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Preparation of gold nanoparticles supported on Nb₂O₅ by deposition precipitation and deposition reduction methods and their catalytic activity for CO oxidation

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ABSTRACT

Nanoparticulate gold catalysts supported on niobium oxides (Nb₂O₅) were prepared by different deposition methods. The deposition precipitation (DP) method, DP method with urea, deposition reduction (DR) method and one-pot method were used to prepare a 1 wt% Au/Nb₂O₅ catalyst. Layered-type Nb₂O₅ synthesized by a hydrothermal method (Nb₂O₅(HT)) was the most suitable as a support among various types of Nb₂O₅ including commercially available Nb₂O₅ samples. It appeared that the large BET surface area of Nb₂O₅(HT) enabled the dispersion of gold as nanoparticles (NPs). Gold NPs with a mean diameter of about 5 nm were deposited by both the DP method and DR method on Nb₂O₅(HT) under an optimized condition. The temperature for 50% CO conversion for Au/Nb₂O₅(HT) prepared by the DR method was 73 °C. Without deposition of gold, Nb₂O₅(HT) showed no catalytic activity for CO oxidation even at 250 °C. Therefore, the enhancement of the activity by deposition of gold was remarkable. This simple Au/Nb₂O₅ catalyst will expand the types of gold catalysts to acidic supports, giving rise to new applications.

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1. Introduction

Nanoparticulate gold catalysts (hereafter denoted as NPGCs) have been attracting much attention over the past few decades [1–5]. NPGCs deposited on base metal oxides act as excellent catalysts, particularly for CO oxidation below room temperature. In order to obtain highly active NPGCs, the diameter of the gold nanoparticles (NPs) should be smaller than 5 nm, which increases the surface boundary between the Au NPs and the support [6,7]. Significant effects of a metal oxide support on catalytic behavior have also been observed, and many kinds of gold-supported catalysts have been developed. A solid acid, which typically shows a low isoelectric point, is attractive as a support, but there have been only a few reports on gold-supported acidic oxides other than silica and

zeolite supports [8–10].

Niobium oxide (Nb₂O₅ or hydrated niobium oxide, Nb₂O₅·*n*H₂O) is widely used in catalysis and in electrochromic and photoelectrochemical devices [11,12]. Nb₂O₅ has been used as a water-tolerant solid acid catalyst for many reactions such as alkylation, esterification, hydrolysis, dehydration and hydration [13,14]. Nb₂O₅ also has potential applications as a support of NPGCs for oxidation of glycerol, which may lead to the development of new processes for glycerol upgrading and for oxidative condensation of furfural and alcohol, aimed at the development of new processes for renewable biomass. Sobczak et al. [15–17] reported Au (or Au–Cu) catalysts supported on Nb₂O₅ and Nb/MCF (silica) by modification of the niobium oxide surface by an amino group. Tong et al. [18] reported a simple Au/Nb₂O₅ catalyst; however, the mean diameter of the

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gold particles was about 9 nm. Recently, we have reported new crystalline niobium oxides (deformed orthorhombic) consisting of NbO_6 octahedra, NbO_7 and micropores based on the 7-membered ring in its structure with corner-sharing in the *c*-direction [19]. This deformed orthorhombic niobium oxide, denoted as $\text{Nb}_2\text{O}_5(\text{HT})$, was synthesized by a hydrothermal process, and catalytic activity based on its crystalline structure was revealed. An advantageous feature as a support is that $\text{Nb}_2\text{O}_5(\text{HT})$ has a large surface area exceeding $200 \text{ m}^2 \text{ g}^{-1}$. Nb_2O_5 is classified as an *n*-type semiconductor and has a redox property, indicating that Nb_2O_5 has the possibility of showing high catalytic activity as a support of an NPGC if gold NPs are deposited on Nb_2O_5 .

