JOURNAL OF CATALYSIS 92, 211–215 (1985)

Study of Supported Platinum Catalysts by Anomalous Scattering

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Received June 7, 1984; revised September 30, 1984

Platinum metal catalysts supported on silica gel and alumina have been examined by wide-angle anomalous X-ray scattering at the Cornell High Energy Synchrotron Source. Complete removal of the support background features is achieved by this method, eliminating errors due to inaccurate background estimation. Platinum diffraction patterns from very high percentage metal exposed catalysts have been obtained for the first time, as well as from platinum supported on alumina. This technique is suitable for examining catalysts under working conditions and is superior to EXAFS for determinations of particle morphology and size distribution. © 1985 Academic Press, Inc.

INTRODUCTION

Wide-angle X-ray scattering has proved to be a very powerful tool in the structural characterization of supported metal catalysts, as numerous studies on platinum (*1–3*), palladium (*4*), and alloys (*5*) supported on silica have shown. A wide range of structural parameters can be obtained, such as catalyst particle size, shape, size distribution, lattice parameter, and atomic vibrational amplitudes of the metal particles, as well as structural changes with changing pretreatment and working conditions. This information is extracted from the positions, shapes, and intensities of the Bragg peaks due to the metal particles and is of crucial importance in the understanding of catalytic activity.

Unfortunately, the ordinary X-ray scattering methods are not atom selective, so that the scattering effects from the metal particles and the support superpose. They can be separated reliably only if the catalyst particle peaks are sufficiently sharp and the scattering from the support sufficiently featureless. There are many important cases, where these conditions are not met. With decreasing particle size, the Bragg peaks broaden and, with particle sizes less than about 15–20 Å, they effectively blend with the support background. At this point, it is difficult to know if the structure of the small particles is crystalline, amorphous, or a different close-packed geometry, as postulated for free metal clusters of a few atoms (*6*). Also, catalysts supported on alumina, regardless of metal particle size, have until now resisted this type of analysis, since alumina, even though poorly crystallized, gives a sharp-featured, intense scattering pattern, whose main peaks overlap many of the metal peaks.

Another experimental technique, which is atom specific and can give structural information about supported metal catalysts is the Extended X-ray Absorption Fine Structure analysis (EXAFS). There is fairly extensive literature on the pros and cons of EXAFS and we will not go into any details here (see, for example, Ref. (*7*) for typical applications of EXAFS in studies of supported metal catalysts). We merely want to point out that EXAFS can only give structural information on the atomic level, but very limited and indirect information on the morphology of the catalyst particles, such as size, shape, crystalline perfection, etc.

It is another technique that we want to describe here, that of anomalous scattering, which appears to be eminently suited to studies of supported metal catalysts. This

0021-9517/85 $3.00

technique is based on the fact that the scattering contrast of a particular atomic species changes significantly when the energy of the scattered photons approaches one of the absorption edges of this species. The pertinent theory has been presented by Fuoss *et al.* (*8*) and is applicable to any atomic configuration involving the anomalously scattering species. Supported metal catalysts present a simpler case, at least to a first approximation: The difference between two scattering patterns, one for a photon energy very near the metal absorption edge and one a few tens of eV away, will be the scattering pattern of the metal particles alone, weighted by the contrast change of the metal atoms. The scattering from the support cancels out, since it does not change appreciably for small changes in photon energy. This same technique could be usefully applied to separate the superimposed patterns of several phases, by using radiation near an edge of an element in each phase, not present in the others.

EXPERIMENTAL

The anomalous scattering experiments were conducted at the Cornell High Energy Synchrotron Source (CHESS), Station A3. The tunable monochromator consisted of a flat silicon (111) crystal, followed by a triangular slotted, sagitally focusing silicon (111) crystal. No mirror was available to eliminate high order reflections, which were intense at the electron energy of 5.5 GeV. A more disturbing effect was that the harmonic content of the beam was not constant, but varied with small changes in the electron orbit as a function of time.

Most of the beam path from the monochromator to the sample was enclosed in beam pipes filled with helium to reduce air absorption. The intensity of the beam was constantly monitored by means of an ion chamber of 8 cm active length, filled with 1 atm of nitrogen. A modified Picker powder diffractometer was employed, mounted with its equatorial plane vertical (since the synchrotron beam is approximately plane polarized in the horizontal plane). A 2-mm $\times$ 2-cm receiving slit was used, followed by a 20-cm active length ion chamber, filled with 2 atm of xenon. Diffracted intensities were several hundred thousand photons per second, which precluded the use of energy discriminating types of detectors (scintillation or proportional counters).

