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Oxidation activity of Au nanoparticles on aerogel supports

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Abstract. We have prepared titania aerogel and titania-coated silica aerogel incorporating thiol-capped Au nanoparticles. Both composite materials showed high CO oxidation activity after they were calcined at 673 K. Compositional and morphological changes driven by calcination were evaluated with thermogravimetry and X-ray diffractometry. From the results, it was suggested that the nanoparticles transformed from a faulted to a near-regular FCC structure presumably in concert with the formation of firm contacts between the nanoparticles and the gel substrates. While the diameters of the Au particles in the titania aerogel considerably increased upon calcination, those in the titania-coated silica aerogel were almost unchanged. As a consequence, the latter composite aerogel showed higher activity for oxidation of CO.

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1 Introduction

Despite the incomparable inertness in its bulk solid state, gold shows surprisingly high catalytic activities even at temperatures below 0 °C when supported as Au nanoparticles (AuNPs) on metal oxide surfaces with diameters less than ≈5 nm [1]. The gold catalyst has been attracting much attention recently because of its many potential applications such as epoxidation of propylene [2] and the water-gas-shift reaction [3].

From the view point of cluster science, size dependence of the oxidation activity is an attractive topic. This theme is studied mainly by using model catalysts such as free clusters [4], deposited clusters [5] and aggregated atoms on oxide substrates [6]. However, in most cases, a large pressure gap exists between the model catalyst and actual catalyst systems. As an alternative approach, we are trying to preform monodisperse AuNPs as passivated colloids in liquid phase and dispersed in a porous substrate. So far, we have reported the fabrication of titania aerogel and titania-coated silica aerogels incorporating AuNPs by adding thiol-capped AuNPs to wet-gels [7], together with their activity for CO oxidation [8].

We will report herein the fabrication, compositional as well as structural analyses of the catalysts and their catalytic activities. it was suggested that the nanoparticles transformed from a faulted to a near-regular FCC structure presumably in concert with the formation of firm contacts between the nanoparticles and the gel substrates. While the diameters of the AuNPs in the titania aerogel considerably increased upon calcination, those in the titania-coated silica aerogel were almost unchanged. As a consequence, the latter composite aerogel showed higher activity for oxidation of CO.

2 Experimental

Details of sample preparation have been previously reported [7,8], and thus are described here briefly. Titania wet-gel was prepared according to the method of Dagan and Tomkiewics [9]. Titania-coated silica (Ti/Si) wet-gel was prepared as follows [10]. Silica wet-gel was first synthesized by the hydrolysis of silicon tetramethoxide (MS39) or silicon methoxide oligomer (MS51, tetramer in average) in methanol using ammonia catalyst. For titania coating, the pore-filling solvent of the silica wet-gel was exchanged to toluene and then the gel was soaked for 24 hours in the toluene solution of titanium tetraisopropoxide (TTIP, 5 mol%) [11]. Dodecanethiol-capped AuNPs ($Au_x(DDT)_y$) prepared by the Brust method [12] were adsorbed on the wet-gels in toluene or tetrahydrofuran so that composite gels incorporating AuNPs were formed [7]. The composite wet-gels were dried using supercritical CO_2. The resulting composites were calcined at 673 K for 4 hours under air flow (flow rate: 2 ml min^{-1}).

Transmission electron microscope (TEM) images were taken on JOEL 2010 with LaB_6 filament operated at

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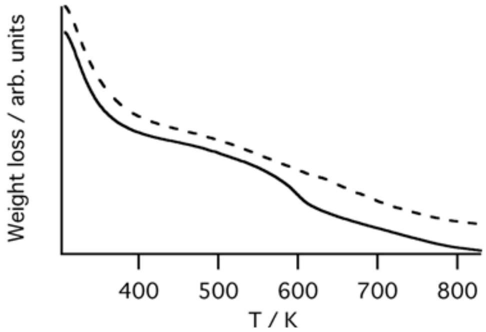

Fig. 1. TG curves for Ti/Si aerogel (dotted line) and Ti/Si aerogel incorporating $\mathrm{Au}_x(\mathrm{DDT})_y$ particles (solid line). Both gels were prepared from MS39 as the starting monomer. The curves are vertically shifted with each other for clarity.

