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Article

Preparation of gold clusters on metal oxides by deposition-precipitation with microwave drying and their catalytic performance for CO and sulfide oxidation

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ABSTRACT

Gold clusters and small nanoparticles supported on metal oxides could be prepared by deposition-precipitation followed by microwave irradiation as a drying method and then calcination. The drying method influenced the size of the Au particles. Au(III) was partly reduced during conventional oven drying, resulting in Au aggregates. In contrast, Au(III) was preserved during microwave drying owing to rapid and uniform heating, and the Au diameter was minimized to 1.4 nm on Al₂O₃. This method can be applied to several metal oxide supports having different microwave absorption efficiencies, such as MnO₂, Al₂O₃, and TiO₂. These catalysts exhibited higher catalytic activities for CO oxidation at low temperature and for selective aerobic oxidation of sulfide than those prepared by conventional methods.

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1. Introduction

Since the discovery of catalysis by gold, unique catalytic performances of Au nanoparticles (NPs) have been reported and are attracting growing interest. In particular, Au clusters, which are smaller than 2 nm in diameter, exhibit high catalytic properties distinct from those of Au NPs because Au clusters possess electronic structures different from those of Au NPs and at the same time provide increased fractions of edge and corner sites [1,2]. Therefore, the preparation methods for Au cluster catalysts have been intensively studied. In this point of view, atomically precise Au clusters such as a glutathi-

one-protected Au₂₅ cluster (Au₂₅(SG)₁₈) have been recently exploited as precursors and deposited on supports [3–10]. The thiolate and phosphine ligands are removed by calcination from Au surfaces, but the Au aggregation often takes place [6–9]. In addition, the ligand remained on the catalyst surface influenced the catalytic activity of Au even though the ligand was removed under detection limit [8–10]. Therefore, to prepare Au cluster catalysts without ligand is still demanded.

One of the most common preparation methods to obtain bare Au NPs on metal oxides is deposition-precipitation (DP); Au(OH)₃ is precipitated exclusively onto metal oxide supports followed by calcination. The preparation conditions, such as pH

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[11], Au precursors [12], calcination temperature [13,14], and treatment gas [15–18], influence the size of the Au particles, and many efforts have been made toward the optimization of these parameters. However, the drying process of the wet solid on which Au(III) is precipitated has not been well studied. Oven drying (OD) is usually used at approximately 120 °C overnight [19–21]. Vacuum- [14] or freeze-drying (FD) [22] has also been exploited, but the reduction of Au(III) occurred to varying extents depending on the conditions [14]. The formation of Au(0) nuclei accelerates the aggregation of Au NPs during the subsequent calcination.

Microwave (MW) heating possesses some unique properties such as rapid, internal, and uniform heating. MW has been used for the formation of Au NPs [23] and the preparation of supported Au catalysts [24–34]. Simultaneous reduction of Au(III) to Au(0) NPs and their deposition onto supports under MW irradiation has been performed in the co-presence of Au(III), supports, reductants, and/or protecting agents [24–30]. However, the diameter of the Au NPs generally exceeded 5 nm with few exceptions [24]. Meire et al. [31] used MW for the reduction of Au(OH)₃ deposited on TiO₂ prepared by DP, but the obtained Au NPs were large and had wide size distributions. MW irradiation was also applied to the co-precipitation of HAuCl₄ and nitrate salts of support metals in the presence of reductants and protecting agents [32–34], but the obtained catalysts showed low activity for CO oxidation [32,33].

MW irradiation has also been applied to other purposes such as MW-assisted deposition of metal precursors [35], ligand removal from Au₂₅(SG)₁₈ on Al₂O₃ and TiO₂ [5], and drying [36,37]. Wittanadecha et al. [36] used MW to prepare Au/C by incipient wetness impregnation (IW) using HAuCl₄. The catalyst contained Au(III) species together with small Au(0) particles (<4 nm). This result indicates that MW heating causes the reduction of Au(III) to Au(0) even in the absence of additional reductants. It is well known that the presence of chloride enhances the aggregation of Au NPs [38], and long MW irradiation time was also reported to cause the reduction of Au(III) [31,36]. Therefore, there is still room to optimize MW irradiation to preserve Au(III) as a drying method.

In this work, we studied the preparation of Au catalysts by DP combined with MW drying (MD). DP is generally used for neutral and basic supports, such as Al₂O₃ and TiO₂, even though acidic supports, such as SiO₂ and MnO₂, can be used for DP using Au(en)₂Cl₃ as a precursor instead of HAuCl₄ [12,19,39]. Therefore, we chose MnO₂, Al₂O₃, and TiO₂ as supports. We found that Au(III) remained almost completely after the optimized MD conditions, whereas the reduction of Au occurred during OD when using Al₂O₃ and TiO₂. The obtained catalysts exhibited remarkably higher catalytic activity than those prepared by DP with OD for the oxidation of CO and sulfide.