Gold catalysts are usually prepared by a deposition method in a liquid phase, such as the deposition precipitation (DP) method or deposition reduction (DR) method, in order to disperse nano-scale gold particles on the support. Control of the charged state of the metal oxide surface is essential for depositing gold NPs with a high degree of and uniform dispersion. However, it was difficult to prepare NPGCs in previous studies when the isoelectric point of the support was below pH 5. To obtain gold NPs on the support surface, electrostatic interactions between gold precursors and the support surface should be strong [20]. A positively charged ethylenediamine-gold complex could be attracted by supports that show a negative electrical charge in water.

The DP method, DP method with urea, DR method and one-pot method were used to prepare 1 wt% $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts in this study to obtain NPGCs. The preparation conditions for the DP method and DR method were optimized by changing gold precursors and reagents for pH control of the precursor solution. The effects of Nb_2O_5 supports on catalytic activity of the $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts obtained were examined through CO oxidation reaction.

2. Experimental

2.1. Catalyst preparation

Niobium oxide was prepared in a manner similar to that reported previously [19]. Layered-structure-type (deformed orthorhombic) niobium oxide was synthesized by a hydrothermal method from ammonium niobium oxalate ($\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$, Aldrich) and was denoted as $\text{Nb}_2\text{O}_5(\text{HT})$. The Nb precursor (6 mmol based on Nb) was dissolved in distilled water (40 mL) and then the solution was treated by hydrothermal synthesis for 1 d at 175°C . The resultant solid was separated and washed with distilled water by using filtration, and then the solid was dried at 80°C . The dried solid was crushed in an agate mortar and heat-treated for 2 h at 400°C in air. Commercially available Nb_2O_5 (Wako) and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Soekawa) were used for comparison after calcination at 400°C in air for 2 h.

Gold catalysts were prepared by the DP method and DR method. $\text{Au}(\text{en})_2\text{Cl}_3$ or HAuCl_4 (0.0507 mmol) was used as a precursor and was dissolved in 51 mL of water followed by the addition of niobium oxide (1 g). The temperatures of the dis-

persed solutions were 50°C for the DP method and room temperature for the DR method. The mixture was stirred for 1 h with pH adjusted to 9 by using 0.1 mol L^{-1} NaOH solution. In the DR method, NaBH_4 was added to the mixture, and the suspension was washed with 3 L of deionized water using suction filtration and dried at 80°C . The dried catalyst was calcined at 300°C for 4 h in air.

Preparation of $\text{Au}/\text{Nb}_2\text{O}_5$ by deposition precipitation with urea was carried out by adding urea (0.06 mol) to the same precursor solution as that used for the DP method without pH control and stirring at 90°C for 4 h. In the one-pot method, the gold precursor and ammonium niobium oxalate ($\text{Au}/\text{Nb} = 1/19$; Nb, 6 mmol) were dissolved in 40 mL of water, and then the solution was treated by hydrothermal synthesis for 1 d at 175°C .

2.2. Catalytic activity test

Catalytic activity was tested through CO oxidation reaction. The catalyst (0.15 g) was set in a fixed bed reactor, and 1 vol% CO in air was flowed (50 mL min^{-1}). H_2O concentration in the flow gas was monitored by a dew-point meter, and the concentrations were 20–100 ppm at $T_{1/2}$ in all experiments. Catalytic activities were compared by the reaction rate per all Au atoms ($\text{TOF}, \mu\text{mol}_{(\text{CO})} \mu\text{mol}_{(\text{Au})}^{-1} \text{ s}^{-1}$), which was obtained under the condition in which conversion of CO is below 15% for differential reactor assumption.

2.3. Characterization

The catalysts were characterized by the following techniques. Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer (RINT Ultima+, Rigaku) using $\text{Cu-K}\alpha$ radiation (tube voltage: 40 kV , tube current: 20 mA). Diffractions were recorded in the range of 4° – 60° at 5° min^{-1} . Morphology was investigated by using a transmission electron microscope (TEM, JEM-2100F, JEOL) at 200 kV . The samples were dispersed in ethanol by ultrasonic treatment for several minutes, and drops of the suspension were placed on a copper grid for TEM observations.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was used to measure oxide surface acidity. The experiment was carried out using an autochemisorption system (Bel Cat, BEL Japan). The experimental procedure was as follows. The catalyst (ca. 100 mg) was set on quartz wool and preheated under helium (50 mL min^{-1}) at 300°C for 1 h. Then ammonia was introduced at 100°C for 30 min. The desorption profile from 100 to 700°C was recorded with a mass spectrometer under a helium flow (50 mL min^{-1}).

