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ESCA Evidence for the Occlusion of Platinum Particles in Reduced PtY Zeolites

Depending on pretreatment conditions platinum particles in several discrete size ranges may be formed in Y-type zeolites. These classes of particles show marked differences with respect to hydrogen adsorption and catalytic properties, as recently reviewed by Gallezot (*1*). Dramatic rate enhancements, for example, have been observed to occur over platinum clusters ≤10 Å in diameter relative to platinum particles of ca. 15 Å on alumina (*2*). Much of the unusual catalytic behavior has been attributed either (a) to particle size effects, or (b) to the influence of the zeolite on the metal, usually by withdrawing electrons.

On the basis of X-ray diffraction, small-angle X-ray scattering, chemisorption, and electron microscopy data Gallezot *et al.* (*3*) have concluded that platinum(0) may exist in three forms in the zeolite. These forms include atomically dispersed Pt^0 in sodalite cages, 6- to 13-Å agglomerates in the supercages, and 25- to 30-Å particles occluded in the zeolite crystals. In each case prior to reduction the platinum, originally in the form of a $Pt(NH_3)_4Y$ zeolite, was reacted in O_2 at temperatures ≥300°C. Dalla Betta and Boudart (*2*) demonstrated that larger particles, on the order of 100 Å, were obtained when the oxidation step was omitted, and the zeolites were simply reduced in H_2. The primary purpose of this study was to determine whether platinum particles larger than 13 Å, which is the nominal diameter of the supercage, remained within the zeolite crystals, as suggested by Gallezot *et al.* (*3*), or formed on the external surface. We have examined, therefore, PtY zeolites for surface enrichment in platinum, using the technique employed first by Minachev and co-workers (*4*), and later by us to confirm the migration of metals or metal oxides to the external surface of zeolites (*5*).

The PtY zeolites, containing 4.5 wt% metal, were prepared using a modified version of the experimental method reported by Dalla Betta and Boudart (*2*). Five grams of NaY zeolite (Linde Lot No. 13544-76) were exchanged three times in 1-liter aqueous solutions of either 0.02 *M* $Ca(NO_3)_2 \cdot 4H_2O$ or 1.0 *M* NaCl. After washing and drying, platinum in the form of $[Pt(NH_3)_4]^{2+}$ was exchanged into the respective zeolite at 80°C. After samples of the exchanged zeolites were dried at 400°C, Pt, Ca, and Na concentrations were determined by plasma atomic emission spectroscopy. Proton concentrations were estimated by difference. The following unit cell formulas were obtained: $Pt_3Ca_{17}Na_8H_8Y$ and $Pt_3Na_{45}H_5Y$.

Samples for the ESCA study were prepared by pressing the zeolite in a stainless-steel die under a force of 1.5×10^5 N. The resulting wafers (47 mg/cm^2) were pretreated so as to produce dehydrated zeolites, which contained the ammine complex, oxidized platinum, small clusters of platinum (6–13 Å), or larger platinum particles. The particular pretreatments are summarized in Table 1. In all cases, oxidation and reduction were carried out in flowing O_2 and H_2, respectively.

The X-ray photoelectron spectra were obtained using a Hewlett–Packard 5950A ESCA spectrometer with monochromatic Al$K\alpha$ X rays. The pretreatment cell was opened under a nitrogen atmosphere, and the sample was transferred into the spectrometer. The Au $4f_{7/2}$ line (84.0 eV) was used as a primary standard and the Si 2*s*

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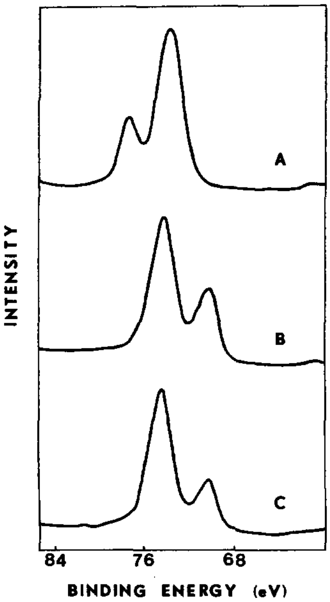

FIG. 1. Pt 4*f* spectra of PtCaY: (A) after oxidation at 100°C for 2 hr; (B) separate sample after reduction at 350°C; (C) separate sample after oxidation at 350°C, evacuation at 25°C, followed by reduction in H_2 at 400°C.

line (154.2 eV) was used as an internal standard. The charging effect was reduced by flooding the sample with electrons of nearly zero kinetic energy.