2. Experimental

2.1. Materials

Metal oxides, Al₂O₃ (Sumitomo Chemical, AKP-G015, 148 m² g⁻¹), and TiO₂ (Nippon Aerosil, P-25, 50 m² g⁻¹) were pur-

chased. MnO₂ (98 m² g⁻¹) was prepared in accordance with the previous literature [19]. As Au precursors, tetrachloroauric acid (HAuCl₄·4H₂O) and bis(ethylenediamine) Au(III) trichloride [Au(en)₂Cl₃] were purchased from Tanaka Kikinzoku Kogyo K.K. and Tri Chemical Laboratories Inc., respectively. Other reagents were purchased and used as received.

2.2. Deposition of Au clusters onto metal oxides

Gold on Al₂O₃ and TiO₂ were prepared by DP with HAuCl₄, because the points of zero charge of these metal oxides were above 7 (1 wt% Au loading) [40]. Briefly, the pH of the aqueous solution of HAuCl₄ (2 mmol L⁻¹) was adjusted to 5 by adding aqueous NaOH solution, after the solution was heated to 70 °C. Then, the support (2 g) was dispersed into the solution, and the suspension was adjusted to pH = 7 by adding aqueous NaOH solution. After stirring at 70 °C for 1 h, the solid was washed with H₂O, filtered, and divided into two groups: MD and OD. MW irradiation was performed by a Shikoku Instrumentation μ Reactor Ex, Max 1000 W, 2.45 GHz for a few minutes depending on the type of support. For OD, the wet solid was dried in air at 120 °C overnight. The dried samples were denoted as drying method_{only}. The dried samples were reduced in a stream of 10 vol% H₂ in N₂ at a flow rate of 50 mL min⁻¹ at 300 °C for 1 h, denoted as drying method_{H₂}. For comparison, FD was also tested under the same conditions except for the drying method. For FD, the wet solid was dried under vacuum overnight after cooling with liquid N₂. Gold on MnO₂ was prepared by DP with Au(en)₂Cl₃ as a precursor, because MnO₂ is negatively charged in aqueous solution at pH 7 (1 wt% Au loading) [19]. The aqueous solution of Au(en)₂Cl₃ was heated to 70 °C. After dispersing the MnO₂ (2 g), the pH of the suspension reached 10. The pH was maintained at 10 during stirring at 70 °C for 1 h. After washing with H₂O, the solid was filtered, dried by MW irradiation or in air at 120 °C overnight, and then calcined in air at 300 °C for 4 h, denoted as drying method₃₀₀.

2.3. Characterization

Au L_{III}-edge X-ray absorption fine structures (XAFS) were measured at BL14B2, SPring-8 (Hyogo, Japan) [41,42]. The XAFS samples were ground with or without boron nitride in an agate mortar and formed into pellets. The aqueous Au(en)₂Cl₃ solution was used as an Au(III) reference for Au/MnO₂. The pH of the solution was adjusted to 10 by adding aqueous NaOH solution. An incident beam from an 8 GeV storage ring with a typical current of 99.5 mA was monochromatized by a Si double-crystal monochromator with a net plane of (311) for the Au L_{III}-edge. The XAFS spectra were recorded in transmission mode using ionization chambers for Au/Al₂O₃ and Au/TiO₂ and in fluorescence mode using a 19-element Ge solid-state detector (19SSD) for Au/MnO₂. The spectral analysis was performed by the XAFS analysis software programs Athena and Artemis [43]. The extraction of the extended XAFS (EXAFS) oscillation from the spectra, normalization by edge-jump, and Fourier transformation were performed by Athena. The curve fitting analysis was performed in R-space by Artemis. In the

curve-fitting analysis, the backscattering amplitude, the phase shift, and the mean-free path of the photoelectron were calculated by FEFF8.4 [44]. The number of neighboring atoms, the interatomic distance between the absorbed atom and the neighboring atom, the Debye–Waller factor, and the absorption edge energy were treated as fitting parameters. The intrinsic loss factor was obtained by the curve-fitting analysis of the EXAFS data of the Au foil.

Transmission electron microscope (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were performed using a JEOL JEM-3200FS operating at 300 kV.