Three supported platinum catalysts were used in this study (see Ref. (*1*) for their preparation): (1) Platinum on silica gel, (1.97 wt%) with a ratio of surface to bulk atoms (percentage metal exposed) of 6.3%. (2) Platinum on silica gel (0.825 wt%) with a ratio of 81%. (3) Platinum on alumina (3.5 wt%) with a ratio of 40%. The percentage metal exposed was measured by hydrogen pulse chemisorption (*9*) and for specimen 1 also by means of wide angle X-ray scattering (*1*).

The silicon monochromator was calibrated in energy by scanning across the Pt L(III) absorption edge (11,564 eV), using sample 2 as an absorber. For all samples, the diffraction pattern was recorded from 20 to 90 degrees 2θ in increments of 0.25 degrees for two different photon energies: 11,558 and 11,508 eV (one more scan at an energy of 11,458 eV was recorded with sample 1). Each measurement lasted approximately 1.5 h and each data point contained well in excess of a million photons. All measurements were performed for a fixed monitor count to eliminate variations in incident beam intensity, were corrected for the calculated variation in ion chamber efficiency as a function of photon energy, and replotted, so that the angle scales correspond to a common reference energy (11,500 eV). Figures 1, 4, and 7 show the diffraction patterns at each of the two incident photon energies for samples 1, 2, and 3, respectively. Figures 2, 5, and 8 show the difference patterns (data at low energy minus data at high energy), again for samples 1, 2, and 3. The intensity scales are in arbitrary units, but the same in all figures.

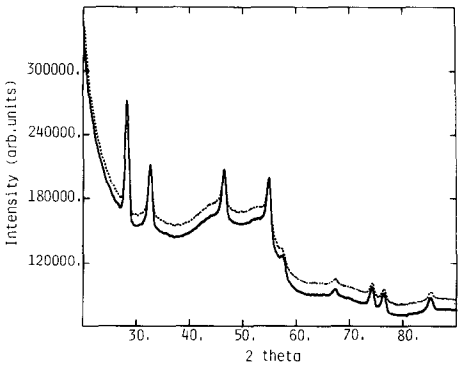

FIG. 1. Diffraction pattern for sample 1 at incident beam energy of 11,508 eV (solid line) and 11,558 eV (dashed line).

DISCUSSION

From Figs. 1 and 2, which show data for our "standard" specimen (large particle size, substantial metal loading, relatively smooth support scattering), a number of observations can be made: The anomalous scattering technique certainly appears to work well. All the support scattering features have been eliminated, such as the large decrease near 55 degrees 2θ. The negative value of the background is probably attributable to differences in harmonic contamination at the two incident beam energies. To obtain an estimate of the harmonic content of the synchrotron beam, the diffraction pattern of sample 1 was recorded on a conventional X-ray unit with Cu$K\alpha$ radiation. The peak-to-background ratio of the platinum 200 peak was found to be approximately 1, whereas for the synchrotron data the ratio was 0.37, indicating that more than half the observed support scattering was due to higher harmonics. Obviously, even small variations in harmonic intensity with changing fundamental beam energy can have large effects on the difference pattern, which is itself a small fraction of the total scattering pattern. It must also be mentioned that the monitor detector is almost totally insensitive to higher harmonics and it only serves to normalize the intensity of the fundamental radiation.

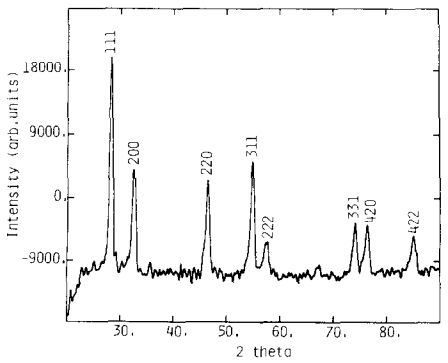

FIG. 2. Difference pattern for sample 1 (data at low energy minus data at high energy).

Except for the negative background in Fig. 2, all platinum peaks are clearly visible and one additional advantage of the anomalous scattering technique can be noted: The high angle peaks in the difference pattern are not as strongly attenuated vs 2θ as in each of the two patterns in Fig. 1. This is because the structure factors in the difference spectrum are proportional to $2ff' + f'^2$, rather than f^2, and f' is not a function of $\sin\theta/\lambda$. Here, f is the atomic scattering factor and f' its correction due to anomalous scattering.

