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Determination of *d*-Band Occupancy in Pure Metals and Supported Catalysts by Measurement of the L_{III} X-Ray Absorption Threshold

The interesting correlation of metallic *d*-band character and catalytic activity originally proposed by Beeck (*1*) and Boudart (*2*) has presented a tantalizing enigma to catalyst chemists. If one plots the percentage *d*-character of the *bulk metal* vs atomic number and the catalytic activity of the *supported metal* vs atomic number the two curves have a similar shape (*3*), lending credence to simple electronic theories of catalysis. However, there has been no generally applicable technique for measuring *d*-electron configuration in metals or catalytic systems. This paper reports an example of the measurement of the *unfilled* *d*-bands in third period transition elements and supported Pt catalysts. In the X-ray absorption technique (*4*) the absorption coefficient vs X-ray wavelength is measured in the neighborhood of characteristic absorption edges of the element of interest. Note that there is no interference problem, the absorption transition probes only the unfilled density of states of the absorbing atom and all the other atoms in the sample are invisible unless they perturb the density of states of the absorbing atom. This ability to isolate a particular atomic species is a unique and valuable attribute of X-ray absorption spectroscopy. The results reported here are the L_{III} absorption edges which involve 2*p*-to-empty-5*d* transitions (quantum mechanically allowed, bound states). This structure near the absorption edge is distinct in origin and interpretation from the extended X-ray absorption fine structure (EXAFS) (*5*) although the samples and experimental technique are similar; indeed the edge spectroscopy appears as a bonus during EXAFS measurements. The sensitivity of the results to *d*-band occupancy and catalytic state suggest that this technique can be used *in situ* to characterize *d*-electron configuration in catalysts.

EXPERIMENTS

The experiments were performed on the EXAFS spectrometer at SSRP which has been described (*6*). The experiment produces a test beam of 10^8–10^{10} photons/sec/eV with a band width of ~1 eV. In this beam the absorption sample is inserted between two ionization chambers whose output ratio is recorded as the energy of the X-ray beam is varied through the appropriate range. The natural logarithm of the ionization chamber ratio vs energy is presented here where the zero of energy of each curve is defined as the first inflection point of the onset of absorption and was determined by differentiating the original absorption curves. The absolute magnitude of the absorption jump above the region of the threshold resonance is proportional to the amount of element present in the absorption path. A straight line was fitted 50–200 eV above the edge (beyond the threshold region) and extrapolated to below the edge to obtain the jump ratio. Each absorption curve was then normalized to unit absorption by dividing by the jump ratio. The resulting curves are shown in Figs. 1 and 2. Data for $PtCl_2$ (not shown) were nearly coincident and slightly higher in amplitude than metallic Pt. The pure metals were in the form of foils ~5 μm thick. The finely ground compounds were mixed with Duco (plastic cement), spread out on Al foil, and the final absorber was sandwiched between supporting Al foils. The catalysts were prepared by impregnating Cab-O-Sil (SiO_2) with a solution of chloroplatinic acid, drying, and reducing in H_2 at 500°C (dispersion by adsorption measurements = 80%). They were contained in a sample cell with X-ray transparent Mylar windows which was air tight. During the actual X-ray measurement the samples were in an evacuated sample chamber at 100°K.

DISCUSSION OF RESULTS

The experimental results for Au, Pt, Ir, and Ta were qualitatively as expected for *d*-band vacancies of 0, 1, 2, and 7, respectibely; i.e., the magnitude of the resonance increases. Since the transitions to the *d*-band were superimposed upon the more featureless X-ray absorption edge of elements without *d*-electron vacancies as in Au, the Au spectrum was subtracted from each curve to obtain just the absorption due to the *d*-band transitions. The peak areas and magnitudes so obtained are given in Table 1, normalized to Pt metal.

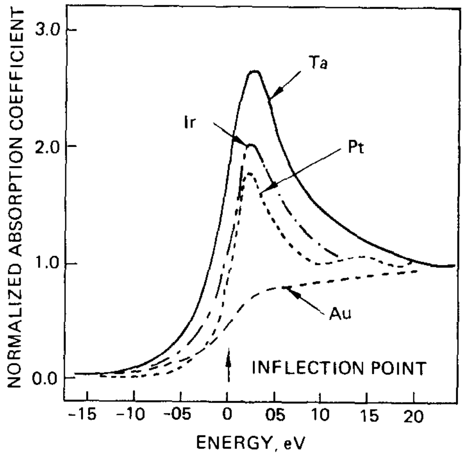

FIG. 1. X-Ray absorption spectra of Au, Pt, Ir, and Ta near the L_{III} absorption threshold. The data were normalized by fitting a straight line 50–200 eV above the peak and extrapolating to below the edge to obtain the jump ratio. Point-by-point division of the L_{III} threshold absorption curves by the jump ratio produced these curves normalized to unit absorption. The zero of energy in each case is the first inflection point after the onset of absorption obtained by numerically differentiating the spectra.

