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LETTERS TO THE EDITORS

Net Charge on Platinum Clusters Incorporated in Y Zeolite

Gallezot *et al.* have reported a PtL_3 absorption edge study (*1*) of 1-nm platinum clusters located in the super cages of NaY, NaHY, and NaCeY zeolites. Their analysis of the absorption edge data led them to the conclusion that despite reduction these clusters are electron deficient due to their small size and due to their interaction with cations other than sodium. This conclusion does not agree with an earlier study (*1*) of a sample containing 60% of its reduced platinum in the form of 1-nm clusters located in the super cages of CaY zeolite. This study led to the conclusion that the platinum bears no charge despite the small size of the platinum and the presence of divalent calcium ions. The object of this letter is to show that the conclusions differ because of the method of analysis of edge data.

Samples of Gallezot *et al.* were examined under atmospheres of hydrogen and oxygen. None was examined under an inert atmosphere to avoid hydrogen's effect on platinum's absorption spectrum (*2, 3*). The analysis by Gallezot *et al.* can be followed by examining Fig. 1a. They normalized their spectra to an absorption step of 1 by dividing each point of the curve by the absorbance at the foot of the white line, point b. Absorption spectra were then compared as to area of the white line, BPb, and as to position of the edge as determined by an inflection point, i. These two parameters were correlated with changes in electron population of platinum's valence band. In particular, an increase in white line area with a shift in edge position toward higher energies was used to indicate a loss of electrons from the band and, hence, electron deficiency.

The following should be considered when using the analysis of Gallezot *et al.* A plot of data from their Table I shows no systematic correlation between edge shift and white line area. White line area by itself is not indicative of electron deficiency. Thus, the spectrum of argon (*4*) contains an intense white line. Argon is not electron deficient. The difficulty in relating white line area to platinum's charge state is that an area increase can be due to either a larger absorbance at P of Fig. 1a or to a smaller absorbance at b. It is important to distinguish these. A larger absorbance at P is always due to formation of electron-deficient platinum from metal via oxidation of electron-deficient platinum from metal via oxidation or chlorination (*3*). Lower absorbance at b can be due to electron deficiency. However, in the absence of increased absorbance at P, lower absorbance at b is indicative only of platinum clusters of small size (*3*).

One can distinguish between causes for white line area increase by using the analysis employed in (*2*). The analysis is based on a comparison of catalyst platinum absorption with that of bulk metallic platinum foil. The P of Fig. 1a is equivalent to −36 sec in Ref. (*2*); b is equivalent to −96 sec in Ref. (*2*). The comparison in the NP range of Fig. 1a is given as a parameter $\Delta A/A_3$:

$$\Delta A/A_3 = \frac{\Delta U_{Pt} - \Delta U_f}{\Delta U_f}. \qquad (1)$$

ΔU_{Pt} is the change in mass absorption coefficient of catalyst platinum absorption coefficient for a given change in X-ray wavelength. ΔU_f is the change in mass absorption coefficient for the foil for the same change in X-ray wavelength. $\Delta A/A_3$ is related to the net charge on platinum atoms. The comparison of absorption coefficients to determine platinum's net

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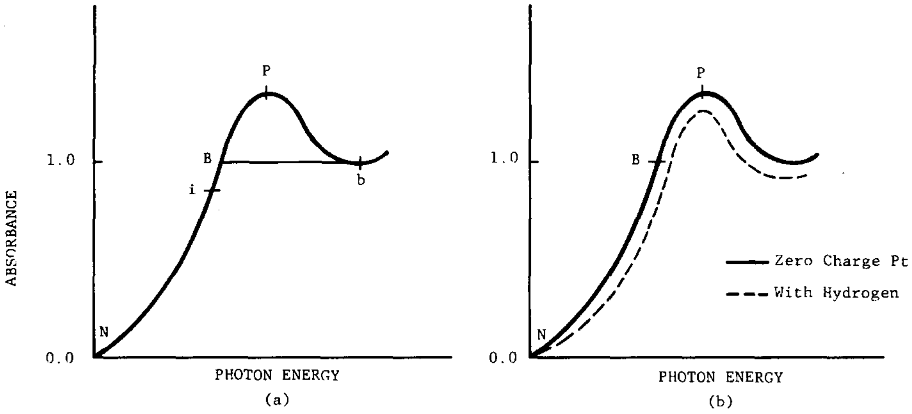