3. Results and discussion

3.1. Selection of Nb_2O_5 supports

Different types of Nb_2O_5 supports were used to prepare 1 wt% $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts, and their effects on catalytic activity for CO oxidation were examined. The layered-type $\text{Nb}_2\text{O}_5(\text{HT})$,

Fig. 1. XRD patterns of Nb₂O₅ (HT) (a), Au/Nb₂O₅ (HT) (b), Au/Nb₂O₅·nH₂O (c), and Au/Nb₂O₅ (d) prepared by the DP method.

hydrothermally synthesized Nb₂O₅, and commercially available Nb₂O₅ and Nb₂O₅·nH₂O were used as supports. GNPCs were prepared by the DP method using Au(en)₂Cl₃ as a cationic gold precursor. The detailed preparation conditions will be discussed later. The DP method is the most conventional and convenient to deposit gold on supports and is particularly useful for basic metal oxides. Since Nb₂O₅ is a typical acidic support, preparation of highly dispersed Au/Nb₂O₅ catalysts by the DP method has not succeeded yet [15–18].

Fig. 1 shows XRD patterns of Nb₂O₅ (HT) and Au/Nb₂O₅ catalysts. Table 1 summarizes the physical properties of the samples obtained and their catalytic activities. The XRD patterns of Nb₂O₅ (HT) showed diffraction peaks at $2\theta = 22.7^\circ$ and 46.2° , which were attributed to (001) and (002) planes of the layered-type structure of Nb₂O₅ (HT), respectively, and the diffraction peak based on Nb₂O₅ (HT) did not change after deposition of gold. The prepared Au/Nb₂O₅ catalysts (Fig. 1 (b–d)) showed diffraction peaks at $2\theta = 38.3^\circ$ and 44.5° based on Au(111) and Au(200), respectively. The crystalline diameters calculated by the Scherrer equation were 4.0 nm for Au/Nb₂O₅ (HT), 6.1 nm for Au/Nb₂O₅·nH₂O and 23 nm for Au/Nb₂O₅. The values of BET surface area of niobium oxides were 208 m² g^{−1} (Nb₂O₅ (HT)), 19 m² g^{−1} (Nb₂O₅·nH₂O) and 5.8 m² g^{−1} (Nb₂O₅). In previous studies, the values of BET surface area of Nb₂O₅ supports were small (85 m² g^{−1} in [17], 7 m² g^{−1} in [15,16] and 1 m² g^{−1} in [18]). These data suggested that the large surface area (208 m²/g) of Nb₂O₅ (HT) was one of the key factors for the formation of NPs of gold dispersed on Nb₂O₅.

Fig. 2 shows the effects of reaction temperature on CO conversion over the catalysts obtained. The Nb₂O₅ (HT) sample

Fig. 2. Effects of reaction temperature on CO conversion on Au/Nb₂O₅ (HT), Au/Nb₂O₅·nH₂O^a, Au/Nb₂O₅^a and Au/SiO₂. (a: commercially available Nb₂O₅. Au/SiO₂: commercial product (Haruta Gold Incorporated) prepared by the DR method (Au: 1 wt%). Reaction conditions: catalyst 0.15 g, flow rate 50 mL min^{−1} (1 % CO/air).

