Investigation by X-Ray Absorption Spectroscopy of Platinum Clusters Supported on Zeolites

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Dedicated to Professor G. M. Schwab on his 80. birthday

The onset of the L_{III} edge of the X-ray absorption spectrum of platinum in Y-zeolites involves an electronic transition from core to band levels producing a so-called white line. The spectral area of this increases and the edge position shifts to higher energies, first when the platinum particle size becomes small enough so that the clusters are in the supercages, second when the clusters are covered with oxygen, and third when multivalent cations are introduced in the zeolite. Both features of the absorption edge indicate that under the three above circumstances, platinum becomes more electron deficient. This conclusion had been inferred earlier from the enhanced catalytic activity of Pt clusters in Y zeolites.

Introduction

The electronic structure of transition metals gradually changes as the number of atoms involved in a particle decreases. This effect of diminishing particle size may be called intrinsic: the band structure splits insert discrete levels [1] and there is a fluctuating increase of the ionization potential from the bulk metal to the single atom value [2]. The perturbation of the electronic structure by the particle environment — including at least the support — should become larger as the particle size decreases. This may be called the support effect. The modification of the electronic structure, whether caused by intrinsic or support effects, should affect the adsorption and catalytic properties of metal clusters. Indeed enhanced catalytic activities were observed on platinum clusters encaged in Y zeolites [3, 4, 5] and the effect was even more pronounced on Pt/SiO_2 with multivalent cations in the vicinity of Pt clusters [6]. The enhanced catalytic activity of platinum clusters was originally attributed to an electron deficient character of the metal [3]. Later, evidence from infra-red [7] and X-ray photoelectron [6, 8] spectroscopy was obtained in support of this electron deficiency of platinum clusters.

The present work was undertaken to confirm these previous findings by X-ray absorption spectroscopy at the platinum L_{III} edge. The onset of the L_{III} edge involves electronic transitions from 2p core levels to the empty 6s and 5d states of the valence band producing a so-called white line in the X-ray absorption spectrum. A quantitative interpretation of the platinum L_{III} white line and the complications which arise in deriving band structure from white line measurements were discussed by Stern et al. [9, 10]. The area of the white line is related to the number of unoccupied electronic levels and an estimate of band occupancy can be derived at least on a relative basis [11].

Experimental

The edge spectroscopy measurements were a by-product of a study of the fine structure of the absorption spectrum extended beyond the edge (EXAFS). These results will be reported elsewhere. Self-supporting wafers of platinum zeolite were treated at one end of a Pyrex cell and then transferred to the other end which was equipped with beryllium windows. Absorption measurements were performed at room temperature on the EXAFS I spectrometer at the Stanford Synchrotron Radiation Laboratory. The intensity of the monochromated X-ray beam was measured before and after passing through the sample by argon-purged ionization chambers. Typically, the spectra were recorded with an integration time of 4 s/point with 300 steps covering a 30 eV region centered on the edge. In order to minimize any thickness effects which would hamper the comparison of the white lines of different samples, all wafers had approximately the same thickness, about 70 mg of zeolite or about 8 mg of platinum per cm^2.

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Shifts of the edge position (in Fig. 1 taken to be the inflection point *i* in the rise at the edge) with respect to that for a platinum calibration foil were obtained by differentiating numerically the absorption curves. The spectra were then normalized to an absorption step of one by dividing each point of the curve by the absorbance value at the foot of the white line (point b in Figure 1). The white line area was then taken as the area under the curve and above an absorbance of unity (shaded region in Figure 1).

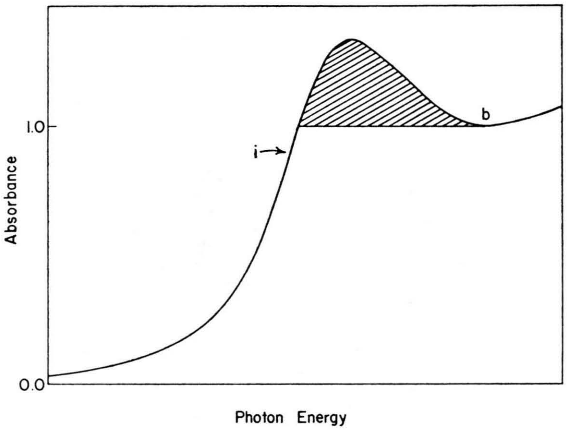

Fig. 1. Typical L_{III} edge spectrum of Pt. Edge position is inflection point (i). The shaded region is integrated to yield the white line area.