FIG. 1. (a) Schematic plot of platinum's absorption edge spectrum; (b) comparison of spectra with and without hydrogen.

charge is based on the contention of Mott and Jones (5) that the coefficients depend in part on the number density of electron-empty energy states. Thus, a loss of platinum electrons due to oxidation increases this density and leads to increased platinum absorption coefficients. This interpretation is supported qualitatively (3) by showing that the absorption coefficients for well-reduced and degassed catalyst platinum are coincident with those of bulk metal in the NP range of Fig. 1a, i.e., $\Delta A/A_3$ is 0. Contact of platinum with electron acceptors, such as oxygen or chlorine, causes ΔU_{Pt} to be larger than ΔU_{f} and $\Delta A/A_3$ to be positive. Contact with hydrogen, an electron donor, causes ΔU_{Pt} to be smaller than ΔU_{f} and $\Delta A/A_3$ to be negative.

The relation between absorption coefficient and platinum's net charge has been made quantitative by using spectra of K_2PtCl_6, K_2PtBr_6, and K_2PtI_6. The net charge on the platinum in this series has been shown to decrease from positive to negative using electron quadrupole resonance (EQR) (6). The relation between EQR and edge data is linear and leads to a relation between net charge on the platinum, Z, and $\Delta A/A_3$:

$$Z = 3.3\Delta A/A_3. \tag{2}$$

The error in the proportionality constant is ±0.5.

The comparison of mass absorption coefficients, U, of catalyst and bulk platinum at b is made using D_{96}:

$$D_{96} = [U_{\mathrm{f}} - U_{\mathrm{Pt}}]_{96}. \tag{3}$$

where f refers to bulk metal and Pt refers to catalyst platinum. D_{96} is sensitive to the charge state of platinum, the presence of platinum clusters smaller than 1.5 nm, and the presence of the intense, negative zeolitic electric field. The percentage of platinum smaller than 1.5 nm, X_{15}, was determined by summing the percentage of platinum smaller than 0.7 nm that dissolves in HF and the percentage of acid-insoluble platinum of size 0.7–1.5 nm. The last was obtained by X-ray diffraction line profile analysis (7). For platinum supported on nonzeolitic supports,

$$D_{96} = 0.19 X_{15} + 2.0. \tag{4}$$

The equation for platinum supported on A and Y zeolites is also linear, but has a larger slope:

$$D_{96} = 0.69 X_{15} + 4.1. \tag{5}$$

The errors in slope are ±0.03 and ±0.02, respectively, for the two equations.

The lower absorbance at b due to small platinum size can be rationalized. At b, the photon excitation is such that the excited electron leaves its parent atom to interact with its neighbors. The absorbance is thus determined by the factors that govern the extended X-ray absorption edge fine structure (EXAFS): the number and type of atoms that surround each excited atom (*8*). Whereas essentially all platinum atoms in bulk metal have a full complement of neighbors, small clusters of platinum contain an appreciable number of atoms that do not have a full complement. Thus, one is comparing the probability of exciting an electron to a position within platinum metal to a different probability of exciting an electron out of a platinum cluster. In the case of zeolite-supported platinum clusters, this probability is apparently affected further by the excited electron's interaction with the intense, only partially shielded negative field of the zeolite.

The analysis just described and used in (*2*) showed that the mass absorption coefficient at P for Pt/CaY is not larger than that of the bulk metal and that the increase in white line area is entirely due to a marked decrease in absorbance at b. The absorption data for this catalyst's platinum coincide with those of bulk metal in the NP range. The determined value of $\Delta A/A_3$ is $+0.02 \pm 0.07$. The charge platinum bears is zero to within the experimental error.

Another difficulty that the interpretation of Gallezot *et al.* may lead to may be seen in Fig. 1b, a schematic comparison of the absorption spectra of metallic platinum and platinum exposed to hydrogen. The analysis of Gallezot *et al.* using the inflection point i indicates a platinum edge shift, suggesting platinum exposed to hydrogen is electron deficient. The decreased absorbances, however, indicate electron-rich platinum.

Because of the above considerations, there is some doubt that Gallezot *et al.* have shown that 1-nm-size platinum clusters in contact with Y zeolite or its cations are electron deficient.

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