

EXAFS and Catalytic Activity of AgPt Bimetallic Cluster Supported on NaY Zeolite

Ryong RYOO, Chanho PAK and Sung June CHO

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taeduk Science Town, Taejon, 305-701, Korea

(Received August 24, 1992)

Platinum clusters with ca. 1 nm in size have been prepared as engaged in supercages of NaY zeolite by the reduction of platinum after ion exchange of $\text{Pt}(\text{NH}_3)_4^{2+}$ into NaY. A series of bimetallic AgPt/NaY samples with Ag/Pt atomic ratios of 0, 0.11, 0.43 and 1.0 have been obtained by the reduction of silver after subsequent ion exchange of Ag^+ into the Pt/NaY sample. The result from measurements for ^{129}Xe NMR spectrum, and hydrogen chemisorption has indicated that the Ag atoms were put together onto the Pt cluster, with the surface enriched by Ag atoms. The extended X-ray absorption fine structure (EXAFS) of the bimetallic cluster measured above Pt *L*_{III} and Ag K edges have been analyzed with reference EXAFS spectra which were experimentally obtained from the metal foils and those for AgPt pair which were theoretically prepared by FEFF codes distributed by Rehr et al. The catalytic activity in ethane hydrogenolysis over the AgPt bimetallic cluster has also been measured.

Keywords: PtAg bimetallic cluster, ethane hydrogenolysis, EXAFS, Pt/NaY zeolite, ^{129}Xe NMR

1. Introduction

According to previous studies on platinum in Y zeolites (Pt/Y)^{1,2}, Pt clusters with ca. 1 nm in size can be prepared as engaged within the supercages (1.3 nm diameter, 0.8 nm aperture) of Y zeolite by proper reduction treatments after the ion exchange of $\text{Pt}(\text{NH}_3)_4^{2+}$ into zeolite, e.g., NaY. The cluster size and the location in supercage became clarified by various physical and chemical characterization methods²) such as transmission electron microscopy (TEM), hydrogen chemisorption, wide-angle X-ray scattering, extended X-ray absorption fine structure (EXAFS) and ^{129}Xe NMR spectroscopy for adsorbed xenon. Recently, the xenon adsorption measurement on Pt cluster indicated that the Pt/NaY sample can be prepared so as to contain about 50 Pt atoms per cluster, independent of the Pt content in the range of 2 – 10 wt%¹). Such a very small cluster size with great uniformity, as well as easy availability and high stability, attracts great attention in the study of metal clusters.

Since various cations can be exchanged into NaY zeolite, a second metal ion, e.g., Ag^+ , can be added onto the Pt/NaY which contains Pt clusters in supercages. Then, the metal ion can be reduced with H_2 , for which the Pt cluster is known to act as a catalyst. If the reduced metal atom has good affinity with the Pt cluster, the two metals may form a *nanosize* bimetallic cluster, which is of great interest with respect to the bulk miscibility of the metals. In the present work, we try to add Ag atoms onto the 1-nm Pt cluster in supercage and to investigate if they form a bimetallic AgPt cluster using

the measurements of EXAFS, ^{129}Xe NMR spectrum, H-chemisorption, xenon adsorption and catalytic activity for ethane hydrogenolysis into methane.

2. Experimental

A sample of Pt/NaY was prepared via a known procedure described elsewhere¹). The sample is designated as $\text{Pt}_{7.1}/\text{NaY}$ according to the Pt content of 7.1 Pt atoms per unit cell of zeolite. Bimetallic AgPt/NaY samples with Ag/Pt atomic ratios of 0, 0.11, 0.43, 1.0 and 2.3 were prepared by the reduction of silver ion with flowing H_2 at 573 K after ion exchanging Ag^+ into the $\text{Pt}_{7.1}/\text{NaY}$ sample in aqueous solution of AgNO_3 at room temperature (RT), respectively. The samples are designated as $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$, where y equals 7.1 times the Ag/Pt atomic ratio. Hydrogen chemisorption, xenon adsorption, and ^{129}Xe NMR spectrum were measured *in situ* as described previously¹).

For EXAFS measurement, about 0.1 g of the sample exposed to air was transformed into a disk of 10 mm in diameter and 1 – 2 mm in thickness by using a mechanical press. The sample was reduced in flowing H_2 at 573 K for 2 h in a Pyrex flow reactor which was joined to a Pyrex cell having Kapton (Eastman Kodak) windows. After the sample was cooled to RT and transferred into the EXAFS cell, the cell was sealed off from the reactor with flame under H_2 atmosphere while H_2 gas was kept to flow to the atmosphere bypassing the sample cell, for safety (to prevent "pop-off"). The X-ray absorption measurements above Pt *L*_{III} and Ag K edges were carried out at

Table I. Hydrogen chemisorption, xenon adsorption and ^{129}Xe NMR chemical shift for $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$.