200 kV. For the TEM observations, toluene solution of $\mathrm{Au}_x(\mathrm{DDT})_y$ or ethanol dispersion of ground nanocomposite aerogel was dried on carbon films. X-ray fluorescence (XRF) and diffraction (XRD) measurements were performed using Shimadzu lab center XRF-1700 and Rigaku RINT 2000/PC, respectively. Brunauer-Emmett-Teller (BET) surface areas and pore size distributions of the composite gels were obtained from N_2 adsorption measurements using Coulter OMUNISORP 360. Thermogravimetry (TG) and differential thermal analysis (DTA) were done using Seiko Instrument Inc. SSC/5200.

Catalytic activity measurements were carried out by using a fixed-bed flow reactor. A ground aerogel sample (100 mg) was placed on a glass wool plug in a quartz tube with an inner diameter of 5 mm. Reactant gas (1 vol% CO in air) was passed through the catalytic bed at a flow rate of 33 ml min^{-1} (Space velocity = 20000 $\mathrm{ml\,h^{-1}\,g\text{-}cat.^{-1}}$). Prior to each experiment, the catalysts were treated in air at 523 K for 30 min.

3 Results and discussion

3.1 Effects of calcination

Calcination is an important step in the preparation of supported Au catalysts since firm contacts between the AuNPs and supports is indispensable for oxidation of CO. Moreover, since, in the present experiments, the starting AuNPs contain thiol molecules, removal of thiols or poisoning sulfate which might be formed in the combustion of thiols [13] should be accomplished by calcination. Thus, to check the validity of the calcination under the present conditions, we evaluated weight and morphology changes driven by the calcination.

Figure 1 shows the temperature dependence of the weight of Ti/Si aerogels with or without $\mathrm{Au}_x(\mathrm{DDT})_y$ measured under atmospheric air. Temperature was raised at the rate of 10 K/min. A significant weight loss, due to the vaporization of adsorbed water, was observed for both samples up to ≈400 K. Further increase of temperature lead to a gradual decrease in the weight of the Ti/Si aerogel which can be attributed to the promotion of condensation reactions with dehydration in the gel [14]. The Ti/Si gel incorporating $\mathrm{Au}_x(\mathrm{DDT})_y$ showed the same trend in the weight loss except for the decrease from ≈560 to ≈610 K. Since a significant decrease in the amount of sulfur was confirmed by a XRF measurement and a exthothermic peak was observed in the corresponding DTA curve, the decrease is probably due to the combustion of thiols.

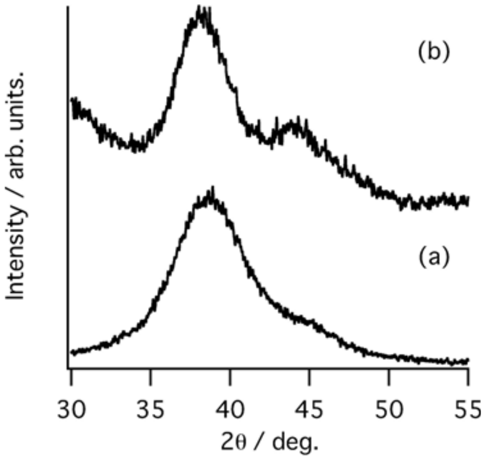

Fig. 2. X-ray diffractograms for $\mathrm{Au}_x(\mathrm{DDT})_y$ particles (curve (a)) and Ti/Si aerogel (from MS39) incorporating $\mathrm{Au}_x(\mathrm{DDT})_y$ particles (curve (b)). The curves are vertically shifted with each other for clarity.