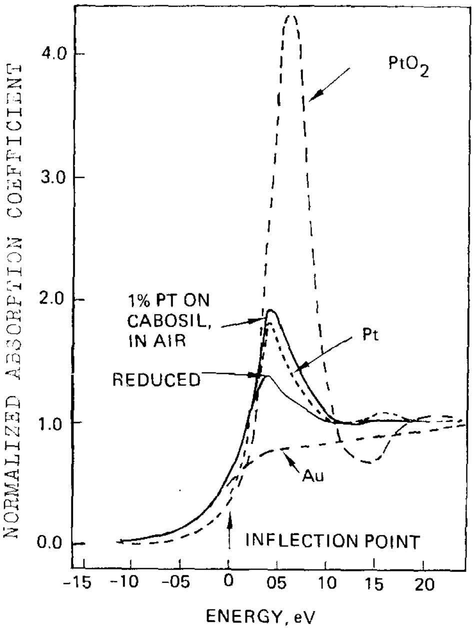

FIG. 2. X-Ray absorption spectra of Pt catalyst samples and α-PtO_2 compared to Pt and Au. Same normalization and energy scale as in Fig. 1.

Good band structure calculations for Au, Pt, and Ir are given by Smith *et al.* (*7*) and by Mathiess (*8*) for Ta. The band structure curves were graphically integrated in the region from the Fermi energy to 10 eV above. This integration contains the total unfilled density of states consisting of a broad *s*-contribution and the peaks in the band structure which are mostly *d*-symmetry. Since all the *d*-states are filled in Au with only a 6*s* vacancy, its integrated density of 0.7 electrons was subtracted from the integration for Pt, Ir, and Ta to approximately isolate the *d*-vacancies as was done with the experimental data (all in Table 1). The com-

TABLE 1

Compilation of *d*-Band Information for Pure Metals, Pt Compounds, and 1 wt% Pt on Cab-O-Sil (Silica) Catalysts

Material	Empty states (electrons/atom)			L_{III} threshold peak	
	Isolated atom *d*-electron count	Band structure integration, 0–10 eV		Area[a]	Amplitude[a]
		Total unfilled states	Unfilled *d*-states		
Au	0	0.7	0.0	0	0
Pt	1	1.5	0.8	1.00	1.0
Ir	2	2.6	1.9	1.51	1.2
Ta	7	6.5	5.8	2.74	1.8
$PtCl_2$	2			1.10	1.1
$\alpha - PtO_2$	4			2.15	3.4
1% Pt, H_2 reduced (~0.6)		Estimated from results in this table		0.69	0.6
1% Pt, exposed to air (~1.0)				1.02	1.1

[a] Au absorption edge was subtracted from each of the L_{III} edges of the other materials.

pounds $Pt^{2+}Cl_2$ and $Pt^{4+}O_2$ were assigned *d*-electron vacancies of 2 and 4 from simple valence electron considerations. The trend in the data of peak height or area with increasing *d*-vacancies is consistent although there is not a linear relationship. The decreased strength of the resonance in the catalyst and sensitivity to air is interesting and significant. Unfortunately, the exact state of the catalysts was not known and could not be accurately determined or controlled during these preliminary measurements. The original catalyst material was prepared by a 500°C reduction in flowing H_2, followed by He purging during slow cooling, then exposed to air while transferring to a sample bottle, and then to the airtight sample cell for X-ray measurements (exposed to air sample). This same sample was treated for 2 hr at 500°C in flowing H_2, cooled under H_2, and transferred to the sample cell in a dry box under dry N_2. Probably this sample retained a layer of chemisorbed H_2 (reduced sample). The decrease in *d*-band absorption with this sample could be due to interaction with the support in such a way that *d*-electron vacancies are filled, a change in Pt band structure because of the high dispersion, or contribution of electrons to the *d*-band by H atoms as in the familiar quenching of Ni ferromagnetism by H (*9*). The exact mechanism will be determined soon in an *in situ* experiment.

These preliminary results show that the technique can be applied to real catalyst systems and chemical information can be obtained by a simple interpretation. Note that all the group VIII and IB metals which are interesting catalytically will have this same degree of sensitivity to *d*-band occupancy at the L_{III} absorption threshold. For example, Bonnelle and Perrin (*10*) have observed the expected increase in the series Cu, Cu_2O, CuO and our work in progress shows the emergence of a strong threshold resonance in Au^{3+} compounds.

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