In order to test the quality of the observed diffraction patterns, the integrated intensities of the platinum peaks were obtained for the low-energy scan, as well as the difference pattern by hand-extrapolating the background under the peaks and subtracting. The resulting integrated intensities were corrected for multiplicity and the Lorentz factor, divided by the appropriate structure factors and plotted in a log plot versus $\sin^2\theta/\lambda^2$, as shown in Fig. 3. Since the difference intensities are on the same scale as the total intensities, it is important to note that the values for f' used in our structure factor calculations are theoretical values, calculated by a method suggested by Cromer and Lieberman (*10*). The agreement between the total and the difference intensities is excellent. From the Debye–Waller factor, previously known (*1*) for sample 1, the slope of ln (I) vs $\sin^2\theta/\lambda^2$

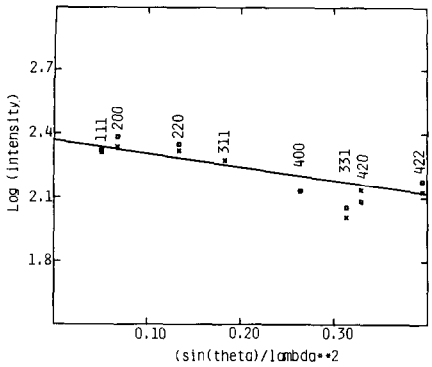

FIG. 3. Log of integrated intensity vs $\sin^2 \theta/\lambda^2$. □, Total integrated intensities. ×, Difference intensities. Solid line, expected slope of $\ln(I)$ vs $\sin^2 \theta/\lambda^2$, assuming known Debye–Waller factor for sample 1.

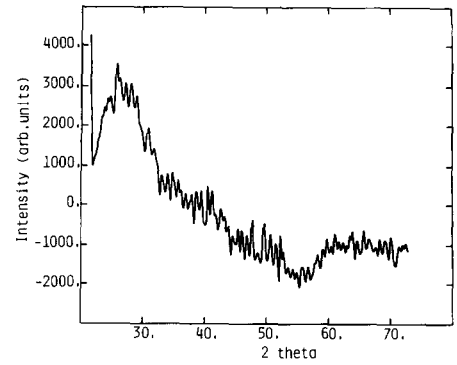

FIG. 5. Difference pattern for sample 2 (data at low energy minus data at high energy).

was calculated and plotted in Fig. 3 (as a solid line). The agreement between this line and the experimental ln (I) vs $\sin^2 \theta/\lambda^2$ is again very satisfactory.

The complete removal of the support scattering features makes possible a much more accurate determination of peak profiles, from which a wealth of information can be extracted, as mentioned in the introduction. To date, the support background was hand-extrapolated under the peaks and subtracted. This procedure cannot work near sharp features of the support scattering and is not very reliable when the catalyst particle size is small and the peaks are broad. Also, particle size distribution determinations, which are very sensitive to the tails of the profiles, become much more prone to error for such hand extrapolations.

In Figs. 4 and 5 a much more demanding situation is shown. The particle size (from hydrogen chemisorption measurements (*9*)) is very small (12–15 Å) and, additionally the catalyst particles, when exposed to air, are oxidized. This was verified by EXAFS measurements, which indicated that the O/Pt ratio was around 1.3, but failed to reveal any information about the structure of the particles. The metal loading of the specimen was quite low and this contributed to substantial statistical error in the difference pattern, shown in Fig. 5. A quantitative analysis of the anomalous scattering for specimen 2 can be much improved by control of the harmonic content of the X-ray beam to eliminate uncertainties in the resid-

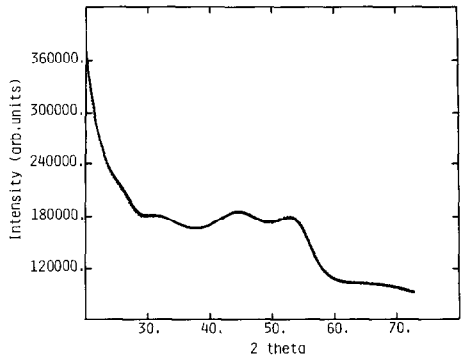

FIG. 4. Diffraction pattern for sample 2 at incident beam energy of 11,508 eV (solid line) and 11,558 eV (dashed line).

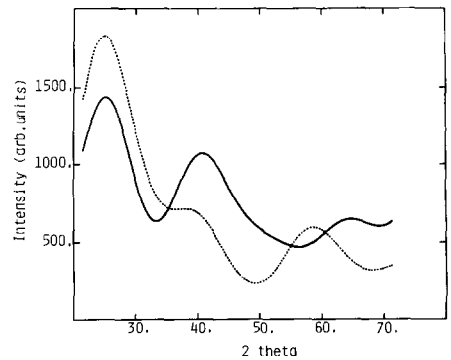

FIG. 6. Synthesized diffraction patterns of 15-Å particle size Pt_3O_4 (solid line) and PtO (dashed line).