In Figure 2, X-ray diffractograms of $\mathrm{Au}_x(\mathrm{DDT})_y$ (average diameter 3.1 nm, curve (a)) and the Ti/Si aerogel incorporating AuNPs after calcination (curve (b)) are shown. Diffraction peaks corresponding to the bulk (111) and (200) peaks were observed at around 38 and 44°, respectively. Remarkably, the intensity ratio of (111) and (200) peaks ($R_{200/111} = I(200)/I(111)$) for $\mathrm{Au}_x(\mathrm{DDT})_y$ ($R_{200/111} = 0.21$) was much smaller than that for the bulk Au ($R_{200/111} = 0.52$). Whetten et al. reported that the diffraction pattern for the thiol-capped AuNP with a mass of 93 kDa is well explained by that of twined-truncated octahedron (t-TO) [15]. The $R_{200/111}$ value for $\mathrm{Au}_x(\mathrm{DDT})_y$ in Figure 2 seems to be very similar to that for the 93 kDa particle in reference [15]. The diffraction pattern for AuNPs in the calcined gel (curve (b)) was modulated by a broad diffraction peak of the amorphous Ti/Si gel: no diffraction peaks corresponding to anatase or rutile crystals were observed. A calculation including the broad background peak gave a $R_{200/111}$ value of 0.41 for the supported AuNPs. Since this value is much closer to that for the bulk gold, it is considered that AuNPs transformed from a faulted to a near-regular FCC form upon calcination. Epitaxial growth of hemispherical AuNPs on a substrate has often been observed for supported Au catalysts by TEM [1]. Thus, AuNPs in the gels are expected to be catalytically activated by the calcination under the present condition (673 K and 4 h).

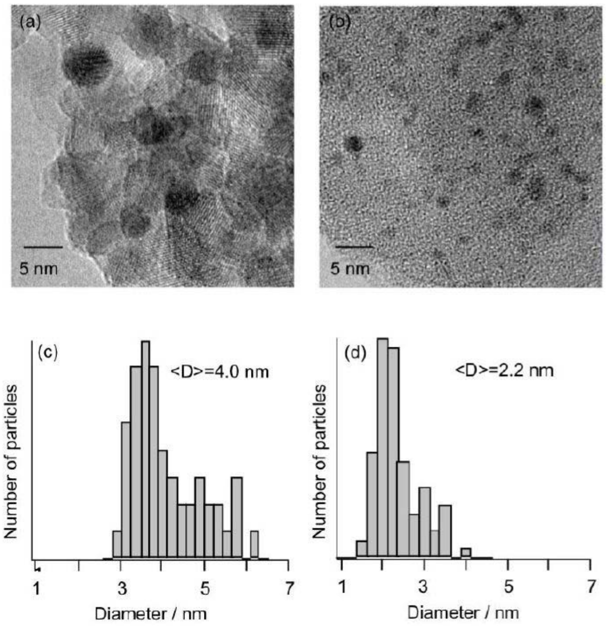

Fig. 3. TEM images and diameter distributions of AuNPs in titania (a, c) and Ti/Si (b, d) composite aerogels. The Ti/Si gel was prepared from MS51 as the starting monomer. The distributions were obtained by measuring the diameters of 200∼300 particles.

3.2 Structures of catalysts

Figure 3 shows the transmission electron microscope (TEM) images and the diameter distributions of Au nanoparticles in titania (a, c) and Ti/Si (b, d) composite aerogels. Before calcination, the titania support had an amorphous structure with a large surface area (650 $m^2 g^{-1}$). However, after the heat treatment, it was found to consist of anatase microcrystals with diameters of 5∼10 nm. The average diameter of AuNPs on this support (4.0 nm, Fig. 3c) was much larger than that of the original particles (2.1 nm). Since the particle size before calcination was similar to that of the original $Au_x(DDT)_y$, the diffusion and coagulation of the AuNPs may have been triggered by the abrupt morphology change of the titania support during the calcination. These results are consistent with those reported by Pietron et al. [16].