As shown in Fig. 1, the Pt $4f_{5/2}$ in the oxidized sample and the Pt $4f_{7/2}$ peak in the reduced sample were well resolved from the overlapping Pt 4*f* and Al 2*p* line. The linewidths at half-maximum were typically 1.8 eV; whereas the Pt 4*d* lines had a halfwidth of ca. 7 eV. After deammination under oxygen, followed by reduction at 350°C, Foger and Anderson (*6*) observed a contribution from the $4f_{5/2}$ line in PtLaY zeolites, which was attributed to an electron-deficient form of platinum identified as Pt^{2+}. In the present study no residual line at 77.3 eV was apparent in spectrum B or C.

From the peak areas and the cross sections reported by Scofield (*7*) atomic ratios have been calculated. These are summarized in Table 1 together with the theoretical ratios obtained by assuming no surface enrichment. Since only a few outer atomic layers of the zeolite particles are sampled by ESCA, surface enrichment of a particular element would normally appear as a large relative increase in the peak for that element. In the previous study with ruthenium, Ru $3d_{5/2}$/Si 2*p* ratios were up to 25 times as large as the theoretical ratio when the samples were heated in the presence of oxygen (*5*). Clearly, the Pt 4*f*/Si 2*p* ratios never exceeded the theoretical ratio except for the sample of PtNaY which was reduced at 350°C for 2 hr, and even in this case the ratio was only 1.7 times the theoretical value. It was satisfying to note that samples which contained $[Pt(NH_3)_4]^{2+}$ or Pt^{2+} had Pt 4*f*/Si 2*p* ratios which were equivalent, within experimental error, to the theoretical ratio.

The failure to observe a surface enrichment of platinum for those samples which were reduced without prior oxidation may be the result of (a) occlusion of the metal within the zeolite, or (b) the formation of very large metal particles on the surface. To test the latter hypothesis electron microscopy and X-ray diffraction studies were carried out on selected samples. A sample preparation was used for the electron microscopy study, which would largely provide information on the nature of the external platinum. In particular, after one of the standard pretreatments a zeolite sample was dispersed, using an ultrasonic bath, in a solution of water with Dowfax 9N15 surfactant. A drop of the suspension was allowed to dry on a standard copper grid which was coated with Formvar and an evaporated carbon film. The platinum particles in the micrographs were identified with the aid of an energy dispersive X-ray fluorescence attachment on a JEOL 100-C transmission scope. The resolution was estimated to be 13 Å. As expected, the samples which were first oxidized and then reduced had only a few particles >13 Å, and for the PtCaY sample most of these were <20 Å in diameter. The PtNaY sample had a few particles in the range 200–300 Å, but most of the *observed* particles were

TABLE 1

Atomic Ratios and Binding Energies for PtCaY and PtNaY Zeolites

Sample	Treatment	Atomic ratios		Binding energies (eV)		
		Pt 4*f*/Si 2*s*	Si 2*s*/Al 2*s*	Pt $4f_{5/2}$	Pt $4f_{7/2}$	Pt $4d_{5/2}$
4.5% PtCaY						
I	Evacuation at 100°C[a]	0.017	2.44	77.1		317.3
II	O_2, 100°C, 2 hr	0.020	2.66	77.3		317.1
III	O_2, 350°C, 2 hr	0.019	2.63	76.8		317.2
IV	H_2, 350°C, 2 hr	0.019	2.67		71.7	314.9
V	H_2, 400°C, 2 hr	0.016	2.66		71.8	315.8
VI	O_2, 350°C, 2 hr; vac 25°C; H_2, 400°C, 2 hr	0.018	2.81		71.8	315.4
VII	O_2, 350°C, 2 hr; He, 350°C, 1 hr; H_2, 400°C, 15 hr	0.012	3.23		72.0	315.2
4.5% PtNaY						
VIII	H_2, 350°C, 2 hr	0.037	2.94		71.5	315.0
IX	H_2, 400°C, 2 hr	0.020	2.86		71.6	315.7
X	O_2, 350°C, 2 hr; vac 25°C; H_2, 400°C, 2 hr	0.013	—		71.6	314.7
Theoretical		0.022	2.43			

[a] A value of 4.8 was observed for the N 1*s*/Pt 4*f* ratio.

<100 Å. Samples which were reduced, without prior oxidation, had many more large particles with a broad size distribution. Particles as large as 450 Å were observed for the PtNaY sample, and in many cases it was evident that these very large particles were on the external surface of the zeolite.

Line broadening of the X-ray diffraction peak corresponding to the 2.26-Å *d* spacing of platinum was observed for samples which were either reduced directly or oxidized and then reduced. Particles smaller than 40 Å gave lines too broad for detection. As a semiquantitative indication of the platinum metal in particles >40 Å the area of the platinum line was compared with the area of a zeolite line corresponding to a *d* spacing of 2.37 Å. From Table 2 it may be seen that all reduced samples contained some particles in the range 90–140 Å, but the number of these particles was much

TABLE 2

Platinum Crystallite Size and Relative Amount of Platinum

Sample[a]	Crystallite size[b] (Å)	Relative Amount (Pt/zeolite)[c]
IV	110	12
VI	130	3.4
VII	90	1.7
IX	140, 700[d]	2.4, 12[d]
X	110	1.8

[a] Sample numbers are the same as those listed in Table 1.