showed no activity for CO oxidation even at 250 °C. In contrast, the activity of the Au/Nb₂O₅ (HT) catalyst for CO oxidation was greatly enhanced, and the temperature for 50% CO conversion ($T_{1/2}$) was 85 °C. The catalytic activity of Au/Nb₂O₅ (HT) was much higher than that of Au/SiO₂, which was an acidic support. The catalytic activities of Au/Nb₂O₅·nH₂O and Au/Nb₂O₅ were much lower than the catalytic activity of Au/Nb₂O₅ (HT). The values of $T_{1/2}$ were 171 °C for Au/Nb₂O₅·nH₂O and 250 °C for Au/Nb₂O₅. The loading amount of gold of Au/Nb₂O₅ (HT) was 0.81 wt% and that of Au/Nb₂O₅·nH₂O was 0.88 wt%. It was difficult to deposit gold NPs for the commercial Nb₂O₅ support, and the amount of gold was 0.10 wt%. To obtain gold NPs on the support surface, electrostatic interactions between gold precursors and the support surface should be strong. The use of Au(en)₂Cl₃, which forms the Au(en)₂³⁺ species in the precursor solution. These results suggested that the interaction between the Au(en)₂³⁺ species and the surface of Nb₂O₅, which show a negative electrical charge in water, was different, even though the support has the same chemical composition (Nb₂O₅), and that the interaction has an important role in the deposition of NPs of gold on Nb₂O₅.

3.2. Comparison of deposition methods

Deposition of gold in liquid phase by the DP, DR, DP method with urea (DP-urea method), and one-pot method was carried out by using Nb₂O₅ (HT), and the catalytic activities were com-

Table 1

Physical properties of Au/Nb₂O₅ prepared by the DP method and their catalytic activities for CO oxidation.^a

Entry	Precursor	Support	BET surface area / m ² g ^{−1}	Au loading ^b / wt%	$T_{1/2}$ ^c / °C	Crystalline diameter ^d / nm
1	Au(en) ₂ Cl ₃	Nb ₂ O ₅ (HT)	208	0.81	85	5.4
2	Au(en) ₂ Cl ₃	Nb ₂ O ₅ ·nH ₂ O ^e	19	0.88	171	7.0
3	Au(en) ₂ Cl ₃	Nb ₂ O ₅ ^e	6	0.10	250	35

^a Catalyst 0.15 g, flow rate 50 mL min^{−1} (1 vol% CO/air). ^b Determined by AAS. ^c Temperature for 50% CO conversion. ^d Calculated by the Scherrer equation from the XRD pattern. ^e Commercially available niobium oxide.

pared. Deposition of gold in a solid state, a method called the solid grinding (SG) method, was also carried out for comparison. The loading amount of gold was 1 wt% for all catalysts. Fig. 3 shows TEM images and the distribution of diameters of gold particles of Au/Nb₂O₅ prepared by the different deposition methods. The crystalline diameter of gold particles of the catalyst obtained agreed well with TEM observation. The mean diameters were 4.1 nm (standard deviation (SD), 1.1 nm) for Au/Nb₂O₅ prepared by the SG method, 4.9 nm (SD, 1.4 nm) for the catalyst prepared by the DR method and 5.0 nm (SD, 2.4 nm) for the catalyst prepared by the DP method.

Then the effects of deposition methods on catalytic activity for CO oxidation were investigated by Au/Nb₂O₅ prepared by the different deposition methods (Fig. 4 and Table 2). The values of TOF at 20 °C and $T_{1/2}$ of those catalysts corresponded to the gold particle size, and the catalytic activity decreased in the order of SG > DR > DP > DP-urea > one-pot methods. The catalytic activity of Au/Nb₂O₅(HT) prepared by the SG method was the highest; however, the precursor of gold, Me₂Au(acac), is currently too expensive to use widely. Therefore, improvement of deposition of gold in liquid phase or the development of an alternative precursor for the SG method will be needed for the deposition of gold NPs on Nb₂O₅.