^1H NMR spectra of the reaction solution of sulfide oxidation were measured on a JEOL ECS-300 spectrometer. Chemical shift values are expressed in ppm relative to internal tetramethylsilane.

The amount of excess surface oxygen was measured by iodometric titration [45]. A mixture of catalyst (0.020 g), KI (ca. 0.02 g), and 0.1 mol L^{-1} HCl aqueous solution (5 mL) was shaken for 5 min. The residue was filtered and washed with H_2O and ethanol. The amount of generated iodine was determined by titration with a sodium thiosulfate aqueous solution (10 mmol L^{-1}).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained by JASCO, FT/IR-6100V equipped with a heat chamber (ST Japan, Model-HC500). The sample powder was pretreated in a flow of N_2 (30 mL min^{-1}) at 250 °C for 1 h. Then the sample was exposed to 10 vol% CO in He (40 mL min^{-1}) at –180 °C for 30 min. DRIFT spectra were obtained by subtracting the background spectrum. After Au sites were saturated with a gas flow of 10 vol% CO/He mixture (40 mL min^{-1}), the catalyst was treated in a flow of N_2 (30 mL min^{-1}) and the spectra were collected at –180 °C.

2.4. Catalytic tests

2.4.1. CO oxidation

The catalytic test for CO oxidation was performed in a fixed-bed flow reactor containing 150 mg of catalyst. The pretreatment was performed at 250 °C for 1 h in a stream of 20 vol% O_2 in N_2 at a flow rate of 50 mL min^{-1} . Then, the reaction gas containing 1 vol% CO in air was passed through the reactor at a flow rate of 50 mL min^{-1} (space velocity of 20,000 mL h^{-1} $\text{g}_{\text{cat}}^{-1}$). The effluent gas was analyzed by gas chromatography using an Ohkura Riken model-802 or a Shimadzu GC-8A with Gasukuropack 54 and Molecular Sieve 13X columns. The moisture content in the reaction gas was monitored by a dew-point meter (Air Liquid DPO-6), and the water concentrations were kept in the range of 20–100 ppm at $T_{1/2}$, which is the temperature at 50% CO conversion in all experiments.

2.4.2. Selective aerobic oxidation of sulfide

To an autoclave was charged methylphenylsulfide (118 μL , 1.0 mmol), 1,2-dichlorobenzene (5.0 mL), Au/ MnO_2 (40 mg), and a magnetic stirring bar. The autoclave was purged and filled with O_2 until the gauge pressure reached 0.5 MPa. The reaction mixture was stirred at 100 °C for 36 h. The mixture was extracted with chloroform and filtered. The filtrate was

analyzed by ^1H NMR using mesitylene as an internal standard.

3. Results and discussion

3.1. Conditions of microwave drying for Au/metal oxide catalysts

The DP with MD was applied to three kinds of metal oxide supports, MnO_2 , Al_2O_3 , and TiO_2 , having different MW absorption efficiencies. Generally, black powders absorb MW efficiently [46,47]. The heating efficiency varies depending on crystal structure, lattice defects, and particle size even when the same oxide is used. To examine the MW absorption efficiency of the metal oxides used in this work, each dry metal oxide (0.4 g) was irradiated with MW at 500 W. A radiation thermometer was set over the MW instrument to monitor the surface temperatures of the metal oxides. After 2 min, the surface temperatures of MnO_2 , Al_2O_3 , and TiO_2 reached 91, 68, and 58 °C, respectively.

The irradiation conditions for Au(III) precursor/ MO_x were optimized by comparing the CO oxidation catalytic activity of Au/ MO_x without calcination for MnO_2 and after H_2 reduction for Al_2O_3 and TiO_2 (Table 1). For 2 g of Au/ MnO_2 , the filtered wet solid was divided into four groups and irradiated with MW using power-fixed (Table 1, entries 1 and 2) or temperature-controlled modes (entries 3 and 4). When the power-fixed mode was applied, higher power gave higher actual temperature and catalytic activity (entry 2). In the temperature-controlled mode, the irradiation power varied automatically in the range of 0–1000 W to reach the target surface temperature. When the actual temperature was at approximately 100 °C, the highest catalytic activity was obtained (entry 4). When Au/ Al_2O_3 and Au/ TiO_2 were dried, the power-fixed mode was better than the temperature-controlled mode in terms of catalytic activity (entries 5 and 7). Higher irradiation power or longer time was required for Al_2O_3 and TiO_2 than for MnO_2 due to lower MW absorption efficiency.

