doi:10.1246/cl.2012.337

Spontaneous Dispersion of Gold Nanoparticles Loaded on USY Zeolites as Analyzed by XAFS, XRD, and TEM

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Structural changes in the gold particles of Au-loaded ultrastable Y (USY) zeolite were analyzed by X-ray absorption fine structure, X-ray diffraction, and transmission electron microscopy. Au particles undergo spontaneous dispersion on the USY support under H_2 atmosphere at a temperature of 773 K to give Au particles with an average diameter of 1.8 nm and narrow size distribution.

Since the pioneering work by Haruta, efforts have been increasingly devoted to the development of supported Au catalysts.[1,2] The interest in these catalysts is fueled by their unique catalytic performance in various reactions.[3,4] The catalytic performance of Au particles is sensitive to the particle size, and consequently, the regulation of the size of Au particles is an important consideration for their use in catalytic reactions.[5] In particular, it has been reported that high catalytic performance is obtained with Au particles when the size of the particles is less than several nanometers.[1] Prior reports focus primarily on the use of reducible metal oxides such as TiO_2 and Fe_2O_3 as supports for Au. Although the number of such studies remains limited, several groups have analyzed the use of zeolites as supports for Au. For instance, Au loaded on Y-type zeolite has been applied to CO oxidation,[6] NO reduction by H_2 has been performed over Au^0 or Au(I) loaded on Na-Y zeolite,[7] and the formation of electron-deficient gold particles inside H-Y cavities has been observed.[8] We have also utilized H-Y zeolites as a support for Au.[9,10] Zeolites are promising supports for metals because the presence of strong acid sites in these materials promotes high dispersion of metal particles. In fact, metal clusters of Pd and Pt with high dispersion were obtained on zeolites having Brønsted acid sites.[11,12] Ultrastable Y (USY) zeolites contain strong acid sites[13] (ca. 150 kJ mol^{-1}) and also exhibit high thermal stability. These acidic sites may be exploited for interaction with Au, and their thermal stability makes USY zeolites attractive for use as Au catalyst supports for high-temperature applications.

In the present study, USY zeolite is employed as a support for Au. Au/USY zeolite was thermally treated in an atmosphere of H_2 at temperatures from 353 to 773 K. The H_2 reduction for the preparation of Au catalysts has also been reported by Haruta.[14] Changes in the Au particle size were analyzed by X-ray absorption fine structure (XAFS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The purpose of this study is to establish a new method for the preparation of Au nanoclusters through the spontaneous dispersion of Au. The data reveal an unexpected behavior of Au in which severely aggregated Au^0 particles are spontaneously dispersed onto USY supports to give nanometer-sized Au^0 particles with narrow size distribution.

Au was loaded onto NH_4-type USY zeolite (Tosoh, HSZ-341NHA) using $HAuCl_4 \cdot 4H_2O$ (Wako Chemical Co.) as the precursor. Specifically, USY was immersed in an aqueous solution of $HAuCl_4$ (7.6×10^{-4} mol L^{-1}), and the slurry was heated to 343 K for 1 h with constant magnetic agitation. The Au-loaded USY zeolite was filtered and washed with deionized water, followed by drying in an oven at 323 K. The typical loading of Au was 3 wt %. Thus obtained Au/USY was treated with a stream of 6% H_2 diluted with Ar (30 mL min^{-1}) at 353–773 K for 30 min. Temperature ramping rate was 5 K min^{-1}. Herein, the Au/USY samples treated with 6% H_2 at 473 and 773 K are denoted as Au/USY-473 K and Au/USY-773 K, respectively.

TEM images were acquired by means of a HITACHI H-9000UHR microscope with an acceleration voltage of 300 kV. Synchrotron radiation experiments (XAFS) were performed at the BL01B1 station with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2011A1106). A Si(111) single crystal was used to obtain a monochromatic X-ray beam. The measurement was performed in the quick mode at room temperature. For the collection of Au L_3-edge data, ion chambers filled with N_2 and N_2(50%)/Ar(50%) were used for I_0 and I, respectively. The energy was calibrated using a Au foil. The data were analyzed using the REX2000 Ver. 2.5.9 program (Rigaku Co.). Fourier transform of $k^3\chi(k)$ data was performed in a k range of 30–160 nm^{-1} for the analysis of the Au L_3-edge EXAFS spectra. The crystal structure was analyzed by XRD under ambient conditions using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation.

