Au L<sub>3</sub>-edge EXAFS data of 2/SiO<sub>2</sub>

<i>T</i> (K)	Au-P				Au-Au				<i>R<sub>f</sub></i> (%)
	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E$ (eV)	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E$ (eV)	
293	1.1	2.28	0.0023	3.6	3.0	2.81	0.0000	10.5	1.7
573					11.7	2.88	0.0004	0.4	0.1

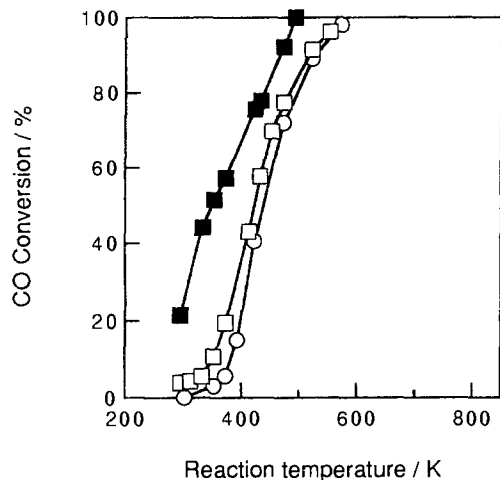


Fig. 3. Temperature dependence of CO oxidation activity of 1/ $\alpha$ - $\text{Fe}_2\text{O}_3$  and 2/ $\alpha$ - $\text{Fe}_2\text{O}_3$ . The data at each temperature were measured after the catalytic reaction reached steady state; 1% CO balanced with air at a flow rate of 34 ml/min ( $\text{SV} = 10000 \text{ h}^{-1}$ ). (■) 1/ $\alpha$ - $\text{Fe}_2\text{O}_3$  treated under air at 673 K, (□) 2/ $\alpha$ - $\text{Fe}_2\text{O}_3$  treated under air at 673 K, (○)  $\alpha$ - $\text{Fe}_2\text{O}_3$  calcined under air at 673 K.

also less active than 1/ $\text{TiO}_2$ , particularly at low temperatures as shown in fig. 4. The gold catalysts showed different activation energies: 1/ $\text{TiO}_2$ : 12 kJ/mol, 2/ $\text{TiO}_2$ : 15–22 kJ/mol (the data are taken at 313–623 K), 1/ $\alpha$ - $\text{Fe}_2\text{O}_3$ : 9 kJ/mol, and 2/ $\alpha$ - $\text{Fe}_2\text{O}_3$ : 21 kJ/mol (calculated from the data at 303–473 K), which were close to the activation energies (16–35 kJ/mol) reported for CO oxidation on Au catalysts prepared by coprecipitation [9]. The Au particle sizes for  $\text{SiO}_2$  and  $\text{TiO}_2$  supports were similar with each other, while 1/ $\text{TiO}_2$  catalyst exhibited much higher activity than the 1/ $\text{SiO}_2$  catalyst. The 1/ $\alpha$ -

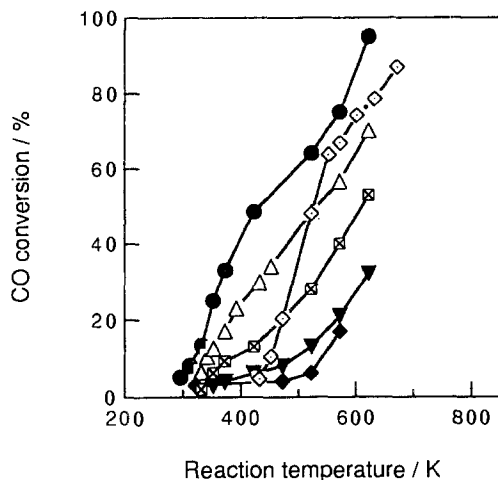


Fig. 4. Temperature dependence of CO oxidation activity of 1/ $\text{TiO}_2$  and 2/ $\text{TiO}_2$ . The data at each temperature were measured after the catalytic reaction reached steady state; 1% CO balanced with air at a flow rate of 34 ml/min ( $\text{SV} = 10000 \text{ h}^{-1}$ ). (●) 1/ $\text{TiO}_2$  treated under CO at 673 K, (△) 1/ $\text{TiO}_2$  treated under 5%  $\text{H}_2$ /Ar at 773 K, (⊗) 1/ $\text{TiO}_2$  treated under air at 673 K, (▼) 2/ $\text{TiO}_2$  treated under 5%  $\text{H}_2$ /Ar at 773 K, (◆) 2/ $\text{TiO}_2$  treated under CO at 673 K, (◇)  $\text{HAuCl}_4$ / $\text{TiO}_2$  calcined under air at 673 K.