In contrast, AuNPs on the Ti/Si composite gel retained their original diameters (2.2 nm, Fig. 3d). It is also noteworthy that the gel supports had an amorphous structure as they had before the calcination: no diffraction peaks from anatase or rutile crystals were observed by XRD as described above. Because the present composites contain no less than 25 mol% of titania, the formation of titania islands on the silica surface would result in the emergence of the anatase structure, as in the pure titania gel. No indication of anatase crystals suggests that silica is covered with thin layers of titania and the morphological changes of the titania layers are inhibited by the firm Si-O-Ti bondings [11], as pure silica aerogel does not show a structural change by the heat treatment.

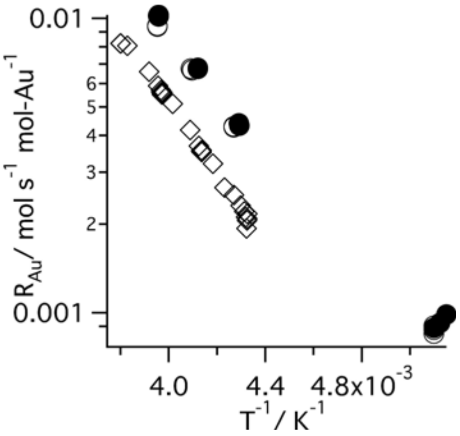

Fig. 4. Conversion rate of CO per Au atom vs. inverse temperature for titania (◇) and Ti/Si (prepared from (●) MS51, (○) MS39) composite aerogels.

Table 1. Compositional and structural parameters as well as CO oxidation activities of the titania and titania-coated silica composite aerogels incorporating AuNPs.

Sample	Au load [wt%]	D_{Au} [nm]	S_{BET} [$m^2 g^{-1}$]	R_{Au} (273 K) [$mol\,s^{-1}$ mol-Au^{-1}]
Au-Titania	5.9	4.0	190	1.3×10^{-2}
Au-Ti/Si (MS51)	4.4	2.2	644	2.1×10^{-2}
Au-Ti/Si (MS39)	4.9	2.5	559	1.9×10^{-2}

3.3 Catalytic activity

Figure 4 shows the conversion rate of CO per Au atom (R_{Au}) over the titania and the Ti/Si silica composite aerogels. It clearly shows that the CO conversion activity is higher for the Ti/Si composite aerogels. Table 1 summarizes the compositional and structural parameters as well as CO oxidation activities of the samples. The structural parameters including the diameters of the AuNPs were very different between the titania and the Ti/Si composite gels: the former has the larger AuNP diameters with the much smaller surface area (S_{BET}). This is due to the structural change of the titania gel (amorphous to anatase form) caused by the heat treatment. The catalytic activity values per Au content (R_{Au}) for the Ti/Si composites were higher than that for the pure titania composite. This can be explained by the conservation of an amorphous structure in the composite, without which the nanoparticles would coagulate with one another since larger AuNPs show less activities [1].

From the view point of catalyst preparation, the present results for the Ti/Si composites are important by the following reasons: (1) the composite gels have a very large surface area even after heat treatment (≈600 $m^2 g^{-1}$) at 673 K; (2) the diameters of the AuNPs do not significantly change upon calcination; (3) the size and the amount of AuNPs in the composite can be independently changed.

The dependence of reactivity on the size of the AuNPs is a major issue to be surveyed in detail for understanding the catalytic activity of supported Au catalysts. By using the Ti/Si gel support, one can easily control the size of the metal nanoparticles in the resultant composite catalyst by changing the size of the original nanoparticles, with a fixed loading amount of gold. The size of thiol-capped AuNPs can be controlled by changing synthetic conditions such as reaction time and temperature [17] or capping molecules [18]. Experiments on the particle size dependence of CO oxidation activity are now under progress.

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