3.3. Stability and acidity of Au/Nb₂O₅(HT) prepared by the DP and DR methods

Fig. 5 shows that time-on-stream change of catalytic activity

Fig. 4. Effects of deposition methods on catalytic activity for CO oxidation over Au/Nb₂O₅(HT). Reaction conditions: catalyst 0.15 g, flow rate 50 mL min⁻¹ (1% CO/air).

for CO oxidation at 100 °C with Au/Nb₂O₅(HT) prepared by the DP and DR methods. In the case of the DP method, the preparation condition was the same as that in entry 1 in Table 2. The precursor used was Au(en)₂Cl₃ and pH value of the precursor

Fig. 3. TEM images and distribution of the diameters of gold particles of Au/Nb₂O₅(HT) prepared by different deposition methods. (a, a') SG method; (b, b') DR method; (c, c') DP method.

Table 2Effects of deposition methods on physical properties of Au/Nb₂O₅(HT) and catalytic activities for CO oxidation.^a

Entry	Deposition condition	Au loading ^b / wt%	T _{1/2} ^c / °C	TOF ^d / ×10 ³ mol _(CO) mol _(Au) ⁻¹ s ⁻¹	Crystalline diameter ^e / nm	Particle diameter ^f / nm
4	SG	1.0	52	5.9	4.1	4.1 ± 1.1
5	DR	0.93	73	5.1	4.9	4.9 ± 1.4
1	DP	0.81	85	1.9	5.4	5.0 ± 2.4
6	DP-urea	0.76	152	—	15.3	—
7	One-pot	3.9	160	—	65.5	—

^a Catalyst 0.15 g, flow rate 50 mL min⁻¹ (1 vol% CO/air). ^b Determined by AAS. ^c Temperature for 50% conversion. ^d Based on all Au atoms at 20 °C.^e Calculated by the Scherrer equation from the XRD pattern. ^f Measured by TEM.

Fig. 5. (a) Effects of reaction time and calcination treatment on Au/Nb₂O₅(HT) catalysts prepared by the DR and DP methods; Distribution of the diameters of gold particles of Au/Nb₂O₅(HT) after the CO oxidation (Au/Nb₂O₅(HT) catalysts prepared by the DR (b) and DP (c) methods). Reaction conditions: catalyst 0.15 g, flow rate, 50 mL min⁻¹ (1 vol% CO/air), reaction temperature 100 °C, heat treatment 250 °C for 1 h in air flow (50 mL min⁻¹).

solution was adjusted to 9 with NaOH solution. The sample obtained was dried under a vacuum condition at room temperature and then calcined at 300 °C for 4 h (see also next section and supporting information).

In the case of the DR method, the condition for preparation was the same as that in entry 5 in Table 2. The precursor used was Au(en)₂Cl₃ and pH value of the precursor solution was adjusted to 9 with NaOH solution, and then NaBH₄ solution was added. The sample obtained was dried at 80 °C and then calcined at 300 °C for 4 h (see also next section and supporting information). The conversion of CO with the Au/Nb₂O₅(HT) catalyst prepared by the DR method was maintained above 98% and that of the catalyst prepared by DP the method was 70% at 100 °C. Then the conversion of CO with both catalysts decreased with prolongation of reaction time. In-situ calcination treatment at 250 °C in air flow was carried out for 1 h after 20-h reaction. The catalytic activity was recovered by calcination treatment. Therefore, deactivation of the catalyst was not due to aggregation of gold NPs. Fig. 5(b) and (c) show the distribution of the diameters of gold particles of Au/Nb₂O₅(HT) catalysts prepared by the DR and DR methods after the CO oxidation. The diameters of gold particles of catalysts after the reaction were almost no change compared to that of the fresh catalysts (Fig. 3). The active lattice oxygen in the perimeter of

gold NPs could be recovered by calcination in air.