In the preparation of Au/USY, Au was readily loaded onto NH_4-USY by employing $HAuCl_4$ as the Au precursor. The initially yellow aqueous solution of $HAuCl_4$ was decolorized, while the zeolites became pale orange within 1 h after the temperature of the solution reached 343 K. This color change is indicative of the loading of Au onto USY. Interestingly, in marked contrast to the NH_4-type USY, Au was not deposited onto either H-USY or Na-Y using an analogous method.

Figure 1a shows the Fourier transforms of Au/USY treated with 6% H_2 at various temperatures (phase shift uncorrected). A peak appeared at 0.17 nm in the untreated sample (as received), which by comparison with the data for Au_2O_3 could be assigned to the Au–O bond. It is plausible that aggregated Au_2O_3 was deposited onto USY, taking into account the fact that the spectrum of as-received Au/USY was similar to that of Au_2O_3 (standard sample) over the entire spectral region. A reduction in the intensity of the Au–O peak accompanied H_2 treatment temperature elevation, and eventually, the peak disappeared at 473 K. Concomitantly, a new peak appeared at 0.27 nm, which was straightforwardly assignable to the nearest neighbor Au–Au

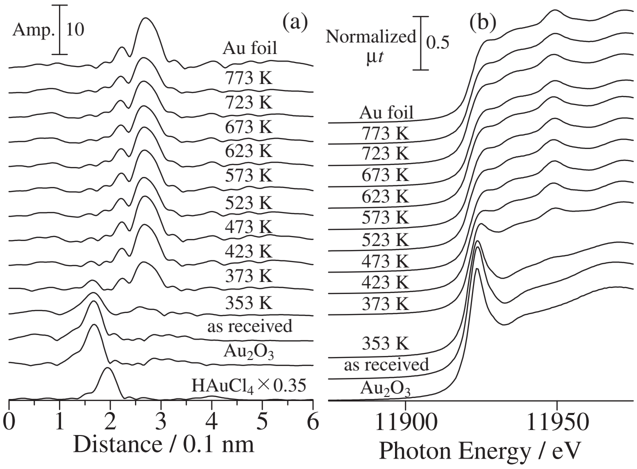

Figure 1. Au L_3-edge EXAFS (a) and XANES (b) of 3 wt%-Au/USY treated at different temperatures under a 6% H_2 atmosphere and reference samples. Data collection was carried out at room temperature.

