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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·nH₂O) 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 NbO₆ octahedra, NbO₇ 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 Nb₂O₅(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 Nb₂O₅(HT) has a large surface area exceeding 200 m² g⁻¹. Nb₂O₅ is classified as an n-type semiconductor and has a redox property, indicating that Nb₂O₅ has the possibility of showing high catalytic activity as a support of an NPGC if gold NPs are deposited on Nb₂O₅.

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% Au/Nb₂O₅ 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 Nb₂O₅ supports on catalytic activity of the Au/Nb₂O₅ 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 (NH₄[NbO(C₂O₄)₂(H₂O)₂]*n*H₂O, Aldrich) and was denoted as Nb₂O₅(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 Nb₂O₅ (Wako) and Nb₂O₅·*n*H₂O (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. Au(en)₂Cl₃ or HAuCl₄ (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, NaBH₄ 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 Au/Nb₂O₅ 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 (Au/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). H₂O 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 (TOF, μmol_(CO) μmol_(Au)⁻¹ 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 Cu-K_α 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 (NH₃-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 Nb₂O₅ supports

Different types of Nb₂O₅ supports were used to prepare 1 wt% Au/Nb₂O₅ catalysts, and their effects on catalytic activity for CO oxidation were examined. The layered-type Nb₂O₅(HT),

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