	$\text{H}/\text{Pt}_{total}^a$	Pt_{surf}^b	δ^c	$\text{Xe}/\text{Pt}_{total}^d$
$\text{Pt}_{7.1}/\text{NaY}$	1.28	1.0	228	0.066
$\text{Ag}_{0.8}\text{Pt}_{7.1}/\text{NaY}$	1.09	0.85	211	0.067
$\text{Ag}_{3.0}\text{Pt}_{7.1}/\text{NaY}$	0.86	0.67	182	0.085
$\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$	0.45	0.35	168	0.107
$\text{Ag}_{16.5}\text{Pt}_{7.1}/\text{NaY}$	0.22	0.17	163	0.132

^aChemisorbed H atoms per *total* Pt atom.

^bSurface fraction of Pt determined by the ratio of H/Pt between $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$ and $\text{Pt}_{7.1}/\text{NaY}$.

^cChemical shift for xenon adsorbed at 26.7 kPa and 296 K.

^dXenon adsorption for saturation on metal cluster at 296 K.

the beam line X11A at the National Synchrotron Light Source, Brookhaven National Laboratory.

Ethane hydrogenolysis reaction rate was measured by using a flow recirculation system. H_2 (Korea Industrial Gases, 99.99%) and He (Korea Industrial Gases, 99.999%) were passed through a MnO/silica and 3A molecular sieve traps before used. Ethane (Matheson, 99.5%) was purified by the freeze-evacuate-thaw technique to 99.9%. The reaction conditions were as follows: $P_{\text{C}_2\text{H}_6} = 1.33$, $P_{\text{H}_2} = 22.5$, $P_{\text{He}} = 77.5$ kPa, circulation rate = 2.3 passes per min, and reaction temperature = 560 ~ 630 K. The product was analyzed by a gas chromatograph (Hewlett-Packard 5890 series II) equipped with a Porapak Q column and a flame ionization detector (FID).

3. Results and Discussion

We reported previously the results from H chemisorption, ^{129}Xe NMR, TEM and xenon adsorption measurements for Pt/NaY samples which contained Pt clusters with ca. 1 nm in size as encaged within supercages. The $\text{Pt}_{7.1}/\text{NaY}$ sample used in the present study was prepared according to the same procedure, and thus the results shown in Table I for the present sample are very similar to the previous data¹.

Our transmission electron micrographs taken (by JEM 2000-EX operating at 200 keV) through thin edges of the $\text{Pt}_{7.1}/\text{NaY}$ zeolite crystal with ca. 1 μm in length showed Pt particles with about 1 nm in size. Platinum particles larger than ~ 1 nm were not seen on the crystal edge. The H chemisorption value 1.28 $\text{H}/\text{Pt}_{total}$ in Table I suggests that nearly all Pt atoms can be exposed on the surface of such small clusters, which is based on the conventional (but not rigorous) assumption for H chemisorption of 1 $\text{H}/\text{Pt}_{surface}$. The chemical shift (δ) in ^{129}Xe NMR spectrum obtained for the adsorbed xenon on $\text{Pt}_{7.1}/\text{NaY}$ was greatly shifted to downfield as compared with NaY, probably due to the interaction between the Pt clusters and the xenon atoms which were adsorbed inside supercages. In addition, the $\text{Xe}/\text{Pt}_{total}$

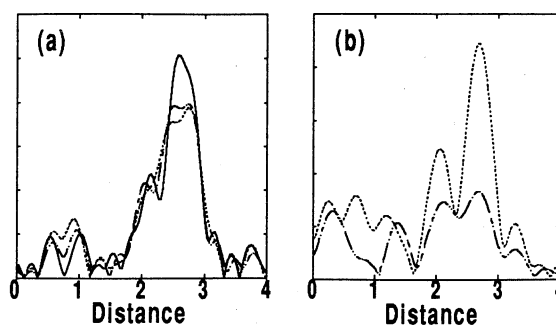


Fig. 1. k^3 -weighted Fourier transforms of EXAFS function above the (a) Pt L_{III} edge and (b) Ag K edge of $\text{Ag}_{3.0}\text{Pt}_{7.1}/\text{NaY}$ (—), $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$ (---) and $\text{Ag}_{16.5}\text{Pt}_{7.1}/\text{NaY}$ (· · ·).

value given in Table I is for the number of xenon adsorption for saturation on the Pt clusters at 296 K which was determined by the decrease in the adsorption isotherm occurred due to the H chemisorption. The xenon adsorption data for $\text{Pt}_{7.1}/\text{NaY}$, 0.066 $\text{Xe}/\text{Pt}_{total}$, in Table I may be compatible with the adsorption of 4 Xe atoms through 4 apertures of a supercage encaging 50 – 60 Pt atoms¹.