bond of Au metal based on comparison with the spectrum of Au foil. The complete disappearance of the Au–O peak indicates the formation of Au^0 at 473 K via H_2 reduction. Formation of Au^0 was confirmed from the XANES regions; the shape of the XANES profile became markedly similar to that of Au foil at 473 K, as shown in Figure 1b. At temperatures above 473 K, the intensity of the EXAFS peak corresponding to the Au–Au bond decreased slightly (Figure 1a). This slight change is suggestive of a decrease in the size of the Au particles, given that the particle size is reflected in the peak intensity. The coordination numbers (CNs) of the atoms in the nearest-neighbor Au–Au bond were measured by curve fitting analysis. The CNs of the Au/USY samples treated at 473 and 773 K were calculated to be 11.8 ± 1.6 and 9.6 ± 1.4, respectively. The change in CNs of nearest-neighbor Au–Au atoms corroborates the suggested decrease in the size of the Au particles at higher treatment temperature. However, EXAFS analysis is rather insensitive for the determination of CNs when the particle size of the metal is larger than several nanometers. Consequently, Au/USY was analyzed by XRD, which is sensitive to changes in the size of Au particles larger than several nanometers. Figure 2 shows the XRD patterns of the 3 and 5 wt% Au/USY samples treated at various temperatures. The peaks that appear at $2\theta = 38.2$ and 44.4° are assignable to the reflections from the (111) and (200) planes of Au^0, respectively. Low intensity diffractions due to the USY zeolites appeared at 38.1 and 44.2°, which overlapped with the diffractions from Au^0. The intensity of the reflections from the (111) and (200) planes increased with increasing treatment temperature, from room temperature to 473 K, for 3 wt% H_2 treated samples (Figure 2a). This change is attributed to formation of Au^0 as confirmed by Au L_3-edge XAFS (EXAFS and XANES). On further increasing the treatment temperature, the intensity of these reflections decreased, accompanied by peak broadening. Particularly, marked reduction of the peaks was observed at 573 K. This change indicated that the aggregated Au^0 particles were dispersed to produce smaller Au^0 particles when the treatment temperature was increased from 473 to 773 K given that the broadness of the diffraction peaks is dependent on the size of the metal particles. The XRD patterns of 5 wt%-Au-loaded USY (Figure 2b) showed a similar marked reduction of the Au(111) and Au(200) peaks indicative of dispersion of the Au^0 particles. However, the reduction in peak intensity was observed at 673 K in the 5 wt% sample, which was 100 K higher than that of 3 wt%-Au/USY, meaning that the extent of Au loading affected the behavior of Au. Figure 3a shows XRD patterns of 3 wt%-Au/USY treated under different atmosphere at 773 K. Steep diffraction peaks appeared in the samples calcined in air or Ar. Addition of 0.5% H_2 resulted in the formation of the dispersed Au as confirmed from the broadening of the diffraction peaks due to the metal Au. Figure 3b gives XRD patterns of the 3 wt%-Au/USY treated at 773 K for 10 min–10 h under atmosphere of 6% H_2. Difference in the diffraction patterns in these samples was not observed, implying that the dispersion of Au took place immediately after the temperature reached 773 K.

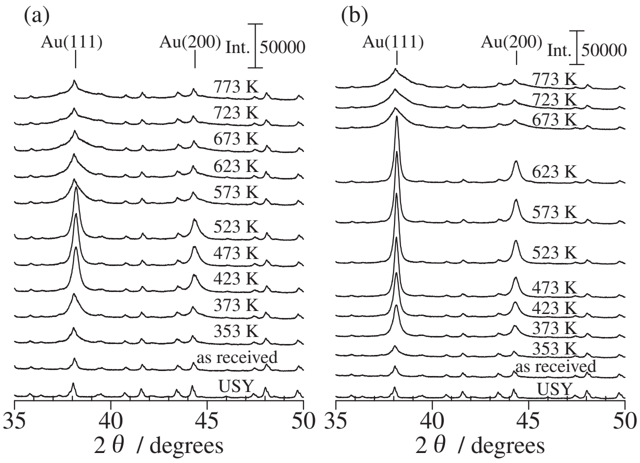

Figure 2. XRD patterns of Au/USY treated at different temperatures under a 6% H_2 atmosphere: (a) 3 and (b) 5 wt%.

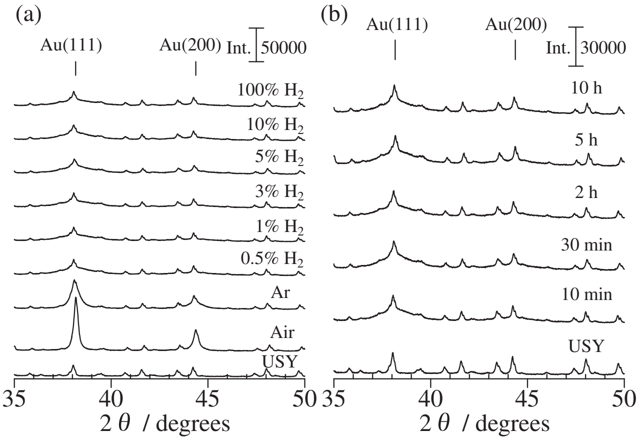

Figure 3. XRD patterns of Au/USY treated at 773 K (a) in different atmosphere for 0.5 h, (b) in 6% H_2 for 10 min–10 h.

