Structure and Catalysis of a SiO_2-Supported Gold-Platinum Cluster $[(PPh_3)Pt(PPh_3Au)_6](NO_3)_2$

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A novel catalyst of $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ **1** supported on SiO_2 was very active in H_2-D_2 equilibration with a TOF of 29.8 s^{-1}, while it showed low activity for ethene hydrogenation and CO oxidation at 303 K. It was found that the catalysis of **1**/SiO_2 was not caused by platinum particle impurity but by the platinum atom which bound to the gold atoms in the cluster. The cluster framework of **1**/SiO_2 was stable during the reactions at 303 K. The change of Au-Pt bond in **1**/SiO_2 by heat treatment and the catalytic performance of produced cluster fragments were characterized by EXAFS, FT-IR and kinetic investigation.

Gold has the filled *d*-band located far bellow the Fermi level and is believed to be least useful for catalytic purpose, though small Au particles on α-Fe_2O_3, Co_3O_4 and TiO_2 exhibit high catalytic activity for low-temperature oxidation of CO.[1] There are some interesting examples, however, that evaporating gold onto platinum single-crystal surface displays markedly different activity and selectivity for conversion of *n*-hexene.[2,3] Conceivably, the "alkali-metal-like" $d^{10}s^1$ electronic configuration of Au atom leads to relatively tractable electronic structure compared to clusters of transition-metals with open *d* shells, which will attract much attention in catalysis of the transition-metal-gold clusters, especially ones containing catalytically important metals such as Pt and Pd. Those studies should provide a better understanding of metal-metal bonding and of the synergism often observed in bimetallic catalysis. Recently, Pignolet et al. reported a possible application of a phosphine-ligand stabilized Au cluster to heterogeneous catalysis by supporting on SiO_2 from surface organometallic viewpoints.[4] Independently, we have successfully obtained a new catalyst by supporting $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ **1** on SiO_2. The aim of this study is to examine the catalytic property of a Pt atom embedded in Au ensemble. The catalysis of **1**/SiO_2 for H_2-D_2 equilibration, ethene hydrogenation and CO oxidation has been investigated along with the surface structure characterization by means of FT-IR, EXAFS and TPR.

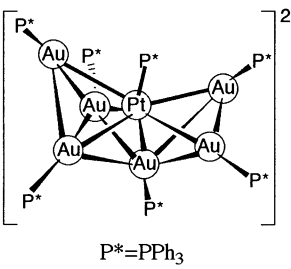

Figure 1. Framework of **1**.

A dark-yellow microcrystalline of $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ **1** was synthesized according to the literature.[5] The framework of **1** is shown in Figure 1. Impregnation of **1** on SiO_2 (Aerosil 300) was conducted with a carefully dried ethanol solution of **1** in atmosphere of Ar (99.9999%), followed by evaporation of the solvent under vacuum for 5 h at room temperature. The loading of **1** on SiO_2 was controlled to be 0.5 Pt wt%. FT-IR studies on **1**/SiO_2 showed that all frequencies attributed to PPh_3 ligands were maintained in intensity when the sample was heated to 473 K at a rate of 4 K/min under vacuum, but the decrease in intensity was observed if temperature was over 473 K, especially above 520 K, indicating that a part of the ligands decompose to change the cluster framework when overheating.

EXAFS measurements have been carried out at room temperature to characterize **1**/SiO_2. The Fourier transforms of EXAFS oscillations at Au L_3-edge and Pt L_3-edge for **1**, **1**/SiO_2, **1**/SiO_2 treated at 473 K and **1**/SiO_2 treated at 773 K under vacuum, are shown in Figure 2.