In the previous reports, Au(III) was partially reduced to Au(0) during MW irradiation. Namely, Wittanadecha et al. [36] reported that Au(III) in Au/C was reduced to Au(0) completely by MW irradiation at 800 W for 2 min. Kawamoto et al. [48] have reported that $\text{Au}(\text{OH})_3$ was converted into Au(0) under air flow via the dehydration of $\text{Au}(\text{OH})_3$ to Au_2O_3 and then the thermal decomposition of Au_2O_3 to Au(0) by TG/DTA analysis. Therefore, excessive heating may cause the reduction of Au(III). As shown in Table 1, the catalytic activity was decreased when the actual surface temperature exceeded 100 °C. It implied that overheating caused partial reduction of Au(III) and aggregation of Au, leading to low catalytic activity. Consequently, the best result for each metal oxide was obtained when the surface temperature reached approximately 100 °C (entries 4, 5, and 7), and these optimum conditions were used in further studies.

3.2. Effect of drying methods on chemical valence and particle size of Au

3.2.1. XANES

Table 1Effect of MD conditions for Au/MnO₂, Au/Al₂O₃ and Au/TiO₂.

Entry	Catalyst	MW irradiation conditions						CO oxidation <i>T</i> _{1/2} (°C)
		Power or target temp.	Ramp rate (°C min ⁻¹)	Holding (min)	Cycle (times)	Total (min)	Actual temp. (°C)	
1	Au/MnO ₂ ^a	500 W	—	2	3	6	85	−28
2		600 W	—	2	2	4	94	−34
3		90 °C	25	1	1	4	110	−45
4		80 °C	25	1	1	3	103	−54
5	Au/Al ₂ O ₃ ^b	600 W	—	2	4	9	101	55
6		90 °C	25	1	2	7	84	61
7	Au/TiO ₂ ^c	1000 W	—	3	4	12	100	−40
8		80 °C	25	1	4	15	88	−31

^a Au/MnO₂_MW_only was used for CO oxidation after pretreatment in air at 250 °C for 1 h.^b Au/Al₂O₃_MW_only was reduced by 10 vol% H₂ in N₂ at a flow rate of 50 mL min⁻¹ at 300 °C for 4 h and then used for CO oxidation after pretreatment in air at 250 °C for 1 h.^c Au/TiO₂_MW_only was reduced by 10 vol% H₂ in N₂ at a flow rate of 50 mL min⁻¹ at 100 °C for 1 h and then used for CO oxidation after pretreatment in air at 250 °C for 1 h.

XANES spectra were obtained in order to elucidate the chemical states of Au in the obtained catalysts. In the Au L_{III}-edge XANES spectra of MD_only and OD_only for Au/MnO₂, white lines were clearly observed at 11.92 keV (Fig. 1(a)), suggesting that a major species was Au(III). The partial reduction of Au(III) on MnO₂ was observed in both samples. For MD_only, the temperature inside the MnO₂ wet solid probably exceeded 100 °C during MW irradiation, causing the reduction of Au(III) due to the high MW absorption efficiency of MnO₂. After the calcination, the white line intensities significantly decreased, suggesting that most of Au(III) was reduced to Au(0) (Table 2).

For Au/Al₂O₃ and Au/TiO₂, the white line intensities of MD_only and FD_only were almost the same as that of Au(OH)₃ (Figs. 2 and 3). In contrast, the intensity of OD_only was decreased. The Au(0) contents were estimated to be 45% and 73% in Au/Al₂O₃_OD_only and Au/TiO₂_OD_only, respectively (Table 2). Therefore, MD prevented the reduction of Au(III) during drying even though the drying temperature was similar to OD. After H₂ reduction, Au(III) was completely reduced to Au(0) in all cases.

3.2.2. EXAFS

To discuss the size of Au particles by XAFS, the radial structure functions (RSFs) of Au/MnO₂ are shown in Fig. 1(b). The FT magnitude of the peaks at 2.52 and 3.00 Å corresponding to Au-Au interaction of all calcined Au/MnO₂ decreased compared with those of Au foil, indicating the formation of Au NPs and/or formation of amorphous Au. In particular, the FT magnitude for Au-Au interaction in MD_250 was significantly lower than in MD_300, OD_250, and OD_300. Curve fitting analysis was performed to estimate the size of the Au NPs, and the EXAFS fitting parameters are shown in Table 3. The Debye–Waller factor, which accounts for the disorder in Au crystal, was almost the same as that of Au foil, excluding the presence of amorphous Au. The coordination numbers (CNs) of the Au-Au interaction of MD_250 and MD_300 were calculated to be 6.9 and 9.9 (Table 3). These values were 9.7 and 10.8 when only the Au(0) component was considered, and the estimated sizes from the CNs were 2.2 and 4.3 nm, respectively (Table 2). In contrast, the CNs of OD_250 and OD_300 were nearly 12 for the Au(0)

Fig. 1. (a) Au L_{III}-edge XANES spectra of Au/MnO₂ and (b) Au L_{III}-edge radial structure functions of Au/MnO₂.