Finally, direct observation of Au/USY by TEM analysis was executed in order to observe the Au^0 particles. The TEM images of Au/USY-473 K and -773 K at a magnification of ×300000 are shown in Figures 4a and 4b, respectively.[15] Large

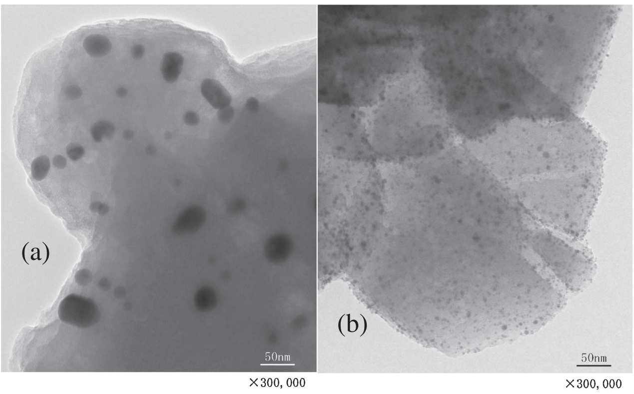

Figure 4. TEM images of (a) Au/USY-473 K and (b) Au/USY-773 K. Loading of Au was 3 wt%.

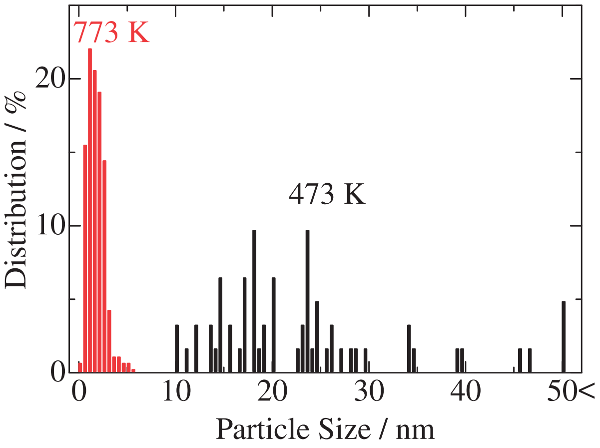

Figure 5. Distribution of Au particles in Au/USY-473 K (black) and Au/USY-773 K (red).

Au^0 particles were observed in the image of Au/USY-473 K (Figure 4a), in which the size of the Au particles was inhomogeneous. Moreover, the shape of the Au particles was nonuniform. In marked contrast to this, and in agreement with the EXAFS and XRD data, the particles of Au^0 in Au/USY-773 K (Figure 4b) were much smaller, and the size distribution appeared to be more homogeneous compared to Au/USY-473 K. Figure 5 shows the particle size distribution of Au^0 determined from the TEM images. The Au^0 particle size ranged from 10 to 150 nm with an average size of 25 nm for Au/USY-473 K. The average size of Au^0 in Au/USY-773 K was calculated to be 1.8 nm, which was 14 times smaller than that of Au/USY-473 K. The distribution of Au^0 particle sizes in Au/USY-773 K ranged from 0.4 and 5.9 nm, which was much narrower compared to that of Au/USY-473 K. The significant difference between Au/USY-473 K and Au/USY-773 K clearly evidences the occurrence of dispersion of Au^0 accompanying elevating treatment temperature. The spontaneous dispersion of Au^0 at 773 K as proved by TEM images coupled with EXAFS and XRD seems to be unusual taking into account the fact that supported metal particles generally undergo sintering to produce aggregates with increasing temperature. Dispersion of Pd and Pt as cations has been observed under an atmosphere of oxygen.[16] We have also reported the spontaneous dispersion of molecule-like PdO on HZSM-5.[17] Unlike these cases, the dispersion of Au^0 onto USY-zeolite support occurred under an atmosphere of H_2 in this instance. Although the origin of the dispersion of Au^0 on USY zeolites has not been fully elucidated at this stage, one hypothesis is that the interaction of Au and H^+ generated as a result of thermal decomposition of NH_4^+ caused the dispersion of Au on the external surface of USY zeolites. This work highlights the possibility of obtaining nanometer-sized metal particles via a simple method and of regulating the size and distribution of Au^0 by variation of the treatment temperature. Therefore, the advantage of this method is the facile preparation of nanometer-sized Au clusters simply by calcination of aggregated one in the atmosphere of H_2. Moreover, the stability of Au/USY at 773 K indicated the possibility for the use of the Au^0 nanoparticle-loaded support catalyst at high temperature.

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