The preparation of zeolites I ($Pt_{8.7}Na_{37.2}H_{1.4}Y$) and II ($Pt_{8.1}Na_{22.6}H_{17.4}Y$) has been described previously [13]. Zeolites III ($Pt_{7.1}Na_{8.5}H_{33.3}Y$) and IV ($Pt_5Ce_9Na_{13}H_6Y$) were prepared like zeolite I but starting from NH_4NaY and CeNaY respectively. As shown previously [3, 14, 15] the final platinum dispersion can be controlled by proper activation and reduction treatment. Treatment A (activation in O_2 and reduction in H_2 at 623 K) gives platinum clusters fitting into the supercages (upper size limit 1.3 nm). Treatment B (activation in O_2 at 623 K and in vacuum at 873 K, reduction in H_2 at 523 K) gives mostly isolated zerovalent platinum, Pt^0 atoms trapped in sodalite cages. Treatment C includes treatment B followed by heating at 973 K in vacuum; it produces the migration and sintering of the Pt^0 atoms into 2.5—3 nm crystallites occuluded in the bulk of zeolite crystals. The X-ray absorption spectra were taken with the samples kept under hydrogen or oxygen.

Results and Discussion

Table 1 gives the sample characteristics, the areas of the white lines relative to that of 3 nm crystallites and values of the edge shift with respect to a platinum foil. To a first approximation an increase in the relative area of the white line corresponds to a decrease in population of the 6s and to a larger extent, of the 5d states in the valence band. A shift of the absorption edge toward higher energies implies a larger positive charge on the metal. There is obviously a close correlation between white line area and edge shift since both reflect a lowering of the electron population in the valence band. For the sake of brevity, the samples will be compared in terms of a qualitative measure of this lowering called electron deficiency (ED).

Table 1. Edge shifts and white line areas of L_{III} absorption edges.

Sample[a] (particle size)[b]	Gas adsorbed[c]	Edge shift[d] (eV ± 0.3)	Relative areas of white lines[e]
Particle size change			
PtNaY (3 nm) IC	H_2	0	1.0
PtNaY (1 nm) IA	H_2	0	1.2
Cation change			
PtNaY (1 nm) IC	H_2	0	1.2
PtNaHY (1 nm) IIA	H_2	0.6	1.3
PtNaCeY (1 nm) IVA	H_2	0.5	1.5
Effect of oxidation			
PtNaY (1 nm) IC	H_2	0	1.2
	O_2	0.2	1.8
PtNaHY (1 nm) IIA	H_2	0.6	1.3
	O_2	0.8	1.7
	O_2 (773 K)	1.1	4.0
PtNaCeY (1 nm) IVA	H_2	0.5	1.5
	O_2	1.1	2.3
	O_2 (773 K)	1.5	4.3
Platinum located in sodalite cages			
PtHNaY (atoms) IIIB	H_2	1.2	1.3
	O_2		1.3

[a] Roman numerals refer to zeolite composition; A, B, C refer to treatment type (see text).

[b] cr stands for 3 nm crystallites, cl for clusters, ia for isolated atoms.

[c] At 298 K unless otherwise specified, and at atmospheric pressure.

[d] Edge shift with respect to Pt calibration foil, positive toward higher energy.

[e] White line area relative to that of 3 nm crystallites under H_2.

The clusters covered by hydrogen in samples IA, IIA and IVA are all electron deficient with respect to the 3 nm crystallites in IC but there are substantial differences among these clusters. The ED of the platinum in sample IIA is larger than in sample IA either because the clusters in IIA are smaller than those in IA [13] or because the support in IIA is more acidic than in IA favoring electron transfer from the metal to the support. The presence of Ce^{3+} ions in sample IVA increases markedly the ED; this is probably due to the high electronic field associated with the cation in the vicinity of the encaged cluster (there is statistically at least one Ce^{3+} ion per supercage). Under oxygen at 298 K the ED of the clusters increases dramatically because the electro-negative oxygen atoms interact strongly with the platinum atoms, displacing them from their positions in the reduced state [13]. This trend to higher ED is continued in sample IVA, possibly due to the presence of Ce^{4+} as well as Ce^{3+} in the zeolite. Heating at 773 K in oxygen increases the electron deficiency of platinum in IIA and IVA. The behavior of isolated platinum atoms in IIIB is very different from that of the clusters. The ED is especially noticeable with regard to edge shift, however no increase in white line area was observed upon contact with oxygen. This lack of effect of oxygen gives further evidence to an earlier conclusion that isolated platinum atoms are located in the sodalite cages [16] where they are inaccessible to oxygen because of the limited aperture (0.22 nm) of the six-membered oxygen rings forming the windows to the sodalite cages.

Conclusion

The results obtained by X-ray absorption show that the electronic properties of very small platinum particles change with size and with environment, but it is not possible to estimate the relative importance of intrinsic and support effects. Both induce an electron deficient character in the metal. The present findings confirm the original conclusion derived from enhanced catalytic cativity [3]. Particularly noteworthy is the effect on electron deficiency of multivalent cations present on the support. This effect was also reported to enhance catalytic activity [3]. Cations may have a role per se in catalytic processes but they also modify the electronic properties of the metal as shown in the present work. This work confirms that isolated atoms — or at most minute groups of atoms — are located in sodalite cages and cannot react with oxygen.

Finally, it must be noted that the main effect reported here, namely the effect of metal-support interaction on the electronic structure of the metal with enhancement of the catalytic activity of the latter was first proposed twenty years ago by G.-M. Schwab and coworkers [16].

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