Table 2Effect of drying and calcination conditions for physical properties of Au/MnO₂, Au/Al₂O₃, Au/TiO₂ and their catalytic activity for CO oxidation.

Entry	Catalyst	Drying and calcination conditions ^a	XAFS		HAADF diameter of Au (nm)	CO oxidation $T_{1/2}$ (°C) ^b
			Au ⁰ (%)	Estimated size (nm)		
1	Au/MnO ₂	MD_only	29	–	–	–
2		OD_only	14	–	–	–
3		MD_250	71	2.2	2.1 ± 0.8	–54
4		OD_250	80	> 5	4.0 ± 7.1	–2
5		MD_300	92	4.3	4.3 ± 2.9	26
6		OD_300	91	> 5	6.8 ± 7.9	74
7	Au/Al ₂ O ₃	MD_only	0	–	–	–
8		FD_only	0	–	–	–
9		OD_only	45	–	2.3 ± 1.8	–
10		MD_H ₂	100	1.6	1.4 ± 1.2	68
11		FD_H ₂	100	1.9	1.9 ± 1.3	72
12		OD_H ₂	100	2.3	3.2 ± 2.6	87
13	Au/TiO ₂	MD_only	6	–	–	–
14		OD_only	73	–	2.1 ± 0.9	–
15		MD_H ₂	100	2.7	2.2 ± 0.8	–42
16		OD_H ₂	100	3.2	2.9 ± 1.1	–13

^a Drying method_300 was calcined in air at 300 °C for 4 h. Drying method_H₂ was reduced by 10 vol% H₂ in N₂ at a flow rate of 50 mL min^{–1} at 300 °C for 1 h.^b CO oxidation was performed after pretreatment at 250 °C for 1 h in a stream of 20 vol% O₂ in N₂ at a flow rate of 50 mL min^{–1}. **Fig. 2.** (a) Au L_{III}-edge XANES spectra of Au/Al₂O₃ and (b) Au L_{III}-edge radial structure functions of Au/Al₂O₃.

component as well as bulk. Even if the CN is 11, the estimated size from the CN exceeds 5 nm. Therefore, the mean diameters of these catalysts were larger than at least 5 nm.

For both Au/Al₂O₃ and Au/TiO₂, the FT magnitude of Au–Au interaction of MD_H₂ was lower than in OD_H₂, as observed in Au/MnO₂; smaller Au NPs were formed in MD_H₂ than in OD_H₂ (Figs. 2(b), 3(b) and Tables 2, 3). Accordingly, the smallest Au clusters, with a diameter of 1.6 nm estimated by XAFS, were deposited on Al₂O₃ using MD followed by H₂ reduction (Au/Al₂O₃_MD_H₂). We also compared MD with FD for Au/Al₂O₃. Although Au(III) was preserved during both drying methods, the Au particle size of MD_H₂ was slightly smaller than that of FD_H₂.

As judged by the Au particle size, MD is the most effective drying method. Although Au(0) was formed in both

Au/MnO₂_MD_only and Au/MnO₂_OD_only, smaller Au NPs were obtained for MD_250 than for OD_250, which is likely due to different Au particle sizes forming after MD and OD. It is likely that Au(III) species were highly dispersed by MD, giving Au cluster catalysts. When Al₂O₃ and TiO₂ were used as supports, OD caused the reduction of Au(III) to form Au(0) nuclei and facilitated the aggregation of Au(0) particles. Once Au(0) nuclei are formed, Au(III) would be preferentially reduced on the nuclei to form Au NPs during the subsequent calcination. MD can be performed in a much shorter time than OD, preventing the reduction of Au(III). FD also prevents the reduction of Au(III), but Au particles are aggregated compared with MD after H₂ reduction. One possible explanation is that structures of adsorbed Au(III) species may change depending on the drying conditions. Moreau et al. [49] proposed the adsorption

Fig. 3. (a) Au LIII-edge XANES spectra of Au/TiO₂ and (b) Au LIII-edge radial structure functions of Au/TiO₂.

mechanisms of Au(OH)₃ on TiO₂. At pH>6, Au(OH)₃ might interact with the surface hydroxy groups of metal oxides and be adsorbed by dehydration. As the dehydration progressed, Au₂O₃, which is unstable, was formed. Although Au₂O₃ was not observed in MD and FD, difference in the adsorbed Au(OH)_x structure may affect the stability of Au(III). A previous report also proposed that the structure of Au(OH)₃ was a linear polymer bridged by OH groups between Au(III) [48]. Therefore, another possibility is that the chain length of [Au(OH)₃]_n, i.e., the size of [Au(OH)₃]_n particles, obtained by MD and FD may be different, although the size of Au(III) species cannot be confirmed by XAFS due to amorphous Au(OH)₃.