The number of chemisorbed H atoms per *total* Pt atom decreased with increasing Ag content as Table I shows. The δ also decreased from the value for $\text{Pt}_{7.1}/\text{NaY}$. Such changes suggest the formation of bimetallic AgPt cluster since Ag atom is known not to chemisorb H atoms on the surface³. The $\text{H}/\text{Pt}_{total}$ ratio decreased more rapidly than the $\text{Ag}/(\text{Ag} + \text{Pt})$ atomic ratio, indicating that the surface was enriched with Ag. The decrease in δ can be due to the inhibition of xenon-Pt interaction by Ag. The increase in Xe/Pt ratio with the Ag content in Table I suggests that the cluster size is increased, say, by expanding into adjacent supercages. A space-filling model for cluster consisting of about 50 Pt atom in supercage will have 4 Xe atoms attached directly on the surface through 4 apertures (4 $\text{Xe}/\sim 50$ Pt ≈ 0.08 Xe/Pt). Similarly, a cluster consisting of about 50 Pt and 50 Ag atoms which occupies two adjacent supercages can adsorb 6 Xe atoms through 6 apertures (6 $\text{Xe}/\sim 50$ Pt ≈ 0.12 Xe/Pt). Thus such crude estimation can explain the change from 0.066 Xe/Pt for $\text{Pt}_{7.1}/\text{NaY}$ to 0.107 Xe/Pt for $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$ in Table I. The metal particles in TEM for $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$ increased uniformly to 1 – 2 nm in size. However, the addition of excessive Ag (i.e., 16.5 Ag) resulted in the formation 20-nm metal aggregates (from TEM).

Figure 1 shows the Fourier transforms of the k^3 -weighted EXAFS spectra ($k^3\chi$) obtained above Pt L_{III} and Ag K edges for $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$ samples. The main peak from the first coordination shell of Pt splits into PtPt peak at 0.248 nm and PtAg at 0.270 nm (not corrected for phase shift), progressively with increasing the Ag loading. Similarly, the peak for Ag shell splits into AgAg at 0.270 nm and AgPt at 0.213 nm, confirming

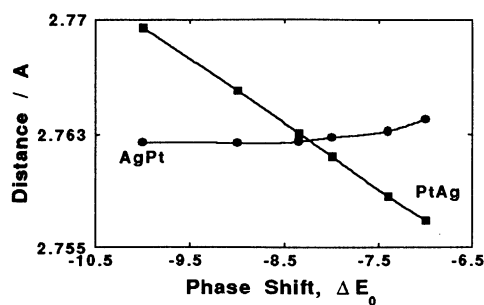


Fig. 2. Effect of phase shift variations, as characterized by a phase shift adjustment parameter ΔE_0 , on values of structural parameters obtained for $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$.

the formation of AgPt bimetallic cluster. To obtain the structural parameters for the Pt or AgPt bimetallic cluster, the data were Fourier-filtered over 0.16 – 0.31 nm, and analyzed by a curve-fitting technique using experimental reference spectra⁴⁾ which were obtained from metal foils and those for PtAg and AgPt pairs which were obtained theoretically from *ab initio* single-scattering calculation according to an automated code, FEFF, distributed by Rehr *et al.*⁵⁾ To prepare reference χ data for AgPt and PtAg pairs, we used the amplitude reduction factor (S_0^2) obtained by fitting the metal foils with FEFF: $S_0^2 = 0.89$ for Pt and 0.78 for Ag. We assumed 0.0072 for the Debye-Waller factor (σ^2) from the combination of $\sigma_{\text{Pt}}^2 = 0.0051$ (fitting $\chi_{\text{Pt foil}}$ with FEFF) and $\sigma_{\text{Ag}}^2 = 0.0092$ in inverse proportion to the reduced mass of atomic pair. But, the curve fitting result was not significantly affected by the choice of σ^2 in the vicinity.

