JOURNAL OF CATALYSIS 32, 163–165 (1974)

The Valence Band Structure of Highly Dispersed Platinum

Recent investigations (*1–3*) of possible particle size effects in heterogeneous catalysis have been directed towards the changes in surface geometry which result when the catalyst crystallites become very small, <20 Å. One might anticipate a small particle size effect due to the electronic state of very small metal crystallites containing only a few (~10) metal atoms. The valence band structure of very small metal crystallites is expected to differ from that of an infinite crystal for a number of reasons: (a) with a ratio of surface to bulk atoms approaching unity (~20 Å diam), the potential seen by the nearly free valence electrons will be very different from the periodic potential of an infinite crystal; (b) surface states, if they exist, would be expected to dominate the electronic density of states; (c) the electronic density of states of very small metal crystallites on a support surface will be affected by the metal–support interactions. It is essential to determine at what crystallite size (or number of atoms per crystallite) the electronic density of states begins to depart from that of the infinite crystal, as the "material state" of the catalyst particle can affect changes in the surface thermodynamics which may control the catalysis and electrocatalysis of heterogeneous reactions as well as the physical properties of the catalyst particle.

In principle, it should be possible to obtain experimental valence band spectra of highly dispersed metals by photoemission. In practice, such spectra have not been obtained because very highly dispersed metals are usually obtained only on nonconductive supports and the resulting charging of the sample causes large chemical shifts and severe broadening of the photoelectron spectra. Recent development, however, by Hewlett-Packard of a charge compensating electron flood gun for the ESCA spectrometer makes the determination of reliable, unbroadened, photoelectron spectra possible. The flood gun impinges a nearly monochromatic beam of low energy electrons onto the sample such that the rate of electron capture by the sample just compensates for the rate of photoemission (*4*). The purpose of this communication is to present valence band spectra of highly dispersed platinum on silica using a Hewlett-Packard ESCA 5950A photoelectron spectrometer with the new electron flood gun.

EXPERIMENTAL METHODS

High surface area platinum supported on silica (Cab-O-Sil, EH-5, Cabot Corp.) catalyst was prepared by an ion-exchange technique similar to Benesi, Curtis, and Studer (*5*). The silica was contacted with a $Pt(NH_3)_4(OH)_2$ solution for 16 hr, then filtered and washed with excess distilled water. After air drying, the catalyst was reduced in hydrogen for 1 hr at 500°C. Chemical analysis indicated that 13.6 wt% platinum was exchanged onto the silica surface.

The platinum surface area was measured by hydrogen chemisorption in a conventional volumetric glass apparatus (*6*). The catalyst was evacuated at 10^{-5} mm Hg for 45 min at 350°C, then reduced for 1 hr at 350°C in hydrogen at 550 mm Hg. After a further heat treatment in vacuum (10^{-5} mm Hg) for 45 min at 350°C, the hydrogen chemisorption on platinum was measured at room temperature. Hydrogen chemisorption measurements under similar conditions on the uncatalyzed silica indicated negligible adsorption occurred on the support.

A platinum surface area of 320 m^2/g Pt was obtained assuming 9 $Å^2/H$ (*5*). A H/Pt ratio of 1.18 calculated from the chemisorption measurements indicated that every platinum atom is a surface atom on the

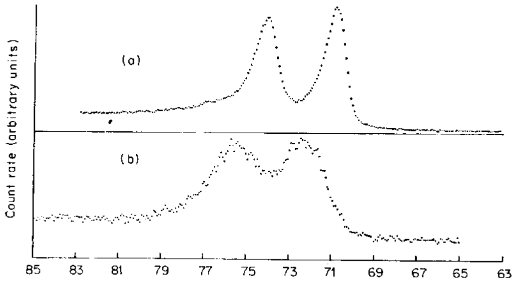

FIG. 1. X-Ray photoelectron spectra of 4*f* electrons for (a) Pt foil; (b) Pt on silica.

platinum particle and the platinum is in the "atomically" dispersed state. Following Dalla Betta and Boudart (7), we believe that this dispersion represents small platinum clusters containing approximately six atoms. Electron microscopy results indicate that there was an extremely narrow range of very small platinum particles (12–20 Å diam.) present in this catalyst. Since the resolution of the electron microscope was to about 12 Å no attempt was made to measure a platinum particle size distribution.