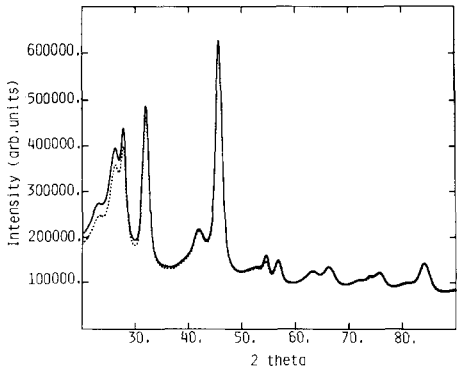

FIG. 7. Diffraction pattern for sample 3 at incident beam energy of 11,508 eV (solid line) and 11,558 eV (dashed line).

ual background, but the results in this first attempt are already impressive. The expected scattering patterns for PtO and Pt_3O_4 were synthesized, assuming a particle size of 15 Å and are shown in Fig. 6. The agreement between either of these patterns and that of Fig. 5 is interesting because Pt_3O_4 clearly fits the observations better, as far as the angular position of the scattering features is concerned. Using particle sizes of 10 and 20 Å produced much worse fits and a synthesized pattern for PtO_2 (not shown in Fig. 6) was totally unlike the observed one. The subject of the structure of 10–15 Å catalyst particles is an important one and it is hoped that valuable insights will be obtained via this technique.

Finally, Figs. 7 and 8 show diffraction patterns for an alumina-supported platinum catalyst. The harmonic contamination of

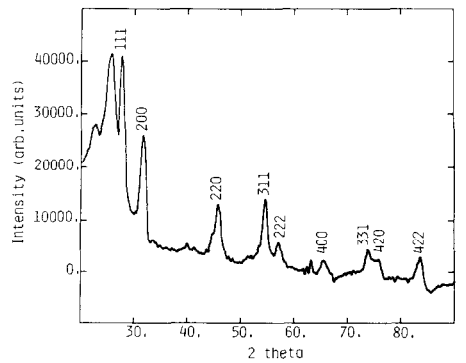

FIG. 8. Difference pattern for sample 3 (data at low energy minus data at high energy).

the beam had more severe effects for this specimen, whose platinum loading was high (twice that of specimen 1 and four times that of specimen 2) and which absorbed and scattered higher harmonics much more efficiently, especially at low scattering angles. Nevertheless, the platinum peaks are all visible and the observed intensities agree rather well with those in Fig. 2. Clearly, much better experimental control is required for alumina-supported than for silica-supported platinum particles, but it is exciting that the possibility exists for structural analysis for this very important class of catalysts.

ACKNOWLEDGMENTS

The authors acknowledge the assistance and general cooperation of the entire CHESS staff, in particular Dr. C. Pryor, Dr. L. Berman, Dr. D. Mills, and Dr. D. Bilderback. Dr. A. Habenschuss of Oak Ridge National Laboratory kindly calculated values of f' for platinum near the L(III) absorption edge, using the program from Ref. (*10*). The catalysts used in this study are those described in Ref. (*9*). This research was sponsored in part by Grant DE-AC02-80ER010744.A-009 from the Department of Energy.

REFERENCES

1. Sashital, S. R., Cohen, J. B., Burwell, R. L., Jr., and Butt, J. B., *J. Catal.* **50,** 479 (1977).
2. Aika, K., Ban, L. L., Okura, I., Namba, S., and Turkevich, J., *J. Res. Inst. Catal. Hokkaido Univ.* **24,** 54 (1976).
3. Nandi, R. K., Pitchai, R., Wong, S. S., Cohen, J. B., Burwell, R. L., Jr., and Butt, J. B., *J. Catal.* **70,** 298 (1981).
4. Nandi, R. K., Georgopoulos, P., Cohen, J. B., Butt, J. B., Burwell, R. L., Jr., and Bilderback, D. H., *J. Catal.* **77,** 421 (1982).
5. Pielaszek, J., and Cohen, J. B., *in* "Proceedings, Denver X-Ray Conf.," p. 27, in press.
6. Renouprez, A., Fouilloux, P., and Moraweck, B., *in* "Growth and Properties of Metal Clusters" (Bourdon, J., Ed.), p. 421. Elsevier, Amsterdam, 1980.
7. Sinfelt, J. H., Via, G. H., and Lytle, F. W., *Catal. Rev.-Sci. Eng.* **26**(1), 81 (1984).
8. Fuoss, P. H., Eisenberger, P., Warburton, W. K., and Bienenstock, A., *Phys. Rev. Lett.* **46,** 1537 (1981).
9. Uchijima, T., Herrmann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50,** 464 (1977).
10. Cromer, D. T., and Lieberman, D. A., *Acta Crystallogr. Sect. A* **37,** 267 (1981).