We obtained a set of the structural parameters for $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$ from the curve-fitting with a given value of phase shift adjustment parameter (ΔE_0) for PtAg. We then compared the changes in AgPt and PtAg nearest pair distances against ΔE_0 (as shown in Figure 2) in the same way described by Meitzner *et al.*⁴⁾ The value of the interatomic distance at the intersection (0.276 nm) is taken to be the best-fit distance for $R_{\text{AgPt}} = R_{\text{PtAg}}$, and the corresponding value of ΔE_0 (-8.3 eV) is used in selecting final values of the structural parameters for other AgPt/NaY samples (listed in Table II). The PtAg and AgPt distances for most AgPt/NaY samples were 0.276 nm, which is significantly shorter than the sum of atomic radii for bulk Pt and Ag metals (0.284 nm). Thus the PtAg distance was rather similar to PtPt distance (0.274 nm) in our AgPt bimetallic cluster. The PtPt and AgAg distances were also decreased from the bulk data. The coordination number (N) in Table II shows that N_{PtPt} decreased by ca. 20% due to the addition of Ag onto $\text{Pt}_{7.1}/\text{NaY}$, and N_{AgPt} and N_{PtAg} increased only to a small extent, whereas N_{AgAg} increased continuously with increasing Ag/Pt ratio. Such results indicate that the core of cluster is richer in Pt than the surface.

The catalytic activity in ethane hydrogenolysis was expressed in terms of the average number of ethane

Table II. Structural parameters of $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$ catalysts from Pt *LIII*-edge and Ag *K*-edge EXAFS.

	atomic pair	$R^a/\text{\AA}$	N^b
$\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.77	6.0
$\text{Ag}_{3.0}\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.75	5.6
	Pt-Ag	2.76	0.3
$\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.74	4.8
	Pt-Ag	2.76	1.4
	Ag-Pt	2.76	1.9
	Ag-Ag	2.81	1.6
$\text{Ag}_{16.5}\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.74	5.0
	Pt-Ag	2.76	1.1
	Ag-Pt	2.81	1.6
	Ag-Ag	2.85	5.0

^a Nearest neighbor distance. ^b Coordination number with uncertainty of ± 1 .

molecules converted per surface Pt atom during 1 s, i.e., the turnover frequency (TOF), for which the fraction of surface Pt atoms was estimated from hydrogen chemisorption with the assumption that Ag atoms does not chemisorb H (in Table I). The TOF was decreased drastically from 1.6×10^{-3} to 3.5×10^{-4} , 6.5×10^{-5} and 1.6×10^{-5} as the Ag/Pt ratio increased to 0.11, 0.43 and 1.0, respectively. The apparent activation energy (E_a) was obtained from the Arrhenius plot between $\ln(\text{TOF})$ and inverse of temperature, and the result was within $60 \pm 5 \text{ kcal mol}^{-1}$ for up to the addition of 7.1 Ag to $\text{Pt}_{7.1}/\text{NaY}$. Such a change in TOF without the change in E_a may suggest that the decrease of catalytic activity was only due to the geometrical effect, i.e., the placement of Ag atoms onto the Pt cluster reduced the number of large ensembles of Pt atoms.

In conclusion, our EXAFS result has confirmed the formation of AgPt bimetallic clusters with the core rich in Pt.

Acknowledgements

This work was supported by Korea Science and Engineering Foundation, the Pohang Light Source, and the U. S. Department of Energy under Contract DE-AC02-76CH00016. We are grateful to the authors (J. J. Rehr, R. C. Albers, J. M. de Leon, S. I. Zabinsky) of FEFF codes. We also thank Prof. M. Choi for helpful discussions.

References

- 1) R. Ryoo, S. J. Cho, C. Pak, J.-G. Kim, S.-K. Ihm and J. Y. Lee: *J. Am. Chem. Soc.* **114** (1992) 76 and references therein.
- 2) M. Boudart, M. G. Samant and R. Ryoo: *Ultramicroscopy* **20** (1986) 125 and references therein.
- 3) M. D. Baker, G. A. Ozin and J. Godber: *J. Phys. Chem.* **89** (1985) 305.
- 4) G. Meitzner, G. H. Via, F. W. Lytle and J. H. Sinfelt: *J. Chem. Phys.* **87** (1987) 6345.
- 5) J. J. Rehr, J. M. de Leon, S. I. Zabinsky and R. C. Albers: *J. Am. Chem. Soc.* **113** (1991) 5135.