JOURNAL OF CATALYSIS 32, 159–162 (1974)

Pt X-Ray Emission Spectra of Platinum Catalysts Supported on Silica

X-Ray emission spectroscopy seems to have been ignored so far as a possible tool to study the chemisorption of H_2 or O_2 on highly dispersed platinum catalysts. The advantage of X-ray emission spectroscopy over more specific surface methods like Auger or photoelectron spectroscopy lies in the fact that with the former method the depth of information is of the order of microns. In the case of catalysts containing only a few percent of platinum it is quite useful to be able to integrate over a larger total sample volume and thus enhance the signal intensity.

It is known, mainly from studies of the lighter elements, that X-ray emission lines due to electronic transitions between core levels may exhibit chemical shifts when the oxidation state or the nature of the ligands are changed (*1*, *2*). The reason for this is that any changes in the electron density distribution in the valence band will also cause the core level binding energies to be shifted by some variable amount. Thus the energy difference between two core levels and, hence, the wavelength of an associated X-ray emission line may be different for a pure metal and its compounds. The shifts normally observed in X-ray spectroscopy, however, are of the order of a few electron volts at most.

If, for highly dispersed Pt, there should be any noticeable wavelength shift due to surface Pt–O or Pt–H, such a shift is most likely to be found among X-ray lines which are due to electronic transitions between low-lying core levels. In the present study attention was therefore focused upon the M-series of platinum corresponding to N–M transitions.

EXPERIMENTAL METHODS

Two silica-supported Pt catalysts were studied. The sample preparation is described elsewhere (*3*). The samples contained 3.7 and 2.3% platinum metal by weight. They will subsequently be referred to as $D14$ and $D62$, since their degree of dispersion D, as defined by the ratio of the number of surface atoms (able to form surface Pt–O or Pt–H) to the total number of metal atoms (*4*), was 14 and 62%, respectively. The calculated average crystallite size was therefore 60 and 12 Å diameter.

A piece of polished Pt metal was used to obtain the spectra from bulk platinum. The catalyst powders were compressed in a multihole stainless-steel micromold assembly (*5*) with a pressure equivalent to about 2000 kP/cm^2. Sufficiently flat surfaces were thus obtained. Aluminum was evaporated onto the surface to a thickness of about 1000 Å in order to avoid charging of the sample under the electron beam.

An ARL electron beam microprobe was used and run at 15 kV, 0.1 μA. In order to keep the electron flux density low and to avoid local heating of the sample the beam was defocused to a diameter of about 200 μm. The vacuum in the sample compartment was of the order of 10^{-5} Torr. A cylindrically bent ADP crystal (ammonium dihydrogen phosphate) with $2d_{101} =$ 10.64 Å served as an analyzer.

At first spectra were taken of the untreated catalysts, which, after having been exposed to air for long time, can be assumed to be fully oxidized Pt–O at the surface. Subsequently the sample compartment was flushed with dry hydrogen for about 20 min at room temperature in order to make Pt–H. The removal of the oxide layer might not have been complete by this treatment since the catalyst particles were tightly compressed and, in addition, covered with the conductive aluminum layer. Also the possibility of Pt–OH formation cannot yet be excluded on the basis of the present preliminary experiments.

Results and Discussion

The most intense lines of the M series, $M\alpha_{1,2}$ and $M\beta$, due to $4f_{7/2,5/2} \rightarrow 3d_{5/2}$ and $4f_{5/2} \rightarrow 3d_{3/2}$ transitions, respectively, did not show any noticeable shifts when the spectra of bulk Pt metal and of supported Pt catalysts were compared. However, two weak doublets $M\zeta_{1/2}$ and $M\gamma$ were formed which did show surprising large differences. All other lines of the M series were either too weak to be studied successfully or obscured by some nearby silicon emission lines.

The $M\zeta_{1,2}$ doublet at 7.738 and 7.790 Å, corresponding to 1602 and 1591 eV, respectively, is due to $4p_{3/2} \rightarrow 3d_{3/2}$ and $4p_{1/2} \rightarrow 3d_{3/2}$ transitions, the intensity ratio of which should be approximately 2:1. In Fig. 1 the $M\zeta_{1,2}$ doublet of bulk Pt-metal (top) is compared with typical $M\zeta_{1,2}$ profiles from the $D14$ and $D62$ samples before and after hydrogenation. In the spectra of both catalysts the $M\zeta_{1,2}$ line of bulk Pt metal can still be seen, but in addition there is a new line at about 1609 eV. This line is shifted to higher energies with respect to bulk Pt metal. It sharpens and increases in intensity upon H_2 treatment.

