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Reply to the Comments of P. H. Lewis "Net Charge on Platinum Cluster Incorporated in Y Zeolite"

P. H. Lewis helped pioneer the use of X-ray absorption spectroscopy (XAS) to study samples of catalytic interest (*1–4*), notably platinum supported on Y-type zeolite (*1*) which was referred to by one of us shortly after it appeared (*5*). We regret the omission of Ref. (*1*) from the reference list of our recent paper (*6*) which also dealt with an XAS investigation of samples of Pt/Y. That paper described the use of edge position and threshold peak area of platinum L_{III} absorption spectra as measures of local electron density on the metal. For reduced, hydrogen-covered platinum in Y zeolites we found that the L_{III} threshold peak increases slightly in area compared to that of bulk platinum when the metal particle size is small enough so that the clusters are in the zeolite supercages with sodium as charge-compensating cations. A further increase in peak area and a shift of the L_{III} edge to higher energy were noted when protons or multivalent charge-compensating cations are present in the zeolite. For these acidic samples, both features of the absorption edge were interpreted to mean that platinum becomes electron deficient, a conclusion suggested also by infrared and X-ray photoemission spectroscopy, by enhanced catalytic activity of the platinum clusters, and by increased resistance of zeolite-supported platinum to sulfur poisoning (for a recent review of the Pt/Y system see (*7*)). In his earlier XAS study of zeolite-supported platinum (*1*), Lewis analyzed his absorption data in a manner different from ours and concluded that platinum particles supported on CaY, after reduction and evacuation, were not electron deficient compared to bulk metal. He also claimed that exposure of the reduced particles to hydrogen rendered them electron rich. He suggests in his comment (*8*) that his conclusions and

TABLE 1

Comparison of Indications of Electron Deficiency on Pt

Sample[a]	Activity for hydrogenolysis[b]	Binding energy of Pt core electrons[c]	Charge transfer to zeolite[d]	Pt L_{III} edge shift[e] (eV)	Pt L_{III} peak area[e]	$\left(\frac{\Delta A_3}{A}\right)^f$
Pt	Normal	Normal	—	0.0	1.0	0.0
Pt/NaY	Normal	Normal	Small	0.0	1.06	0.05
Pt/CaY	Enhanced	—	—	0.3	1.3	0.04
Pt/HY	Enhanced	Increased	Large	0.6	1.6	0.07
PtO_2	—	—	—	2.3	6.5	1.45

[a] See Ref. (*6*) for descriptions of the Pt/Y samples. PtO_2 refers to Adams' catalyst.

[b] Dalla Betta, R. A., and Boudart, M., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 2, p. 1329. North-Holland, Amsterdam, 1973.

[c] Foger, K., and Anderson, J. R., *J. Catal.* **54,** 318 (1978).

[d] Vedrine, J. C., Dufaux, M., Naccache, C., and Imelik, B., *J. Chem. Soc. Faraday Trans. I* **74,** 440 (1978).

[e] See Refs. (*6*) and (*11*).

[f] Calculated on the spectra reported in Ref. (*11*) according to Lewis' procedure given in Ref. (*8*).

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ours differ because of differences in data handling.

Unfortunately there has been no theoretical work which directly and quantitatively answers the question of how best to analyze X-ray absorption edge data for platinum in order to obtain chemical information like local charge density on the metal. Quantum mechanical calculations for simpler systems have been performed (*9, 10*) and extensions of the work are promised. It would seem prudent to limit discussion of the relative merits of methods for interpreting XAS edge data, which at this time could only be argued heuristically and qualitatively, until a reliable theoretical framework appears. Empirically, we note that the measures of electron density employed by us in (*6*) and (*11*) correlate well with independent spectroscopic and chemical evidence for electron deficiency on clusters of platinum in the supercages of acidic Y zeolites. However, when we analyze our XAS data according to the scheme described by Lewis (*8*), his parameter, $\Delta A_3/A$, does not differentiate among the samples of Pt/Y (see Table 1). Thus we prefer our own procedure of handling the spectral data.

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