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Formation and Catalysis of Gold Nanoparticles Generated through the Physical Mixing of AuCl(PPh₃) and Oxides

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Abstract AuCl(PPh₃) was mixed with various kinds of inorganic supports with a mortar. Thermal treatment of the mixture resulted in the formation of gold nanoparticles, particularly when NaY zeolite and CeO_2 were employed as the supports for gold. Catalytic performance in the aerobic oxidation of benzyl alcohol was in good correlation with the degree of the dispersion of gold.

Key words gold, nanoparticle, zeolite, alcohol, oxidation

Recently, much attention has been paid to the goldloaded catalysts because gold nanoparticles have been found to exhibit high catalytic activity in various reaction including oxidation of CO and alcohols.¹ Several preparation methods of supported gold catalysts have been developed such as deposition-precipitation,² ion exchange,³ and chemical vapor deposition (CVD).⁴ Among these methods, CVD seems to be one of the most attractive ones because highly dispersed gold nanoparticles (NPs) are feasibly obtained on various supports. As a matter of fact, Au NPs are readily obtained through solid grinding of Me₂Au(acac) and active carbon or metal organic framework.^{4b} The catalysts were applied to the oxidation of alcohols and glucose. Despite the feasibleness of the solid gridding, kinds of gold complexes suitable for CVD are limited. In addition, the gold complexes are unstable in air in many cases. From industrial and environmental points of view, finding of a readily available and stable gold complexe as the precursor of Au NPs is highly desirable. Here, we report that Au NPs are obtained just by mixing of the chloro(triphenylphosphine)gold(I) [AuCl(PPh₃)] and supports, followed by thermal treatment in the atmosphere of hydrogen. The advantage of the AuCl(PPh₃) is that the complex is stable in air, readily available; therefore widely utilized as the precursor for the synthesis of gold(I) complexes⁵ and Au NPs.^{6–8} Among employed supports, we focused on NaY zeolite and CeO₂ as the support for gold in this study.

NaY (Tosoh, HSZ-320NAA), CeO₂ (JRC-CEO-2), SiO₂ (fumed silica, Sigma), Al₂O₃ (JRC-ALO-3), ZrO₂ (JRC-ZRO-6), TiO₂ (JRC-TIO-11), and activated carbon (AC, Wako Co.) were employed as the support of gold. The CeO₂, Al₂O₃, ZrO₂, and TiO₂ supports were reference catalysts supplied from the Catalysis Society of Japan.⁹ Under typical conditions, AuCl(PPh₃) (Aldrich) and supports were ground in a mortar for 0.5 hours. The loading of gold was 3 wt%. The mixture was thermally treated in the stream of Ar, 6% H₂ diluted with Ar or O₂ for 0.5 hours. The flowing rate of gas was fixed at 30 mL min⁻¹. The obtained solid was subjected to the characterization and catalytic reaction.

Figure 1 (a) shows X-ray diffraction (XRD) patterns of gold loaded on different kinds of supports other than zeolites thermally treated at 773 K in 6% H₂. Reflections assignable to the Au(111) and Au(200) appeared at 2θ = 37.8 ° and 44.0°, respectively. It can be seen in the figure that the intensity and broadness of the reflections changes depending on the kind of supports. Namely, sharp reflections appeared on gold loaded on AC and SiO₂. On the other hand, the intensity of these peaks were much smaller over gold loaded on Al₂O₃, TiO₂, ZrO₂, and CeO₂, which had basic character. In particular, the intensity of the diffraction was the smallest and broader in Au/CeO₂, suggesting gold particles were well dispersed on the CeO₂ surface because the broadness of the diffraction could be correlated with the particle size.¹⁰ The possible effect of CeO₂ for the dispersion of Au NPs might be that the vacant sites of CeO₂ played a crucial role for the dispersion of gold as has been evidenced by the DFT analysis.¹¹

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Figure 1 XRD patterns of (a) Au loaded on different kinds of supports other than zeolites. The samples were treated at 773 K for 30 min in a 6% H₂ flow prior to the measurement. (b) Au loaded on zeolites (ZSM-5 and Y zeolite) thermally treated at 773 K under different atmosphere.

Figure 1 (b) shows the XRD patterns of gold mixed with various kinds of zeolites. Intensity of the reflections assignable to the Au(111) and Au(200) planes were the smallest when NaY was employed as the support for gold, although the reflection from Y-type zeolite partially overlapped the region. The XRD patterns of Au/NaY treated in the atmosphere of Ar and O₂ were included in Figure 1 (b). Intensity of the reflections arising from Au(111) and Au(200) planes were smallest when the Au/NaY was thermally treated in the atmosphere of 6% H₂. The fact agrees with the previous studies on Au/USY zeolites prepared in the liquid phase where the Au NPs with diameters of ca. 2 nm were obtained through the thermal treatment in the atmosphere of H_{2} .¹²

