Emergence of hydrogenation catalysis in PVP-stabilized gold superatoms by doping a single heterometal atom

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Abstract: A single M atom (M = Pd and Rh) was successfully doped into gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) as revealed by mass spectrometry. Doping effect on the catalysis of Au:PVP was evaluated using hydrogenation of styrene as a test reaction. It was revealed that single M atom doping on Au:PVP led to the emergence of hydrogenation catalysis. Moreover, AuRh:PVP exhibited much higher catalytic activity than that of AuPd:PVP, which was ascribed to synergistic effect between Au and Rh.
Keywords: Au clusters, Single-atom doping, Hydrogenation

1. Introduction

Magic stability and intrinsic chemical properties of bare gold clusters have been explained in terms of *superatom concept*.[1,2] According to the concept, Au clusters gain exceptionally high stability when the superatomic orbitals (1S, 1P, 1D, 2S, 1F, 2P, 1G, ...) formed over the cluster framework are filled up by valence electrons with the magic numbers of 2, 8, 18, 20, 34, 40, 58 and so forth. Recent mass spectrometric studies demonstrated that gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) preferred the sizes of 34, 43, 58, and so on.[3] Coincidence of magic numbers with those of bare Au clusters suggested that Au:PVP is an ideal platform to study catalytic properties of gold superatoms in the real world.[4]

We have reported that Au:PVP acts as active catalyst for aerobic oxidation.[4] Although the electronic structures of Au:PVP can be modified by the exposure to hydrogen molecules,[5] hydrogenation catalysis of Au:PVP is very poor. This study aims to provide Au superatoms with hydrogenation catalysis by doping an element that has high affinity to hydrogen. In order to gain molecular level understanding on the doping effect, a single atom of Pd or Rh was doped on Au:PVP by co-reduction method. The effects of doping on magic numbers and on catalysis for hydrogenation of styrene were studied.

2. Experimental

Au:PVP was prepared by mixing aqueous solutions of $HAuCl_4$ and $NaBH_4$ in the presence of PVP (Au atom : PVP monomer = 1 : 40) using a microfluidic mixer.[6] AuM:PVP (M = Pd or Rh) was produced by co-reduction of $HAuCl_4$ with $PdCl_2$ or $RhCl_3$, respectively, with the molar ratio of 97:3. Au:PVP and AuM:PVP were characterized by optical spectroscopy, X-ray absorption fine structure (XAFS) analysis, transmission electron microscopy (TEM) and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. Hydrogenation catalysis of Au:PVP and AuM:PVP was characterized by using styrene as a substrate in ethanol solution under mild reaction conditions: H_2 pressure of 0.1 MPa and temperature at 303 K.

3. Results and discussion

UV-Vis spectra of Au:PVP and AuM:PVP showed no localized surface plasmon resonance (LSPR) band, indicating that these clusters are smaller than ~2 nm in diameter. From the TEM analysis, the diameters of Au:PVP, AuPd:PVP and AuRh:PVP were estimated to be 1.2±0.2, 1.1±0.3 and 1.3±0.3 nm, respectively, suggesting that a heteroatom was doped into Au clusters while retaining the average size.

In order to estimate the number of dopant atoms in AuM:PVP, MALDI mass spectra were recorded with relatively intense laser power. Smooth distributions of mass peaks of $Au_nM_1^-$ centered at n~33 were observed, whereas other peaks such as Au_n^- and $Au_nM_2^-$ were not observed. These results indicated the exclusive doping of a single M atom to Au:PVP. **Figures 1a** and **1b** show MALDI mass spectra of AuPd:PVP and AuRh:PVP, respectively, recorded with minimal laser fluence for detecting the ionized species. The most abundant species are assigned to $Au_nM_1Cl_m^-$ (M = Pd or Rh) in which Cl atoms originating from the synthetic precursor are adsorbed. In contrast to the smooth size distribution in the mass spectra recorded at higher laser fluence, magic numbered clusters are clearly observed at $Au_{33}Pd_1Cl_m^-$ and $Au_{34}Rh_1Cl_m^-$ in **Figures 1a** and **1b**, respectively. Compared with a magic numbered pure gold cluster of $Au_{34}Cl_m^-$ (**Figures 1c**),[2,7] these findings suggest the different effects between Pd and Rh on the superatomic electronic structure. EXAFS analysis at M K-edge (M = Pd or Rh) indicated that both dopant atoms were located at an exposed surface of Au superatoms.

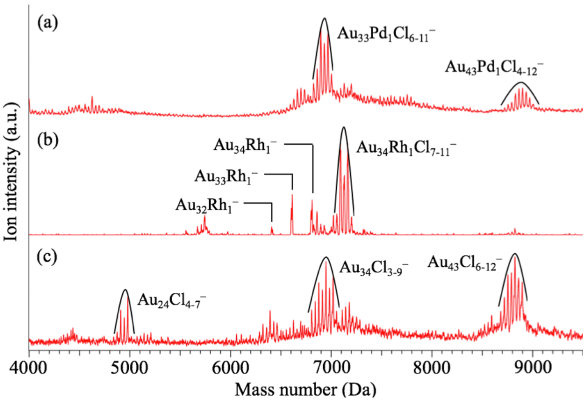
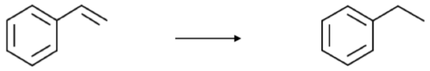


Figure1. MALDI mass spectra of (a) AuPd:PVP, (b) AuRh:PVP, and (c) Au:PVP recorded under soft ionization condition.

The catalytic activity of Au:PVP and AuM:PVP for hydrogenation of C=C bond was characterized by using styrene as a representative substrate. Catalytic activity was compared by the conversion after 1h (**Table 1**) in order to minimize the influence of degradation of the clusters. AuM:PVP catalyzed hydrogenation of styrene under mild reaction conditions (entries 2 and 3) although Au:PVP exhibited almost no catalytic activity (entry 1). These results show that single heterometal atom doping to Au superatoms leads to the emergence of hydrogenation catalysis. Entries 2 and 3 show that AuRh:PVP was much more active than AuPd:PVP in hydrogenation catalysis. The higher activity of AuRh:PVP is ascribed to synergistic effect between Au and Rh, given that Rh:PVP (average diameter = 2.7 nm) was less active than Pd:PVP (3.6 nm) for hydrogenation of styrene under the same conditions.

Table 1. Hydrogenation of styrene catalyzed by Au:PVP and AuM:PVP (M = Pd, Rh)



1 **2**

Entry	Catalyst	Conversion (%)
1[a]	Au:PVP	<1
2[a]	AuPd:PVP	3
3[a]	AuRh:PVP	15

[a]Reaction conditions; substrate: 50 μmol; catalyst: 1 atom% of metal atom; Ethanol: 5 mL; H_2: 0.1 MPa; 303 K; 1h.

4. Conclusions

We successfully doped a single heterometal atom, Pd or Rh, into Au:PVP. Different magic numbers observed for the bimetallic superatoms suggested different roles of Pd and Rh on the electronic structures. The single-atom doping was found to lead to the emergence of hydrogenation catalysis and AuRh:PVP was much more active than AuPd:PVP. The higher catalytic activity of AuRh:PVP was expected to originate from synergistic effect between Au and Rh.

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