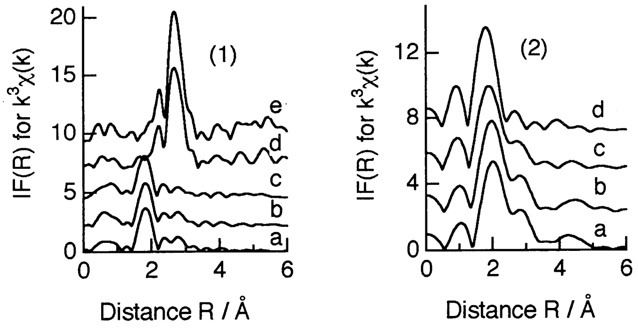

Figure 2. Fourier transforms of the EXAFS oscillations at Au L_3-edge (1) and Pt L_3-edge (2); (a): **1**; (b): **1**/SiO_2; (c): **1**/SiO_2 treated at 473 K; (d): **1**/SiO_2 treated at 773 K; (e): Au foil.

The EXAFS fitting results are listed in Table 1. The EXAFS analysis revealed that there was no change in the cluster framework of **1** after deposition on the SiO_2 surface. However, cluster fragmentation irreversibly occurred when **1**/SiO_2 was treated at 473 K under vacuum. The bond numbers of Pt-Au and Au-Au(Pt) decreased to about 68% and 75% of the original cluster **1**, respectively. Moreover, the cluster framework of **1** was suggested to be completely destroyed to form gold particles and $PtP^{\#}_m$ (m≈3, $P^{\#}$ for phosphine species) when heated to 773 K.

Table 1. Curve-fitting results for the EXAFS data of **1**/SiO_2[a]

Sample	Au-P		Au-Au(Pt)		Pt-P		Pt-Au	
	N	R/Å	N	R/Å	N	R/Å	N	R/Å
1/SiO_2	1.0	2.30	4.0	2.83	1.0	2.28	6.0	2.69
	±0.1	±0.01	±1.0	±0.02	±0.2	±0.02	±1.0	±0.03
1/SiO_2[b]	0.6	2.28	3.0	2.83	1.3	2.27	4.1	2.69
	±0.1	±0.02	±0.9	±0.02	±0.3	±0.02	±1.0	±0.03
1/SiO_2[c]	—		10	2.87	3.3	2.28	—	
			±1.0	±0.02	±0.6	±0.02		
1[d]	1.0	2.30	4.0	2.83	1.0	2.28	6.0	2.69

[a] Fitting results were determined by comparing the EXAFS results with the crystallographic data of **1**;[4] [b] treated at 473 K; [c] treated at 773 K. [d] cluster **1**; Au-Au (Au foil): 2.88 Å.

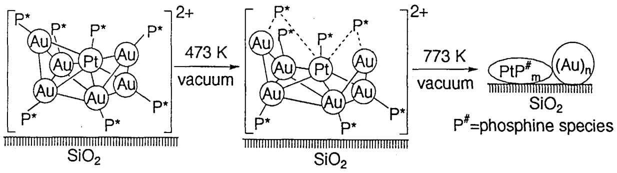

Figure 3. Schematic framework transformation in **1**/SiO_2 by heating. Dotted lines tentatively represent bonding of P* to Pt and Au.

Change of the cluster framework in **1**/SiO_2 was proposed in Figure 3.

H_2-D_2 equilibration on a series of catalysts related to **1**/SiO_2 was tested at 303 K in a fixed-bed flow reactor system equipped with a mass spectrometer. Ar was used as a diluent gas with a flow rate of 50 ml/min (H_2=D_2=2.0 ml/min). The catalytic reaction rates are defined as turnover frequency (mol of HD)(mol of cluster)$^{-1}$(s)$^{-1}$, which are shown in Table 2.