In order to monitor the formation process of Au NPs on NaY zeolite, Au L₃-edge EXAFS and FTIR spectra of the Au/NaY were measured (Figure 2). In the EXAFS of the 473 K treated sample the small peak appeared at 0.20 nm together with the large Au–Au bond at 0.26 nm (Figure 2, a). The curve fitting analysis revealed that the small peak could be assigned to the Au-P and Au-Au bonds, respectively, while the Au-Cl bond was not detected (Table S1). On further increase in the treatment temperature, intensity of the peak assignable to the nearest neighboring Au-Au bond increased (0.26 nm, phase shift uncorrected). Intensity of the Au-Au bond of the 673-873 K treated samples almost agreed with that of gold foil implying the formation of gold(0) was almost complete at 673 K. On the other hand, the two peaks assignable to the stretching vibration modes of the benzene ring were observed between 1420 and 1480 cm⁻¹ in the IR spectrum of AuCl(PPh₃) (Figure 2, b). A similar spectrum was observed in the as-prepared sample with physical mixing, although the peak position slightly shifted to the higher wavenumber. Intensity of the two peaks gradually decreased with increase in the temperature and vanished at 773 K. The change suggested that the Ph₃P was completely removed from Au/NaY at 773 K. At the same time, the color of the solid changed from white to red on





Figure 2 (a) Au L_3 -edge EXAFS Fourier transformed and (b) FTIR spectra of 3 wt% Au loaded on NaY treated at different temperatures in the atmosphere of 6% H_2 .

Figure 3 (a) shows the transmission electron microscope (TEM) image of Au/NaY zeolite which was treated in 6% H₂ at 773 K. Formation of Au NPs were seen in the sample with an average diameter of 3.8 nm with narrow distribution of the diameter (Figure 3, c). The TEM image directly shows that the formation of Au NPs is achieved through the use of AuCl(PPh₃) as the gold source. Figure 3 (b) shows the enlarged TEM image of Figure 3 (a). The Au NPs were preferentially deposited at the surface (edge), suggesting the Au NPs were preferentially located on the external surface of NaY zeolite. This may be due to the bulkiness of the AuCl(PPh₃); the Au complex could not enter into the micropore of NaY zeolite when it was vaporized in the course of thermal treatment. In order to obtain insight into the mechanism for the formation of Au NPs, the 473 K treated $AuCl(PPh_3)/NaY$ in 6% H₂ was rinsed with water, followed by filtration. The analysis of the filtrate by inductively coupled plasma revealed the dissolution of Na⁺. The amount of Na⁺ detected in the filtrate was equimolar to that of gold present in Au/NaY, suggesting that the reaction between Cl- in AuCl(PPh₃) and Na⁺ of NaY took place at 473 K. Therefore, it could be assumed that the formation of Au NPs proceeded via the steps given in Equation 1.

Probably, the first step (1) took place at 473 K considering that the temperature was close to the melting point of $AuCl(PPh_3)$ (493 K). In agreement with the assumption, the curve-fitting analysis revealed that the 473 K treated sample could be fitted by the combination of Au–P and Au–Au bond, while the Au–Cl was not detected as described earlier (Table S1). The absence of the Au–Cl bond suggested the formation of Au NPs proceeded after the reaction between



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Figure 3 (a, b) TEM images of Au/NaY thermally treated in 6% H₂ at 773 K; (c) distribution of the diameter of Au NPs.

Cl⁻ of the gold complex and the Na⁺ present on the external surface of zeolite.

Finally, oxidation of benzyl alcohol (BzOH) was carried out over Au/NaY and Au/CeO₂. The reaction was performed at 323 K in the atmosphere of air. Benzaldehyde was obtained as the primary product (selectivity: ca. 90%) together with a small amount of benzyl benzoate and dibenzylether. The possible role of K_2CO_3 might be the suppression of the inhibition caused by the formation of benzoic acid,¹³ because benzoic acid was not detected in the analysis with gas chromatography.

Figure 4 (a) shows the dependence of the conversion of BzOH on the thermal treatment temperature of Au/NaY. The conversion of BzOH reached maximum when the sample was treated at 773 K in 6% H₂. Probably, the highest activity was attained as a result of the completion of the removal of the PPh₃ ligand and the generation of the gold(0)as proved by EXAFS and FTIR spectroscopy. Data on the conversion of BzOH over the Au/NaY treated in the stream of Ar and O₂ are included in the figure. The highest conversion of BzOH over Au/NaY treated in Ar and O2 were much lower than that of Au/NaY treated in 6% H₂. The fact coincided with the data of XRD patterns in that the intensity of the reflections from gold(0) were the smallest when Au/NaY was treated in 6% H₂. We have carried out the reaction over the Au/NaY by varying the concentration of H₂ for the thermal treatment. But the conversion was almost independent of the concentration of H_2 in the range of 6–100%. The effect of H_2 for the formation of Au NPs was not clearly understood at this stage. But one hypothesis was that H_2 promoted the reduction of gold(I) to gold(0) at lower temperature compared to those treated in Ar and O_2 , so that the coalescence of gold(0) was suppressed in the atmosphere of H_2 . Catalytic performance of Au/CeO₂ is displayed in Figure 4 (b). The highest conversion of BzOH was obtained when Au/CeO₂ was treated in 6% H_2 at 773 K in a similar manner to the Au/NaY. Moreover, the activity was higher than those



treated in O₂ and Ar, similarly to the case of Au/NaY zeolite.

Figure 4 Dependence of the conversion of benzyl alcohol on the temperature for thermal treatment of (a) Au/NaY and (b) Au/CeO₂ treated in different atmosphere. *Reagents and conditions*: BzOH (1 mmol), K₂CO₃ (1 mmol), toluene (5 mL), catalyst [1.5×10^{-3} mmol (Au)], 323 K, 30 min, air.

In conclusion, we found that the Au NPs were readily obtained by mixing the AuCl(PPh₃) and various kinds of supports, followed by thermal treatment. Among employed supports, the NaY and CeO₂ seemed to be most promising because high catalytic activity could be obtained in the aerobic oxidation of benzyl alcohol.

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Supporting Information

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