Fig. 6 shows NH₃-TPD spectra of Nb₂O₅(HT) and Au/Nb₂O₅(HT) catalysts prepared by the DP and DR methods. The temperatures of preheat-treatment under He (50 mL min⁻¹) were 300 °C for the Nb₂O₅(HT) catalyst and 250 °C for the Au/Nb₂O₅(HT) catalyst. A broad desorption peak of NH₃ was observed for Nb₂O₅(HT), and its peak temperature was

Fig. 6. NH₃-TPD spectra of Nb₂O₅(HT) (a) and Au/Nb₂O₅(HT) catalysts prepared by the DP (b) and DR (c) methods.

about 230 °C. The amount of absorbed NH_3 was 0.48 mmol g^{-1} . The shapes of desorption peaks for $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ catalysts prepared by the DP and DR methods were similar to those for $\text{Nb}_2\text{O}_5(\text{HT})$. The amounts of absorbed NH_3 were 0.39 mmol g^{-1} for the $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ catalyst prepared by the DP method and 0.30 mmol g^{-1} for the catalyst prepared by the DR method. More than 64% of the acid sites were functioning to adsorb NH_3 after the deposition of gold NPs. NH_3 -TPD measurement showed that acid sites existed on the surface of the $\text{Au}/\text{Nb}_2\text{O}_5$ catalyst even after deposition of gold NPs.

3.4. Optimization of the preparation conditions for $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ and unique contact structure of gold NPs

$\text{Au}/\text{Nb}_2\text{O}_5$ catalysts were prepared by the DP and DR methods with changes in the preparation conditions. The preparation amount of gold was 1 wt% for all catalysts. Table 3 shows the effects of the conditions on the activity for CO oxidation and on the diameters of gold particles. Crystalline diameter of gold was calculated by using the Scherrer equation from the XRD pattern, and mean diameters of gold particles and their distribution were estimated by TEM observations.

In the DP method, entry 9 (Table 3) is a typical condition for preparation of a gold catalyst by using HAuCl_4 as a precursor; however, this condition was not effective for the deposition of gold (Au loading 0.18 wt%). The mean diameter of the gold NPs was 7.5 nm with a large distribution (SD, 5.9 nm), and $T_{1/2}$ was 262 °C. $\text{Au}(\text{OH})_4^-$ species were formed from the HAuCl_4 precursor in the precursor solution at pH 9 [21] and could not interact with niobium oxide, of which the isoelectric point of its surface is estimated to be 2.8 [22]. The use of $\text{Au}(\text{en})_2\text{Cl}_3$, which forms the $\text{Au}(\text{en})_2^{3+}$ species in the precursor solution, enhanced the amount of gold loading and the catalytic activity (entry 1). The amount of gold for the catalyst obtained was 0.81 wt% and $T_{1/2}$ was 85 °C with mean diameter of gold NPs of 5.0 nm as described above.

In the DR method, HAuCl_4 was used as a precursor for entry 10 (Table 3) and $T_{1/2}$ for the sample obtained was 110 °C. The amount of gold for the catalyst obtained was 0.26 wt%; however, small gold particles (MD, 4.3 nm; SD, 1.1 nm) were deposited with a relatively large population. TOF based on all Au atoms at 20 °C was 0.010 s^{-1} , which is higher than that of the

Fig. 7. TEM images (a, b) and HAADF-STEM images (c, d) of the $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ catalyst prepared by the DR method using the HAuCl_4 precursor.

catalyst prepared by using the $\text{Au}(\text{en})_2\text{Cl}_3$ precursor (entry 5; TOF, 0.0051 s^{-1}). TEM observation of $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ catalyst prepared by using the HAuCl_4 precursor solution showed that gold NPs were deposited on the basal planes of the rod-type $\text{Nb}_2\text{O}_5(\text{HT})$ support (Fig. 7). The $\text{Nb}_2\text{O}_5(\text{HT})$ catalyst obtained by the hydrothermal method from ammonium niobium oxalate shows a layered-type structure, in which NbO_6 octahedra were corner-sharing in the c -direction, and consists of NbO_6 octahedra, NbO_7 and a 7-membered ring in the a - b plane, indicating the formation of a high-dimensional structure [19]. Strong Brönsted acidity based on the basal planes has been reported. Kundu et al. [23] suggested that the differences in surface energies owing to the polar character of the $\{0001\}$ facets of ZnO resulted in a preferential reduction of Au on the basal planes. These kinds of structural differences would affect the interaction between $\text{Au}(\text{OH})_4^-$ species and the surface of Nb_2O_5 , and Au^{3+} was reduced by NaBH_4 to form NPs on the basal planes of the rod.

