JOURNAL OF CATALYSIS 80, 479–481 (1983)

Catalyst Size Distributions from X-Ray Diffraction

Both the average metal crystallite size and the size distribution can be obtained from Fourier analysis of X-ray diffraction peaks from supported metal catalysts. The average size is obtained from the first derivative of the cosine coefficients (after correction for instrumental effects and microstrain), and the distribution from the second derivative. The advantage of this procedure over, say, electron microscopy is the good sampling associated with a large cross-section of X-ray beam. Furthermore, the weighting of the distribution determining the average size is the same as for chemisorption, so that direct comparisons are possible, $\langle L^3\rangle/\langle L^2\rangle$ where L is the size. (This is not the case when the half-breadth or integral breadth of a peak is employed.) As an example of such an investigation with catalysts, see Ref. (*1*). Because the weighting of the distribution is different in microscopy, direct comparisons of X-ray and EM results must be made carefully to take this into account. Some investigators have verified the X-ray procedures for the case of mixed samples of two known but different size distributions (*2, 3*). The calculated and measured distribution agreed. But this has not been done for catalysts, that typically have low metal loading and large background scattering from the support. This is the purpose of this brief report.

The preparation and characterization of the Pt/SiO_2 catalysts employed here are described in Ref. (*4*). Catalysts of 6.3 and 21.5 pct metal exposed (with metal loadings of 1.97 and 1.48 weight percent, respectively, and with the ratio of catalyst weights 3.5/1) were thoroughly mixed. The experimental details for recording the diffraction peaks and processing the data are given in Ref. (*1*). The 111 and 222 peaks for the 6.3 pct metal exposed were measured, to correct the Fourier coefficients for microstrain, while only the 111 (was measured) for 21.5 pct metal exposed because there is no strain at this percentage exposed (*1*). (In this reference it is shown that the coefficients of the 111 and 222 overlap in this case.) For obtaining the size distributions, several procedures have been described (*3, 5*) but we have found it quite adequate simply to fit the Fourier cosine coefficients with spline functions before taking the second derivative. The size distributions for the individual catalysts are shown in Fig. 1. Note that the asymmetry is quite different in these two distributions. To calculate the size distribution of the mixture, let $M_{\rm I}$ be the weight of the 6.3 pct exposed catalyst, $M_{\rm II}$ the weight of the 21.5 pct metal exposed. Then, let $A = M_{\rm I}/M_{\rm II}$. Also, let n be the total number of columns normal to the diffracting planes in all crystallites. Then, with $K = n_{\rm I}/n_{\rm II}$, ρ the Pt density, $V_{\rm L}$ the volume of a particle, and $P_{\rm L}$ the size distribution function, representing the fraction of columns of length L In the sample:

$$A = \frac{M_{\rm I}}{M_{\rm II}} = \frac{n_{\rm I} \sum_L \rho\, V_{\rm L}{}^{\rm I} P_{\rm L}{}^{\rm I}}{n_{\rm II} \sum_L \rho\, V_{\rm L}{}^{\rm II} P_{\rm L}{}^{\rm II}} \equiv \frac{n_1}{n_2} Z \equiv KZ. \quad (1)$$

Therefore

$$n_{\rm II} = n_{\rm I} Z/A, \quad (2)$$

and

$$K = A/Z.$$

In the mixture

$$nP_{\rm L} = n_{\rm I} P_{\rm L}{}^{\rm I} + n_{\rm II} P_{\rm L}{}^{\rm II}, \quad (3a)$$

0021-9517/83 $3.00

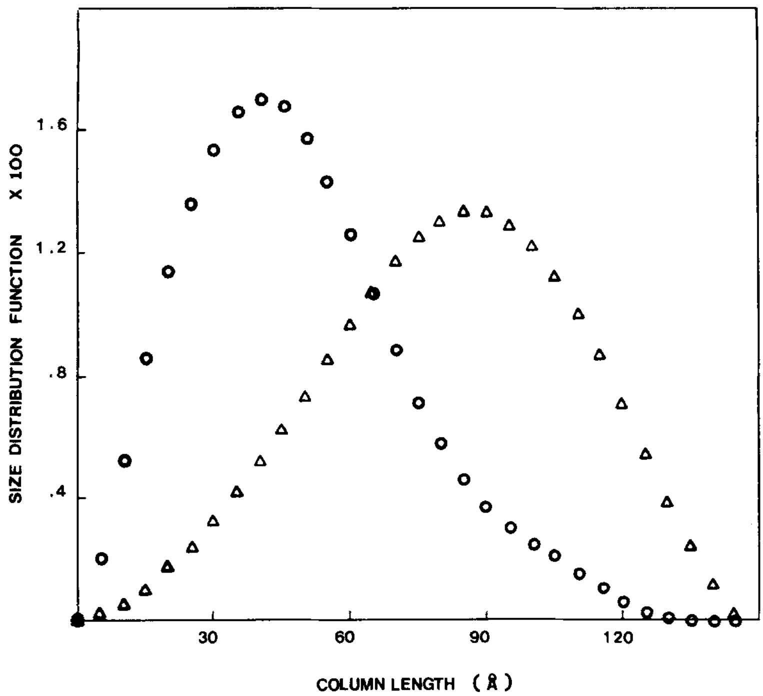

FIG. 1. Size distributions of component catalysts: ○, 6.3 pct metal exposed; △, 21.5 pct metal exposed.

