

Electron Spectroscopy for Chemical Analysis (ESCA) Intensity Ratios—a Probe of Catalyst Structure

One of the most important unknowns in studies of heterogeneous catalysts is the manner in which the catalytically active component "interacts" with the physical structure of the support material. Since ESCA (electron spectroscopy for chemical analysis) is a tool for surface characterization, the intensities of the observed electron lines reflect the surface structure of supported metals and oxides. In this communication we describe the results of ESCA measurements on rhodium/carbon catalysts which yield information about the depth of metal penetration into the internal porosity of carbon supports of greatly different physical properties. Previously, we have shown (1) that ESCA can be used to monitor changes in metal dispersion when rhodium catalysts prepared on high surface area activated charcoal are sintered.

For this work three carbon supports (all used as fine powders) with quite different physical properties were chosen, as shown in Table I. Carbon A was a low surface area, relatively nonporous graphite while carbon B was a typical microporous, high surface area activated carbon. Carbon C had a moderately high surface area but contained pores considerably larger than carbon B. Pore size distributions were obtained from nitrogen desorption isotherms using the BJH approximation (2). BET surface areas were calculated using a single point on the nitrogen adsorption isotherm. The applicability of the BJH and BET models to highly microporous solids has been discussed in the literature and, although we make no claim as to their

validity for our samples, we feel the comparative results are interesting.

Catalysts were prepared by hydrogen reduction of a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ containing the slurried carbon powder. By varying the amount of rhodium salt used, catalysts with different metal levels, nominally 3, 6 and 12.5% by weight, were prepared. The water-white filtrate obtained after fabrication indicated that all of the rhodium had been deposited on the support, and this was confirmed by elemental analysis.

ESCA spectra were measured on a Hewlett Packard 5950A spectrometer using monochromatic Al $K\alpha$ radiation. The catalyst samples were examined as smears on double-sided tape or gold plated sample mounts and the Rh/C intensity ratios were determined from the areas under the C 1s line and the Rh 3d lines using 20 eV sweeps.

As shown in Fig. 1, Rh/C intensity ratios vary directly as the metal loading, in the range studied, for each carbon support. Intensity ratio differences between the supports are pronounced and cannot be ascribed simply to differences in total carbon surface area since the results for the highest surface area support, B, are intermediate between A and C. We interpret these observations to be a direct reflection of differences in the catalysts brought about by the pore structure of the carbon supports.

Assuming a cross-sectional area of 7.6 \AA^2 for each metal atom (3), 1 g of 12.5 wt% Rh/C catalyst would contain enough metal

TABLE 1
Physical Properties of Carbon Supports

Carbon	Surface area, N ₂ BET (m ² /g)	Av pore radius from BJH distribution (Å)
A	10	—
B	850	11
C	560	53

to form a monolayer covering about 56 m². This would be sufficient to completely cover the surface of carbon A with a layer approximately 5–6 atoms (15–20 Å) thick, but would at most cover only 10% of the surface of carbons B and C. The high Rh/C intensity ratio observed for A is therefore attributed to the fact that a large fraction of the Rh is accessible for ESCA detection. Rh in the center of large Rh particles will not be observed by ESCA, however, since electron escape depths for metals are estimated to be on the order of 10–20 Å.

In our earlier work (1), we discussed the difference between the oxidation–reduction behavior of small and large rhodium clusters. Larger particles behave like bulk metal in showing an asymmetric photoelectron line due to adsorbed oxygen but not the well split oxide line exhibited by

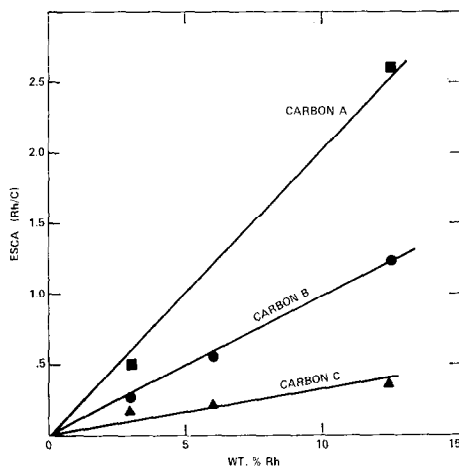


FIG. 1. Rhodium/carbon intensity ratios for catalysts on three different carbon supports.

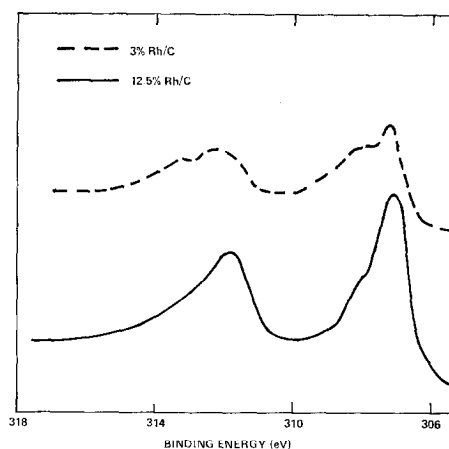


FIG. 2. The rhodium 3d electron lines observed from 3% Rh/carbon A(---) and 12.5% Rh/carbon A(—). The surface oxide component for the 12.5% Rh catalyst is somewhat more pronounced than in the case of untreated Rh foil (4).

smaller particles. Figure 2 demonstrates this effect for carbon A. The spectrum of the 12.5% Rh sample (solid curve) resembles that of bulk metal (4), while the 3% Rh sample (broken curve) shows a resolved line from a Rh₂O₃-like material indicative of smaller crystallites. For carbons B and C both metal and oxide lines are observed (1).

The highly microporous nature of carbon B could result in preferential deposition of rhodium on the outer portions of the particle during the catalyst fabrication step when soluble Rh(III) is rapidly reduced to metal. This effect should be much less important for carbon C, which contains considerably larger pores and would thus be more evenly coated with rhodium. Non-uniformity throughout a catalyst grain, greatest for carbon B, will not be directly evident from ESCA intensity ratios since such measurements reflect the composition of only the outermost portion of each particle. But the lower Rh/C intensity ratio for carbon C, at the same metal loading, is indicative of a more uniform metal distribution throughout the carbon particle and, contrary to what might be expected,

probably indicates a higher metal dispersion as well.

The determination of the metals distribution within the particles of a supported metal catalyst is an area in which ESCA can provide unique information (1, 5). The above results point out, however, that an understanding of the physical nature of the support is required for the proper interpretation of the ESCA spectra.

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Received February 26, 1976; revised September 13, 1976