Table 3

CO oxidation over $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts prepared by the DP and DR method.^a

Entry	Method	Precursor	Support	pH ^b (reagent)	Au loading ^c / wt%	$T_{1/2}$ ^d / °C	TOF ^e / $\times 10^3 \text{ mol}(\text{CO}) \text{ mol}(\text{Au})^{-1} \text{ s}^{-1}$	Crystalline diameter ^f / nm	Particle diameter ^g / nm
1	DP	$\text{Au}(\text{en})_2\text{Cl}_3$	$\text{Nb}_2\text{O}_5(\text{HT})$	9(NaOH) ^h	0.81	85	1.9	3.8	5.0 ± 2.4
8	DP	$\text{Au}(\text{en})_2\text{Cl}_3$	$\text{Nb}_2\text{O}_5(\text{HT})$	9(NaOH)	0.79	108	1.6	5.6	5.2 ± 2.9
9	DP	HAuCl_4	$\text{Nb}_2\text{O}_5(\text{HT})$	9(NaOH)	0.18	262	0.0	—	7.5 ± 5.9
5	DR	$\text{Au}(\text{en})_2\text{Cl}_3$	$\text{Nb}_2\text{O}_5(\text{HT})$	9(NaOH)	0.93	73	5.1	4.9	4.9 ± 1.4
10	DR	HAuCl_4	$\text{Nb}_2\text{O}_5(\text{HT})$	9(NaOH)	0.26	110	10	—	4.3 ± 1.1
11	DR	$\text{Au}(\text{en})_2\text{Cl}_3$	$\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ⁱ	9(NaOH)	0.76	194	0.9	19	—
12	DR	$\text{Au}(\text{en})_2\text{Cl}_3$	Nb_2O_5 ⁱ	9(NaOH)	1.00	315	0.0	44	—
13	DR	HAuCl_4	$\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ⁱ	9(NaOH)	0.08	227	—	—	—
14	DR	HAuCl_4	Nb_2O_5 ⁱ	9(NaOH)	0.02		(7% at 280 °C) ^j	—	—

^a Catalyst 0.15 g, flow rate 50 mL min^{-1} (1 vol% CO/air). ^b pH value of the precursor solution. ^c Determined by AAS. ^d Temperature for 50% conversion.

^e Based on all Au atoms at 20 °C. ^f Calculated by the Scherrer equation from the XRD pattern. ^g Measured by TEM. ^h Catalyst was dried in a vacuum condition at room temperature. ⁱ Commercially available niobium oxide. ^j CO conversion.

Fig. 8. Schematic representation of the deposition of gold NPs on $\text{Nb}_2\text{O}_5(\text{HT})$ by different deposition methods.

The effects of supports were compared by using a commercially available niobium catalyst (entries 11–14). The catalytic activities of gold supported on commercially available $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($\text{Au}/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and Nb_2O_5 ($\text{Au}/\text{Nb}_2\text{O}_5$) were less than the catalytic activity of $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$. The value of $T_{1/2}$ was 194 °C for $\text{Au}/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and conversion was 29% at 250 °C for $\text{Au}/\text{Nb}_2\text{O}_5$ by using $\text{Au}(\text{en})_2\text{Cl}_3$ precursor. These activities are similar to those of the catalyst prepared by the DP method.

The deposition methods in the liquid phase are summarized schematically in Fig. 8. The use of the $\text{Au}(\text{en})_2\text{Cl}_3$ precursor was effective for the deposition of gold NPs on $\text{Nb}_2\text{O}_5(\text{HT})$ by both the DP and DR methods. The use of the HAuCl_4 precursor was not effective for the deposition of gold by the DP method; however, in the DR method, gold NPs were deposited on basal planes of rod-type $\text{Nb}_2\text{O}_5(\text{HT})$ particles. Because Brönsted acid sites are located at the basal planes of $\text{Nb}_2\text{O}_5(\text{HT})$, utilization of the combination reaction of the a - b plane of $\text{Nb}_2\text{O}_5(\text{HT})$ with gold NPs will be expanded in the future to many reactions.