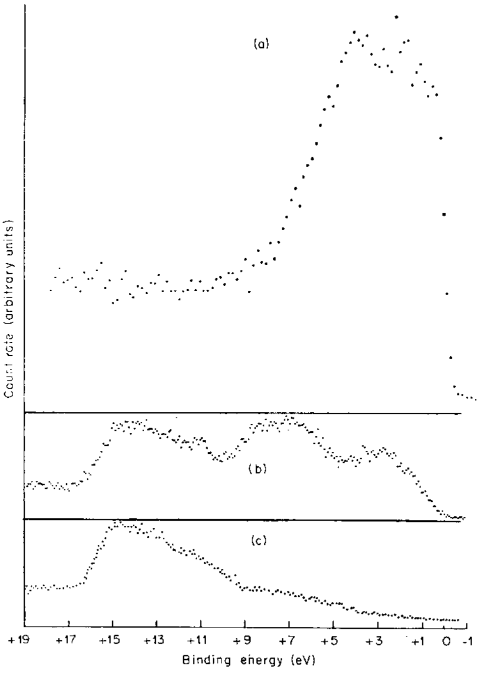

FIG. 2. X-Ray photoelectron spectra of valence band region of (a) Pt foil; (b) Pt on silica; (c) silica.

The powder was pressed into a thin disk for mounting in the spectrometer. Prior to collecting the photoemission, the sample was pretreated by a combination of high temperature hydrogen reduction and argon ion bombardment. The residual vacuum in the spectrometer sample chamber was 5×10^{-9} Torr.

The binding energy was calibrated using the *d*-band edge of a platinum foil cleaned by argon ion bombarding. Figure 1a shows the valence band spectrum of platinum foil with the Fermi level set at the *d*-band edge. With this definition of the Fermi level, the Pt $4f_{7/2}$, $4f_{5/2}$ binding energies, shown in Fig. 2a, were 70.9 and 74.2 eV, respectively. Figure 1b shows the 4*f* electron binding energies for Pt/SiO_2, Fig. 2b the valence band of Pt/SiO_2, and 2c the valence band of SiO_2. The valence band spectra have not been corrected for inelastic scattering.

DISCUSSION

The region from 10 to 17 eV of the Pt/SiO_2 spectrum is obviously due to the SiO_2 valence band, centered 14 eV below the Fermi level. The Pt 4*f* electron binding energies in Pt/SiO_2 indicate an apparent chemical shift of +1.5 eV. Most of this shift is apparently produced by partially uncompensated charging of the sample, which caused the 4*f* line widths to be increased from 1.2 eV for Pt foil to 2.5 eV for Pt/SiO_2. This charging is also reflected in the shift of the valence band edge to a point 1.5 eV below the Fermi level. It is possible that some of the chemical shift of the 4*f* levels is real, representing the platinum–silica interaction. The photoelectron spectrum of ion-exchanged Pt on graphitized Vulcan XC-72 (H/Pt = 0.4), a highly conductive support for which there should be no charging, showed a chemical shift of +0.4 eV. This would indicate a net electron transfer from platinum to the support. Such an interaction was postulated by Dalla Betta and Boudart (7) for highly dispersed platinum on silica–aluminates.