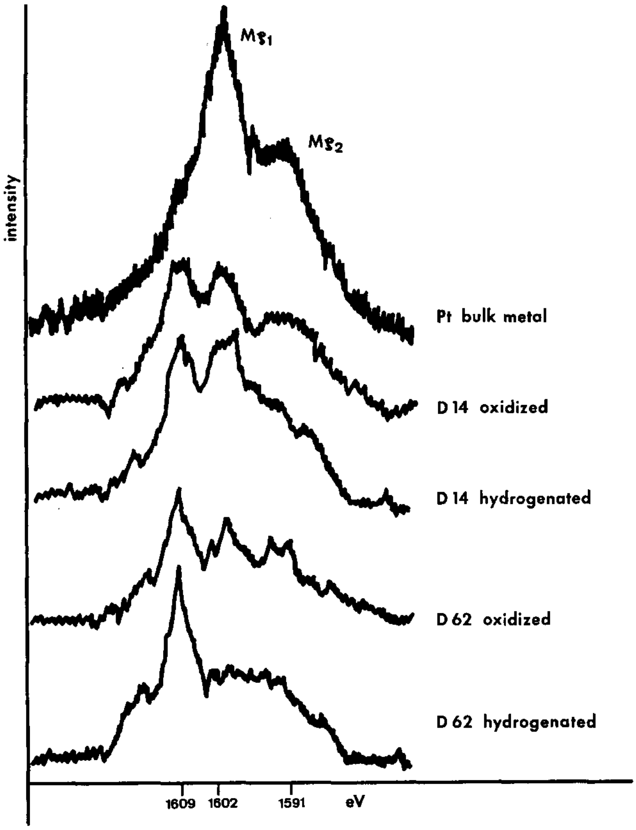

FIG. 1. The Pt $M\zeta_{1,2}$ doublet of bulk Pt metal and silica-supported Pt catalysts $D14$ and $D62$, e.g., 14%, respectively, 62% dispersed.

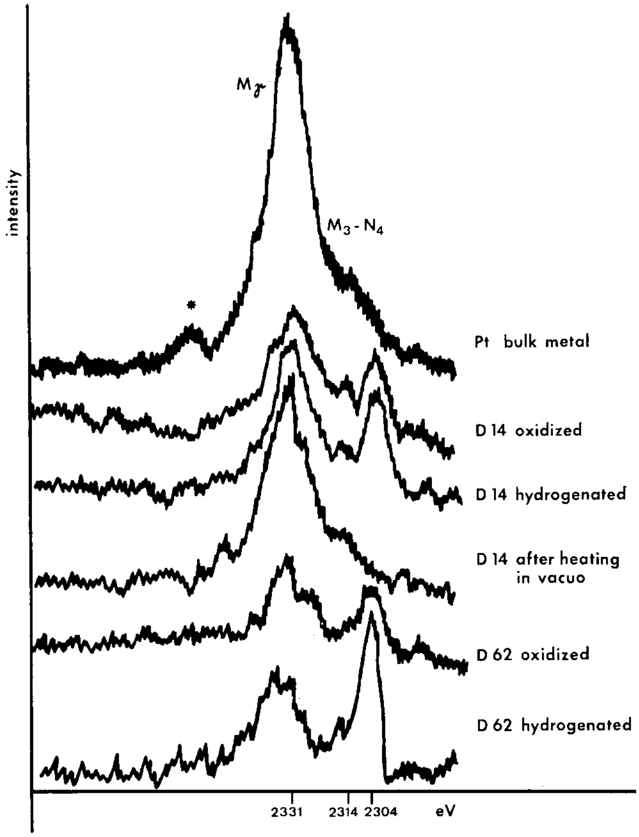

FIG. 2. The Pt $M\gamma$ line of bulk Pt metal and silica-supported Pt catalysts $D14$ and $D62$, e.g., 14%, respectively, 62% dispersed.