3.2.3. HAADF-STEM

The HAADF-STEM images of Au/MnO₂ are shown in Fig. 4. In both MD_only and OD_only, Au particles were scarcely found,

but a few Au clusters ca. 1 nm in diameter were observed (Fig. 4(a) and (b)). After MD_only and OD_only were pretreated in air at 250 °C or calcined in air at 300 °C for 4 h, Au NPs were formed and clearly observed. The mean diameters of Au for MD_250 and MD_300 were estimated to be 2.1 and 4.3 nm (Fig. 4(d) and (h)). These values were consistent with XAFS and smaller than those for OD_250 and OD_300, respectively. Careful HAADF-STEM observation revealed large Au NPs (>30 nm) in OD_250 and OD_300, which resulted in a broader size distribution (Fig. 4(f) and (j)). It should be mentioned that MD can prevent the aggregation of Au during calcination to give smaller Au particles than OD in spite of the fact that partial reduction of Au(III) occurred during both MD and OD.

As shown in Figs. 5 and 6, Au NPs were observed in OD_only but not in MD_only for Au/Al₂O₃ and Au/TiO₂. After reduction by H₂, the Au NPs on both supports were aggregated to larger

Table 3

EXAFS fit parameters for Au/MnO₂^a, Au/Al₂O₃^b, and Au/TiO₂^c.

Entry	Sample		Shells	CN ^d	<i>R</i> (Å) ^e	σ ² (Å ²) ^f	<i>R</i> _{factor} ^g
1	Au foil		Au-Au	12.0	2.865 ± 0.002	0.0081 ± 0.0003	0.0007
2	Au(en) ₂ Cl ₃		Au-N	4.0	2.023 ± 0.017	0.0034 ± 0.0025	0.0126
3	Au/MnO ₂	MD_250	Au-Au	6.9	2.848 ± 0.010	0.0087 ± 0.0004	0.0141
4			Au-N	1.0	1.982 ± 0.020	0.0013 ± 0.0029	
5		OD_250	Au-Au	9.8	2.858 ± 0.005	0.00869 (share)	0.0020
6			Au-N	0.8	2.013 ± 0.018	0.0041 ± 0.0028	
7		MD_300	Au-Au	9.9	2.863 ± 0.004	0.00869 (share)	0.0073
8		OD_300	Au-Au	10.4	2.856 ± 0.007	0.00869 (share)	0.0017
9	Au/Al ₂ O ₃	MD_H ₂	Au-Au	8.8	2.811 ± 0.004	0.0123 ± 0.0006	0.0023
10		FD_H ₂	Au-Au	9.2	2.824 ± 0.004	0.0118 ± 0.0006	0.0022
11		OD_H ₂	Au-Au	9.8	2.836 ± 0.002	0.0107 ± 0.0003	0.0007
12	Au/TiO ₂	MD_H ₂	Au-Au	10.1	2.832 ± 0.005	0.0100 ± 0.0008	0.0032
13		OD_H ₂	Au-Au	10.4	2.848 ± 0.005	0.0094 ± 0.0008	0.0028

^a *k*³: *k*-range = 2–10 Å⁻¹, *r*-range = 1.9–3.4 Å for Au–Au and 1.1–1.9 Å for Au–N. Intrinsic loss factor, *S*₀² = 0.83 (Au–Au) from Au foil and 0.90 (Au–N) from Au(en)₂Cl₃.

^b *k*³: *k*-range = 2–11 Å⁻¹, *r*-range = 2.0–3.3 Å for Au–Au. Intrinsic loss factor, *S*₀² = 0.81 (Au–Au) from Au foil.

^c *k*³: *k*-range = 2–10 Å⁻¹, *r*-range = 1.95–3.35 Å for Au–Au. Intrinsic loss factor, *S*₀² = 0.84 (Au–Au) from Au foil.

^d First shell coordination number.

^e Bond length.

^f Debye-Waller factor.

^g Goodness-of-fit index.