4. Conclusions

Layered-type $\text{Nb}_2\text{O}_5(\text{HT})$, hydrothermally synthesized Nb_2O_5 , and commercially available Nb_2O_5 and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ were used as supports for the preparation of 1 wt% $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts. The $\text{Nb}_2\text{O}_5(\text{HT})$ sample was inactive for CO oxidation; however, the catalytic activity was significantly enhanced by the deposition of gold NPs. Moreover, the catalytic activity of

$\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ was much higher than these of the catalysts prepared from $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and Nb_2O_5 . The $\text{Nb}_2\text{O}_5(\text{HT})$ sample was effective as a support because of its large surface area.

NPGCs supported on $\text{Nb}_2\text{O}_5(\text{HT})$ were prepared by different deposition methods. The DP method, DR method, DP-urea method and one-pot method were used to prepare $\text{Au}/\text{Nb}_2\text{O}_5$ catalysts. Conditions for preparation were optimized in the DP and DR methods. The use of $\text{Au}(\text{en})_2\text{Cl}_3$ is suitable as a gold precursor for Nb_2O_5 in both deposition methods. The mean diameters of gold particles were 5.0 nm (SD, 2.4 nm) for $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ prepared by the DP method and 4.9 nm (SD, 1.4 nm) for $\text{Au}/\text{Nb}_2\text{O}_5(\text{HT})$ prepared by the DR method in the optimized conditions. In the case of the DR method, gold nanoparticles (MD, 4.3 nm; SD, 1.1 nm) were deposited on the basal plane of $\text{Nb}_2\text{O}_5(\text{HT})$. The activity of gold NPs on the basal plane of $\text{Nb}_2\text{O}_5(\text{HT})$ was very high, but improvement is still needed to increase the amount of gold loading.

NH_3 -TPD measurement showed that acid sites existed on the surface of the $\text{Au}/\text{Nb}_2\text{O}_5$ catalyst after deposition of gold NPs. Therefore, application of the $\text{Au}/\text{Nb}_2\text{O}_5$ catalyst can be expanded in the future to many reactions by utilization of the combination of acidic sites and oxidation reaction sites.

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Graphical Abstract

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Preparation of gold nanoparticles supported on Nb_2O_5 by deposition precipitation and deposition reduction methods and their catalytic activity for CO oxidation

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Nanoparticle gold catalysts supported on layered-type niobium oxide (1 wt% $\text{Au}/\text{Nb}_2\text{O}_5$ for CO oxidation) were prepared by the deposition precipitation method and deposition reduction method.

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沉积-沉淀法和沉积-还原法制备Nb₂O₅负载的金纳米粒子及其催化CO氧化活性

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摘要: 采用不同的沉积法制备了氧化铌(Nb₂O₅)负载的金纳米粒子催化剂, 即沉积-沉淀(DP)法、尿素辅助的DP法、沉积-还原(DR)法和一步法制备了1 wt% Au/Nb₂O₅催化剂。在众多类型Nb₂O₅ (包括商业Nb₂O₅)中, 采用水热法制备的层间型Nb₂O₅ (Nb₂O₅(HT))最适合用作载体。结果表明, 较大比表面积的Nb₂O₅(HT)使得金以纳米颗粒形式分散于其上。在优化的条件下, 以DP和DR法沉积于Nb₂O₅(HT)上的金纳米粒子平均粒径为5 nm。采用DR法制备的Au/Nb₂O₅(HT)催化剂上CO转化率为50%时的温度为73 °C。不沉积金的条件下, 即使在250 °C, Nb₂O₅(HT)对CO氧化反应也没有催化活性。因此, 金的沉积对活性的促进作用非常明显。该简易Au/Nb₂O₅催化剂将金催化剂的类型扩展到酸性载体, 这将增加新的应用。

关键词: 金纳米粒子; 氧化铌; 固体酸; CO氧化; 多相催化剂

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