From Table 2, it was observed that the catalytic activity of **1** under molecular solid-gas condition was promoted about 15 times by supporting on SiO_2.[6] The dramatic increase may be mainly attributed to a high surface area of the support. It was also found that the catalytic activity of **1**/SiO_2 was higher than that of the ones treated at 473 or 773 K. $[Au_9(PPh_3)_8](NO_3)_2/SiO_2$ was inactive for H_2-D_2 equilibration, which implies that the Pt atom in **1** plays a key role in activation of H_2. This is contrasted to activation of H_2 on Pt catalysts which demands multimetal sites at Pt surface. Lower activity of **1**/SiO_2 treated at 473 K compared to **1**/SiO_2 is possibly referred to the increase in the number of Pt-P bonds and to the decrease in the number of Au-Pt bonds which may participate in the activation of H_2. The monometallic catalysts of $Pt(PPh_3)_4/SiO_2$ and that pretreated at 473 K were inactive (Table 2). In case of **1**/SiO_2 treated at 773 K, the H_2-D_2 equilibration may be caused by Au particles[7] or Pt sites with phosphine ligands. However, $Pt(PPh_3)_4/SiO_2$ treated at 773 K showed a remarkably high activity for H_2-D_2 equilibration, which may be ascribed to fragmentation of $Pt(PPh_3)_4$ to form metallic particles on SiO_2 because of irreversible H_2 adsorption (H/Pt=0.32). No chemisorption of H_2 was observed with $Pt(PPh_3)_4/SiO_2$ and the one treated at 473 K. Increasing activity by treatment of **1**/SiO_2 at 773 K might be due to partial clusterization of Pt though no Pt-Pt bond was observed by EXAFS.

Table 2. H_2-D_2 equilibration (a), ethene hydrogenation (b) and CO oxidation (c) over several catalysts at 303 K

Catalyst	TOF / s^{-1}		
	(a)	(b)	(c)
1	2.0	—	—
1/SiO_2	29.8	$8x10^{-4}$	$7x10^{-5}$
1/SiO_2 treated at 473 K	11.1	$5x10^{-4}$	$3x10^{-5}$
1/SiO_2 treated at 773 K	25.7	$6x10^{-4}$	$1.5x10^{-5}$
$Pt(PPh_3)_4/SiO_2$	0.0	0	—
$Pt(PPh_3)_4/SiO_2$ treated at 473 K	0.0	0	—
$Pt(PPh_3)_4/SiO_2$ treated at 773 K	1299.1	$7x10^{-2}$	—
$[Au_9(PPh_3)_8](NO_3)_2/SiO_2$	0.0	—	—

From pulse reactions, the following results were obtained: 1) About 80% decrease in the rate of H_2-D_2 equilibration was observed when ethene was mixed into a gas flow of H_2-D_2. When ethene was mixed with D_2, the HD formation rate was 1/20 of that in H_2-D_2 equilibration and a very weak signal in m/e 29 (C_2H_3D) was observed. It is, therefore, unlikely that H_2-D_2 equilibration on **1**/SiO_2 is caused by undetectable metallic platinum particle impurity. 2) No H_2-D_2 equilibration proceeded when CO pulse was admitted into a gas flow of H_2-D_2. By CO adsorption, the yellowish **1**/SiO_2 immediately turned to the orange-red one, which resembles the CO adduct of **1** in solution.[4] It is also deducible that the H_2-D_2 equilibration takes place on the coordination space enough for hydrogen dissociation on the Pt atom of **1**/SiO_2. $Pt(PPh_3)_4/SiO_2$ treated at 473 K was inactive, whereas, **1**/SiO_2 treated at 473 K catalyzed H_2-D_2 equilibration. The Au-Pt bonds may contribute to the formation of active Pt sites.

The rapid H_2-D_2 equilibration catalyzed by **1**/SiO_2 impelled us to carry out the ethene hydrogenation at C_2H_4/H_2=13 : 13 kPa in a closed circulating system. It was found that the hydrogenation of ethene to ethane proceeded over **1**/SiO_2 at an initial rate of $8x10^{-4}$ s^{-1} at 303 K (Table 2). TPR spectra of **1**/SiO_2 before and after ethene hydrogenation were almost the same each other, suggesting that no change occurred in the cluster framework of **1**/SiO_2 during the reaction.

We also performed CO oxidation reaction under CO/O_2=13 :13 kPa at 303 K. The low reaction rate (TOF of $7x10^{-5}$ s^{-1}) in Table 2 is due to strong CO adsorption as proved by the color change, which prevents O_2 adsorbing. The catalytic reaction mechanism on one Pt atom embedded in the Au cluster is not clear at present, but behavior of **1**/SiO_2 upon CO and O_2 adsorption related to structure characterized by FT-IR and EXAFS will be reported separately.[8]

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