Fig. 4. HAADF-STEM images of Au/MnO₂ (a) MD_only, (b) OD_only, (c) MD_250, (e) OD_250, and (g) MD_300, TEM image of (i) OD_300, and distributions of the diameter of Au NPs in (d) MD_250, (f) OD_250, (h) MD_300, and (j) OD_300.

NPs than that of OD_only. For MD and FD, cluster-sized particles were obtained even after reduction by H₂. The size of Au/Al₂O₃_MD_H₂ was estimated to be 1.4 nm, which was in

Fig. 5. HAADF-STEM images and distributions of the diameter of Au NPs in Au/Al₂O₃ (a, b) OD_only, (c, d) MD_H₂, (e, f) FD_H₂, and (g, h) OD_H₂.

accordance with XAFS results (Fig. 5).

3.3. CO oxidation

Fig. 7 shows the results of CO oxidation on Au/MnO₂ and MnO₂. MnO₂ is also catalytically active for CO oxidation without the deposition of Au, but the $T_{1/2}$ was 103 °C. With the deposition of Au NPs, the $T_{1/2}$ of all Au/MnO₂ decreased by more than 30 °C. The catalytic activities of MD_250 and OD_250 were much higher than that of MnO₂. MD_250 exhibited the highest catalytic activity. The $T_{1/2}$ of MD_250 was −54 °C, which was approximately 50 °C lower than that of OD_250. Although the catalytic activity decreased after calcination due to the aggregation of Au, the catalytic activity of MD_300 was remarkably

Fig. 6. HAADF-STEM images and distributions of the diameter of gold NPs in Au/TiO₂ (a, b) OD_only, (c, d) MD_H₂, and (e, f) OD_H₂.

Fig. 7. CO oxidation in air on Au/MnO₂ catalysts. (●) MD_250; (▲) OD_250; (○) MD_300; (△) OD_300; (◆) MnO₂.

higher than that of MnO₂ and OD_300; the $T_{1/2}$ was 26 °C (Table 2).

Fig. 8 shows the results of CO oxidation on Au/Al₂O₃ and Au/TiO₂. The catalytic activity increased with a decrease in the size of Au as in the case of Au/MnO₂. The catalytic activities of both MD_H₂ were higher than those of OD_H₂ (Table 2). The catalyst that possessed the highest ratio of Au clusters exhibited the highest catalytic activity (MD_H₂). MD also gave better results for Au/Al₂O₃ than OD and FD did. As a result, MD can be used to deposit small Au particles regardless of the type of metal oxide support and Au precursor, leading to high catalytic

Fig. 8. CO oxidation in air on Au/TiO₂ (○) MD_H₂ and (△) OD_H₂, and Au/Al₂O₃ (●) MD_H₂, (■) FD_H₂, and (▲) OD_H₂.

activity.

To further elucidate the difference in catalytic activity between Au clusters and NPs, DRIFT spectra of Au/Al₂O₃_MD_H₂ and Au/Al₂O₃_OD_H₂ were obtained using CO as a probe molecule (Fig. 9). Al₂O₃ also adsorbed CO and the corresponding peaks were observed at 2183, 2152, and 2132 cm⁻¹. After Au deposition, the additional peaks were observed. In the case of Au/Al₂O₃_MD_H₂, the peaks corresponding to the adsorbed CO were observed at 2122 and 2093 cm⁻¹. These were assigned as Au^{δ+}-CO and Au⁰-CO, respectively [50,51]. On the other hand, in the case of Au/Al₂O₃_OD_H₂, the peak at 2093 cm⁻¹ ascribed to Au⁰ was observed while the peak for Au^{δ+} was negligible. It is widely accepted that cationic Au species are present at the perimeter. Therefore, the presence of Au^{δ+} in large amount for Au/Al₂O₃_MD_H₂ suggested the markedly increased Au perim-

Fig. 9. DRIFT spectra of CO adsorbed on (a) Au/Al₂O₃_MD_H₂, (b) Au/Al₂O₃_OD_H₂, and (c) Al₂O₃.

eter atoms. The perimeter interface is known as the active sites for CO oxidation [2], but one of our authors [52] and Lu et al. [53] reported that the amount of cationic Au species and catalytic activity did not directly correlate. Therefore, the contribution of change in the oxidation state of Au might not be a determination factor. It is likely that the improved activity of Au clusters in this paper is ascribed to markedly increased Au–MO_x interface, edge and corner sites for CO adsorption.