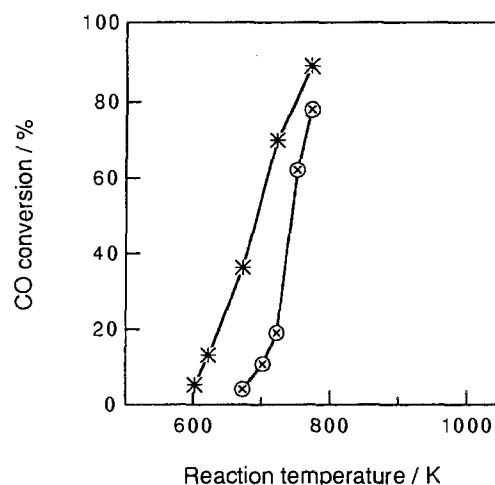


Fig. 5. Temperature dependence of CO oxidation activity of 1/ $\text{SiO}_2$  and 2/ $\text{SiO}_2$ . The data at each temperature were measured after the catalytic reaction reached steady state; 1% CO balanced with air at a flow rate of 34 ml/min ( $\text{SV} = 10000 \text{ h}^{-1}$ ). (\*) 1/ $\text{SiO}_2$  treated under air at 673 K, (⊗) 2/ $\text{SiO}_2$  treated under air at 673 K.

$\text{Fe}_2\text{O}_3$  catalyst with an averaged particle size of 120 Å was more active than the 1/ $\text{TiO}_2$  catalyst with an averaged particle size of 160 Å. Thus the catalytic activity varied with the kind of support and the particle size. In this study, the catalysts derived from gold complexes 1 and 2 supported on  $\alpha$ - $\text{Fe}_2\text{O}_3$  among the three metal oxides were found to be most efficient for CO oxidation. There may exist synergistic interaction between Au particles and oxides which changes by the kind of precursors and the pretreatment conditions. The present study demonstrates importance of the kind of precursor for catalyst preparation in a synergistic mode with the oxide support [20], which would require precise characterization of the obtained catalyst at atomic or molecular scales.

#### 4. Conclusion

We reported here the first example of supported gold catalysts prepared from a phosphine-stabilized mononuclear gold complex  $\text{Au}(\text{PPh}_3)(\text{NO}_3)$  (1) and an ennea-nuclear gold cluster compound  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (2), which were active for CO oxidation after treatments under air or CO or 5%  $\text{H}_2$ /Ar atmosphere. These gold complexes can be used as precursors to develop a novel and relatively simple way to prepare supported gold catalysts. The catalytic activity of the gold particles on oxides depended on precursor, support, and treatment conditions. The catalysts derived from 1 showed a higher activity than those derived from 2. Work is in progress to obtain much smaller gold particles on oxides and to find a new way to get stronger interaction between precursor and oxide for the genesis of high catalytic performance at low temperatures.

Table 4  
CO oxidation kinetics at temperature of 313 K <sup>a</sup>

Catalyst	Pretreatment	Activity TOF <sup>c</sup> (10 <sup>-3</sup> s <sup>-1</sup> )	Au crystalline size (Å)	Ref.
1/TiO <sub>2</sub>	773 K, 5% H <sub>2</sub> /Ar <sup>b</sup>	2.5	~ 160	this work
1/Fe <sub>2</sub> O <sub>3</sub>	673 K, air <sup>b</sup>	8.2	> 120	this work
2/TiO <sub>2</sub>	773 K, 5% H <sub>2</sub> /Ar <sup>b</sup>	0.4	~ 180	this work
5% Au/Fe <sub>2</sub> O <sub>3</sub>	673 K, air	7.0	160	[9]
12% Au/Fe <sub>2</sub> O <sub>3</sub> <sup>d</sup> (Au/Fe = 1/19)	673 K, air	> 13	36	[9]
2.4% Au/TiO <sub>2</sub> (110 m <sup>2</sup> /g)	673 K, air	83 <sup>e</sup>	~ 100	[18]
2.4% Au/TiO <sub>2</sub> (40 m <sup>2</sup> /g)	673 K, air	33 <sup>f</sup>	~ 40	[18]
2.2% Pd/Al <sub>2</sub> O <sub>3</sub>		0.08 <sup>g</sup>	37	[19]

<sup>a</sup> Measured with a gas flow rate 34 ml/min containing  $P_{\text{CO}} = 7.6$  Torr balanced by air.

<sup>b</sup> Heating at a rate with 5 K/min, keeping at final temperature for 4 h.

<sup>c</sup> TOF (turnover frequency) is defined as the number of reacted CO molecules divided by the total number of Au included in the catalyst.

<sup>d</sup> Prepared by coprecipitation, washed with hot water.

<sup>e</sup> Measured at 308 K.

<sup>f</sup> Measured at 273 K.

<sup>g</sup>  $P_{\text{CO}} = 26$  Torr,  $P_{\text{O}_2} = 132$  Torr.

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