Comparing Fig. 2b with c, it is clear that the valence band region from 0 to 10 eV binding energy is due to the platinum clusters. The valence band for small platinum clusters differs significantly from that of an infinite platinum crystal, Fig. 2a, and from the theoretical density of states for Pt (*8*). Neither the theoretical density of states nor the bulk platinum valence band have the accumulation of states in the 5 to 10 eV binding energy region seen in the valence band of small platinum clusters. The free-atom relativistic Hartree-Fock energy eigenvalues for Pt $5d_{3/2}$, $5d_{5/2}$ are 12.2 and 10.5 eV vacuum referenced (*9*) or 7.2 and 5.5 eV relative to the Fermi level. Moore's (*10*) tabulation, however, of free-atom spectra indicates the *d* electron binding energies are 3 eV lower than the calculated eigenvalues. If a +1.5 eV correction is added due to an apparent uncompensated charging of the sample, the localized free-atom Fermi referenced binding energies would be at 5.7 and 4.0 eV on the energy scale of Fig. 2. Thus, the accumulation of states observed in the 5 to 10 eV region probably do not represent atomic states that arise from localization of valence electrons in clusters containing only a few atoms. The structure in the 5 to 10 eV may be interpreted either as a surface state or as a bonding valence state representing Pt–support bonding. In either case, this structure is due to very small Pt crystallites having a large fraction of atoms as surface atoms located along metal–gas interfaces or metal–support interfaces. Superimposed over the small crystallite state is the density of states for larger clusters of platinum, since there were observed clusters up to 20 Å diam. which would contain on the order of 100 to 300 metal atoms. Judging from the measured width of the valence band, it seems likely that the electronic density of states for these larger clusters has the same gross features as that of bulk platinum, and that clusters 20 Å and larger have the same electronic properties as the bulk metal.

The interpretation of these results is still in the formative stage. We are currently attempting a calculation of the electronic density of states by the multiple scattering, x-α, method of Connolly and Johnson (*8*), using the computer program of J. W. Connolly, for octahedral platinum clusters containing 6, 19 and 44 atoms, covering a particle size range of 6–12 Å. It is hoped that these calculations will reveal the nature of surface states, if any, and the particle size at which the localization of the valency electrons takes place. For corroboration of the theoretical density of states, valence band spectra from an even narrower distribution of crystallite sizes than presented here are required.

ACKNOWLEDGMENT

We thank Howard Harrington and the Hewlett-Packard company for use of the HP 5950A ESCA spectrometer with the electron flood gun.

REFERENCES

1. POLTORAK, O. M., AND BORONIN, V. S., *Z. Fiz. Khim* **40**, 2671 (1966).

2. ANDERSON, J. R., AND SHIMOYAMA, Y., *in* "Proceedings of the Vth International Congress on Catalysis" paper No. 48, North-Holland, Amsterdam, 1973.

3. BETT, J., LUNDQUIST, J., WASHINGTON, E., AND STONEHART, P., *Electrochim. Acta* **18**, 343 (1973).

4. HARRINGTON, H., HEWLETT-PACKARD, private communication.

5. BENESI, H. A., CURTIS, R. M., AND STUDER, H. P., *J. Catal.* **10**, 328 (1968).

6. BETT, J. A. S., KINOSHITA, K., ROUTSIS, K., AND STONEHART, P., *J. Catal.* **29**, 160 (1973).

7. DALLA BETTA, R., AND BOUDART, M., *in* "Proceedings of the Vth International Congress on Catalysis" paper **100**, North-Holland, Amsterdam, 1973.

8. CONNOLLY, J. W. D., AND JOHNSON, K. H., MIT Solid and Molecular Theory Group Report No. 72, 1970; and JOHNSON, K. H., *Phys. Rev.* **152**, 429 (1966).

9. MANN, J. B., Los Alamos Scientific Laboratory Rept. LA No. 3690, 1972.

10. MOORE, C., "Atomic Energy Levels," Vol. 3, p. 101. Nat. Bur. Stand. Circ. 467, Washington, DC, 1958.

PHILIP N. ROSS
KIM KINOSHITA
PAUL STONEHART

Materials Engineering and
Research Laboratory
Pratt & Whitney Aircraft
Middletown, Connecticut 06457

Received July 23, 1973