The new line at 1609 eV is moderately intense in the case of the $D14$ sample, e.g., for the sample with 14% of its Pt atoms at the surface. In the case of the more highly dispersed $D62$ sample the intensity of the 1609 eV line is higher than the intensity of the $M\zeta_{1,2}$ doublet of the Pt metal. After hydrogenation of the $D62$ sample the new line becomes most prominent, while at the same time the bulk metal doublet is reduced to a broad diffuse hump.

Tentatively this new line at 1609 eV can be assigned to a $M\zeta_1$ line or $4p_{3/2} \rightarrow 3d_{3/2}$ transition originating from surface Pt atoms in a bound state, either as Pt–O or Pt–H.

The $M\gamma$ line at 5.319 Å or 2331 eV is due to a $4d_{3/2} \rightarrow 3p_{3/2}$ transition making a doublet with the weak M_3–N_4 line at 5.357 Å or 2314 eV, due to a $4d_{5/2} \rightarrow 3p_{3/2}$ transition. In Fig. 2 the $M\gamma$ doublet of bulk Pt metal (top) is compared with typical spectra of the $D14$ and $D62$ samples.* Again an additional line is found in the spectra from the highly dispersed Pt catalysts, but this time the new line is shifted to lower energies by as much as 27 eV with respect to $M\gamma$ of Pt bulk metal. The line lies at 2304 eV. It sharpens and increases in intensity upon H_2 treatment. Comparing the spectra of the $D14$ and $D62$ samples, the intensity ratio between $M\gamma$ of Pt bulk metal and this new line reflects reasonably well the degree of dispersion and lends support to the assump-

---

* The weak line marked with an asterisk is an artefact due to the P absorption edge in the analyzing crystal.

tion that this line too is due to surface Pt atoms in a bound state, either as Pt–O or Pt–H.

One crucial experiment to ascertain the nature of this new line is to heat the hydrogenated Pt catalyst, since Pt–H is known to decompose *in vacuo* at about 450°C yielding Pt metal. The heating was carried out *in situ* by increasing the electron beam current and exposing the same sample area to the electron bombardment for an extended period of time. The 2304 eV line was found to decrease soon in intensity and to vanish completely after some time as shown in Fig. 2 by the fourth curve from the top. Thus, a further piece of evidence is added to support the conclusion that surface Pt atoms in a bound state are responsible for this very strongly shifted $M\gamma$ X-ray emission line.

A possible explanation for the large shifts observed might be drawn from the fact that chemically strongly bound surface layers such as Pt–O and Pt–H can be treated as dipole layers, exerting strong influences upon the closed shell Pt $4p$, $4d$ and/or Pt $3p$, $3d$ levels. It is, however, surprising that the Pt $4f$ level seems not to be influenced at all as shown by the absence of any noticeable shift in the position of the Pt $M\alpha_{1,2}$ and $M\beta$ lines. Preliminary attempts failed to observe directly the shift of the $4d_{3/2}$ level (involved in the $M\gamma$ line) by measuring the extremely soft weak N_4–N_6 X-ray line due to an inner-shell $4f_{5/2} \rightarrow 4d_{3/2}$ transition. Even though this line could be seen in the recorded spectrum of bulk Pt metal at the expected wave length of 48.1 Å, corresponding to 258 eV, it was consistently absent in the case of the highly dispersed Pt catalysts. Further studies are under way.

ACKNOWLEDGMENTS

This work was carried out during a short stay at the Dept. of Chemical Engineering of the Stanford University. I thank Professor Michel Boudart for supplying the Pt catalyst samples. Professor R. A. Huggins gave permission to use the ARL microprobe, and Dr. Charles Taylor gave his very valuable assistance in obtaining the spectra.

REFERENCES

1. SANDSTRÖM, A. E. *in* "Handbook of Physics" (S. Flügge, ed.), Vol. 30, pp. 158ff. Springer Heidelberg, 1957.

2. LÄUGER, K., *J. Phys. Chem. Solids* **32**, 609 (1971).

3. SCHLATTER, J. C., AND BOUDART, M., *J. Catal.* **25**, 93 (1972).

4. BENSON, J. E., AND BOUDART, M., *J. Catal.* **4**, 704 (1965).

5. Designed by Dr. Charles M. Taylor, Dept. Geology Stanford University, Stanford, CA 94305.

FRIEDEMANN FREUND

Mineralogisch-Petrographisches Institut
Zülpicher Strasse 49
D-5000 Köln 1, West Germany
Received June 8, 1973