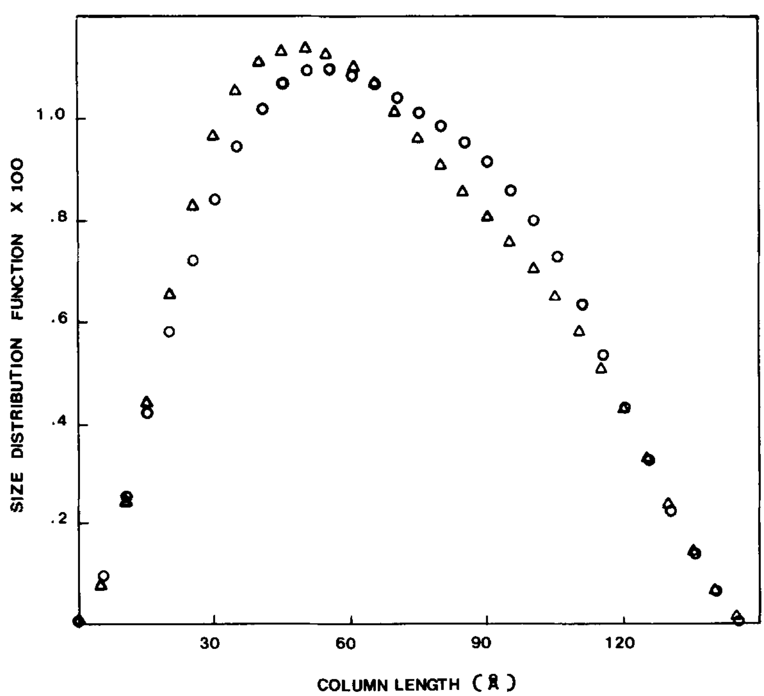

FIG. 2. Size distribution of catalyst mix, 3.5/1, 6.3 pct/21.5 pct: △, experimental; ○, from Eq. (5).

$$P_L = \frac{n_I P_L^{I} + n_{II} P_L^{II}}{n_{II}} = \frac{K P_L^{I} + P_L^{II}}{K + 1} \quad (3b)$$

$$= x P_L^{I} + (1 - x) P_L^{II}, \quad (3c)$$

i.e., the size distribution of the mixture is a linear combination of the size distributions of the components.

Now taking

$$Z = \frac{\sum_L L^3 P_L^{I}}{\sum_L L^3 P_L^{II}} \quad (4)$$

we obtain from the distributions in Fig. 1:

$$P_L = 0.56 P_L^{I} + 0.41 P_L^{II}. \quad (5)$$

In Fig. 2 is shown the measured size distribution and that calculated from Eq. (5). There is good agreement between the measured and calculated size distributions, which indicates that Fourier analysis is suitable for determining size distributions in real catalysts.

For the silica gel used as a support (70–80 mesh) and the CuK_α employed for the measurement (with a cross-sectional area of 240 mm^2) some 13,500 gel particles are sampled. This sampling can be increased by an order of magnitude by employing MoK_α radiation.

ACKNOWLEDGMENTS

This research was supported by DOE, office of Basic Energy Sciences, under Grant DEA-C02-77ER04254. The X-ray measurements were obtained in the Northwestern University Materials Research Center's X-ray diffraction facility, supported in part by NSF, under Grant DMR-MRL-76-80847.

REFERENCES

1. Sashital, S. R., Cohen, J. B., Burwell, R. L., Jr., and Butt, J. B., *J. Catal.* **50,** 479 (1977).
2. Quinn, H. F., and Cherlin, P., *Adv. X-Ray Anal.* **5,** 94 (1962).
3. Le Bail, A., and Louer, D., *J. Appl. Crystallogr.* **11,** 50 (1978).
4. Uchijima, T., Hermann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50,** 464 (1977).
5. Päusescu, P., Mănăilă, and Popescu, M., *J. Appl. Crystallogr.* **7,** 281 (1974).

J. PIELASZEK[1]
J. B. COHEN[2]
R. L. BURWELL, JR.
J. B. BUTT

Department of Materials Science and Engineering
The Technological Institute
Ipatieff Catalytic Laboratory, and Materials Research Center
Northwestern University
Evanston, Illinois 60201

Received September 14, 1982; revised December 14, 1982

[1] On leave from the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

[2] To whom correspondence should be addressed.