[b] Obtained using the formula $D = K\lambda/\beta \cos \theta$, where D is the crystallite diameter, K is the shape factor (0.90), λ is the wavelength of the X rays (1.5405 Å), β is the width at half-maximum of the Pt line corresponding to the 2.26-Å *d* spacing, corrected for instrumental broadening, and θ is the angle of diffraction (19.8°).

[c] The relative amount of Pt was obtained by taking the ratio of the Pt 2.26-Å line to the zeolite 2.37-Å line.

[d] Sample IX exhibited a bimodal platinum phase.

smaller for those zeolites which were first oxidized. In agreement with the electron microscopy results the PtNaY zeolite (Sample IX), which was directly reduced in H_2, had a substantial mass of very large particles.

A simple model has been considered to determine whether particles in the size ranges observed by electron microscopy and X-ray diffraction could give rise to the observed Pt 4*f*/Si 2*p* ratios if the particles existed on the external surface of the zeolite crystallites. In the model the zeolite particles were taken to be cubes, 0.5 μm on a side, which was a reasonable average value as indicated by electron micrographs. It was assumed that all of the platinum was present on the surface in the form of spheres, either 100 or 300 Å in diameter. Furthermore, only platinum atoms in a hemispherical shell, 20 Å thick, gave rise to the ESCA line. The escape depth for platinum under the conditions of this experiment is approximately 30 Å (*8*). Finally, the Si 2*p* line was assumed to be derived from four layers of Si atoms. Ratios of Pt 4*f*/Si 2*p* of 0.2 and 0.07 were then calculated for the 100 and 300 Å platinum particles, respectively.

The experimental Pt 4*f*/Si 2*s* ratios from Table 1 are an order of magnitude less than the value from the model, assuming 100-Å platinum particles; therefore, it seems likely that a substantial fraction of these particles are indeed occluded within the zeolite. For the larger particles the reverse may be true; i.e., most of the particles >200 Å probably exist on the external surface of the zeolite crystals. Verdonck *et al.* (*9*) have shown that ruthenium agglomerates are built up in holes of the zeolite crystals when water is present during reduction. The water is believed to generate these holes by hydrolysis of the zeolite lattice. Since the partial pressure of water was small in the present study it seems that the defects must have existed prior to reduction. The generation of defects by the formation of 100-Å platinum particles would be a very unlikely process due to the amount of energy required.

The experimental Si 2*s*/Al 2*s* ratios were generally larger than the expected ratio of 2.43 obtained from chemical analysis. However, approximately half of the values are within a standard deviation of 10% of the theoretical value, which is within the limits of accuracy for different nontransition elements of similar kinetic energy. Vedrine *et al.* (*10*) also observed an absence of superficial enrichment in silicon for their PtY zeolites. The samples having ratios greater than 2.7 probably have undergone a true enrichment in silicon at the surface.

In addition to providing information on the location of platinum particles in zeolites binding energies for both the large and small particles have been obtained. If one takes the binding energy for Pt $4f_{5/2}$ to be 3.75 eV greater than that for Pt $4f_{7/2}$ (*6*), then the results shown in Table 1 indicate that although a difference in binding energy of 1.3 ± 0.4 eV exists between the Pt^{2+} and Pt^0, no significant difference occurs between the samples reduced according to the different procedures. In Y-type zeolites Vedrine *et al.* (*10*) noted binding energies of 72.8 ± 0.3, 72.2 ± 0.3, and 72.2 ± 0.3 eV for atomically dispersed platinum, 10-Å platinum, and 20-Å platinum, respectively. Obviously, the three values are within experimental error. Thus, apart from the effort of Foger and Anderson (*6*) in lineshape analysis there does not appear to be definitive ESCA evidence to support more extensive withdrawal of electrons from platinum in PtCaY when compared with PtNaY or in small particles when compared with large particles.

In summary, except for one PtNaY sample which was reduced directly in H_2 at 350°C, no ESCA evidence was found for the migration of platinum to the external surfaces of zeolite crystallites. Electron microscopy and X-ray diffraction data, however, demonstrated that a significant amount of the metal was present as particles between 20 and 150 Å in diameter for samples which were not oxidized prior to reduction. Since the regular large cavities in zeolite-Y are only 13 Å in diameter, we conclude that most of the particles in this 20- to 150-Å size range are occluded in other voids which exist within the zeolite crystallites. In addition, differences in metal-support interaction were not evident from binding energy data for the several types of reduced platinum examined in this study.

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