3.4. Selective aerobic oxidation of sulfide

We recently reported that MnO_x and Au/MnO_x catalyzed the selective aerobic oxidation of sulfides to sulfoxides [19]. Since the active species is MnO_x in this reaction, MnO_x with higher amounts of excess surface oxygen has higher catalytic activity, and the deposition of Au enhanced the catalytic activity of MnO_x owing to the enhanced activation of oxygen at the interface between Au and MnO_x. Therefore, minimizing the size of Au particles increases the active Au–MnO_x interface and will offer highly active catalysts. The catalytic activities for the selective oxidation of sulfide to sulfoxide were also tested (Table 4). With the deposition of Au NPs, sulfide conversion and sulfoxide selectivity were improved as previously reported (entries 4 and 5). An increase in excess surface oxygen by the deposition of Au was confirmed by iodometric titration. The amount of excess surface oxygen was not directly related to catalytic activity for Au/MnO₂. This is due to slight differences in excess surface oxygen among Au/MnO₂. Given that MD_only containing Au(III) and Au clusters of 1 nm in diameter exhibited the highest catalytic activity, Au(III) also contributes to the activation of oxygen at the Au(III)–MnO₂ interface, and highly dispersed Au(III) and Au clusters markedly improved the catalytic activity. Although there was no difference in Au particle size between MD_only and OD_only in the TEM results, the yield was improved by using MD_only. Au(III) species derived from Au(en)₂Cl₃ may present not only as mononuclear but also polynuclear complexes as is the case for [Au(OH)₃]_n. Accordingly, the size of Au(III) species might be different between MD_only and OD_only and affect the catalytic activity because of the different lengths of perimeter interfaces between Au and MnO₂.

Table 4
Selective aerobic oxidation of methyl phenyl sulfide by Au/MnO₂.^a

Entry	Catalyst	Excess surface oxygen (mg g ⁻¹)	Conv. (%)	Yield (%) ^b	
				Sulfoxide	Sulfone
1	MD_only	42	65	64	1
2	OD_only	43	56	54	2
3	MD_300	41	59	57	2
4	OD_300	41	52	50	2
5	MnO ₂	36	30	26	4

^a Reaction conditions: sulfide (1.0 mmol), catalyst (40 mg), 1,2-dichlorobenzene (5 mL), *p*_{O₂} (0.5 MPa, gauge pressure), 100 °C, 36 h.

^b Determined by ¹H NMR spectroscopy using mesitylene as an internal standard.

4. Conclusions

Small Au NPs and clusters could be deposited on metal oxides by deposition-precipitation followed by MW irradiation and calcination. The catalysts prepared by MD exhibited higher activities for both gas and liquid phase oxidations than those prepared by OD and FD. The MD can be applied to several metal oxides regardless of the efficiency of MW absorption and performed in a much shorter time than OD. This method is very simple and convenient because there is no need to prepare clusters beforehand and to remove ligands and protecting agents. (1) In the case of Au/MnO₂, although Au(III) was partly reduced to Au(0) after MD and OD, smaller Au NPs were obtained by MD than by OD, which lead to high catalytic activity for sulfide oxidation. (2) In the case of Au/Al₂O₃ and Au/TiO₂, MD can be performed at a relatively lower temperature than OD and more quickly than FD. Therefore, the reduction of Au(III) and the aggregation of Au(0) particles can be prevented during drying, yielding Au cluster catalysts. In particular, the Au particle size was minimized to 1.4 nm on Al₂O₃ using MD followed by reduction with H₂.

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Graphical Abstract

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Preparation of gold clusters on metal oxides by deposition-precipitation with microwave drying and their catalytic performance for CO and sulfide oxidation

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Small gold nanoparticles and clusters could be deposited on metal oxides by deposition-precipitation followed by microwave drying and calcination. The MW drying can be applied to several metal oxides regardless of the MW absorption efficiency.

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沉积-沉淀-微波干燥法制备金属氧化物负载的金簇合物及其在CO氧化和硫化物氧化反应中的催化性能

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摘要: 采用沉积-沉淀法再辅以微波干燥和焙烧制备了金属氧化物负载的金簇合物和小的金纳米粒子。干燥方法影响了金颗粒尺寸。在炉干燥过程中Au(III)因部分还原而致使Au聚集。相反, 在微波干燥下, 因快速和加热均一而使Au(III)得以保持, 在Al₂O₃上负载的Au颗粒尺寸小至1.4 nm。该法可用于具有几种不同微波吸收效率的金属氧化物载体, 如MnO₂, Al₂O₃和TiO₂。这些催化剂在低温CO氧化和硫化物选择有氧氧化反应中的催化活性比常规方法制备的更高。

关键词: 金纳米粒子; 金簇合物; 微波; 一氧化碳氧化; 有氧氧化

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