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Determination of Particle-Size Distributions of Heterogeneous Catalysts on High-Electron-Density Supports by Neutron Small-Angle Scattering: Dispersed Nickel Oxide on α-Alumina

The particle-size-distribution functions (p.s.d.f.) of heterogeneous catalysts can be characterised using electron microscopy (*1*) or small-angle scattering (s.a.s.) (*2*), whereas crystallite-size-distribution functions (c.s.d.f.) (*3*) can be obtained from lineshape analysis of diffraction profiles if the contributions due to strain are properly accounted for. In a limited number of cases magnetic methods may also be applicable to obtain related information. Of the first two techniques only small-angle scattering allows the experimenter to obtain information which is representative of a possibly heterogeneous material, but despite this advantage it has not found wide usage in catalyst characterisation (*2*). One difficulty with small-angle X-ray scattering is that it cannot be applied indiscriminately to all combinations of catalysts and supports. Here we demonstrate how neutron small-angle scattering provides an alternative tool, having significant advantages over X-ray s.a.s., especially for examining catalysts with high-electron-density supports.

In principle, the technique of filling pores (*4*) with a fluid of identical scattering power to that of the support suppresses the s.a.s. component arising from the pores. Nevertheless, perfect matching is not always practicable, especially with high-electron-density supports. There may also be an additional term in the scattering due to the difference between the catalyst–pore and catalyst–support interfaces. This contribution, unlike the former, cannot be assessed by a null experiment on the fluid-impregnated support alone. It is apparent that to obtain accurate measurements of the scattering from the active phase, it is necessary to measure the scattering from the support in the absence of the active phase. This requirement cannot be satisfied readily by coprecipitated catalysts.

For catalysts of very high electron density, such as platinum, on supports such as silica or alumina, the electron density differences between the metal and the support are sufficient for all the contributions to the background intensity to be neglected. However, generally, the scattering power of the support and the active phase will be much closer, and it is then necessary to use the pore-masking technique. This has proved a successful ploy for X-ray s.a.s. with low-electron-density supports, but it has not been successfully used with higher-electron-density supports such as α-alumina (1.95 faradays cm^{-3}) because of the difficulty of obtaining matching fluids. Somorjai *et al.* (*5*) pointed out, that liquids or conveniently fusible solids, with high electron densities, [such as CHI_3 (1.68 faradays cm^{-3}), and $SbBr_3$ (1.79 faradays/cm^3)] are difficult to introduce into the pores of an alumina support, because they do not wet the surface. In addition, nonreproducible attenuation of the X-ray beam results unless all surplus maskant is scrupulously removed from the outer surfaces of the sample.

If neutrons are used as the probe, problems with maskants are not important because the neutron-scattering-length densities of readily available CD_3OD, D_2O, and mixtures of these with their protonated counterparts, can be adjusted to be identical to the neutron scattering densities of

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TABLE 1

Neutron Scattering-Length Densities (n.s.l.d.) of Supports and Maskants

Material	Density (g cm^{-3})	n.s.l.d. (10^{-10} mol cm^{-2})
ZnO	5.6	0.079
α-Al_2O_3	3.9	0.095
γ-Al_2O_3	3.1	0.087
D_2O	1.10_5	0.106
H_2O	1.00	−0.009
CD_3OD	0.89	0.097
CH_3OH	0.79	0.006

high-electron-density supports (Table 1). Moreover, the absorption cross sections of the fluids are so low, that there is no problem arising from fluid on the sample in excess of that required for pore filling. At the same time the neutron-scattering-length densities of a number of commercially important catalysts are sufficiently different from those of their supports that high scattering intensities should be observed (Table 2).

We used the neutron s.a.s. spectrometer at AERE Harwell to investigate an experimental dispersion of nickel oxide on α-alumina using individual pellets of 5.4-mm-diameter as samples. The support had a surface area of 1.5 m^2 g^{-1}, a pore volume of 0.25 cm^3 g^{-1}, and a NiO loading of 6.5%. The sample was outgassed at 150°C, and examined after having had its pores filled with CD_3OD by condensation under vacuum. Pellets of the unimpregnated α-Al_2O_3 were similarly degassed, and then examined both before, and after, its pores had been filled with CD_3OD.

The s.a.s. data, obtained with 10-Å incident neutrons (Fig. 1) in the form of a plot of log (intensity) vs scattering angle, demonstrates the large decrease in the scattering, from the alumina, due to pore masking and also the large increases in scattering arising from the impregnation of the alumina by the nickel oxide. The particle-size-distribution function shown in Fig. 2 was obtained from these data by the analysis of Vonk (*6*), in which, by a least-squares procedure, the data are fitted to a sum of curves representing the scattering by spheres. This distribution function is the volume-weighted-diameter-distribution function $\Sigma d^3 \cdot d / \Sigma d^3$, and so is comparable with results obtained by a Scherrer analysis of X-ray diffraction line broadening.

Scattering due to support and CD_3OD was subtracted from that of the supported nickel oxide and CD_3OD, making due allowance for changes in the total transmission. In this way we remove the contribution due to scattering from closed pores which are unfilled by methanol, and from density fluctuations present in the alumina. We also subtracted the limiting value of the scattering at high angles arising from the incoherent scattering. The data do not, of course, cover all scattering angles, and the experiment is therefore a probe for a limited range of particle sizes. In our experiments this range is between 22 and 640 Å. Using different neutron wavelengths or detector positions, this range can be extended.

Dispersed nickel oxide on α-alumina is a particularly favourable system to study since it is possible to determine the c.s.d.f. of the solid by X-ray diffraction. Consequently, we have sought to validate the neutron results by comparing the p.s.d.f. obtained from them with a c.s.d.f. obtained by X-ray diffraction. Only one diffraction peak from the nickel oxide (220) was suit-

TABLE 2

Neutron Scattering-Length Densities of Some Supported Catalyst Combinations

Catalyst	n.s.l.d.	Support Combination	$(\Delta\rho)^2$ (10^{-24} mol^2 cm^{-4})
NiO	0.144	(NiO/α-Al_2O_3)	2.4×10^{-3}
Ni	0.156	(Ni/α-Al_2O_3)	3.7×10^{-3}
Cu	0.107	(Cu/ZnO)	0.8×10^{-3}
CuO	0.116	(CuO/ZnO)	1.4×10^{-3}
MoS_2[a]	0.037	(MoS_2/γ-Al_2O_3)	1.3×10^{-3}

[a] In this case, since it is a γ-Al_2O_3 support which is of interest commercially, the experiment should be equally feasible with X rays.

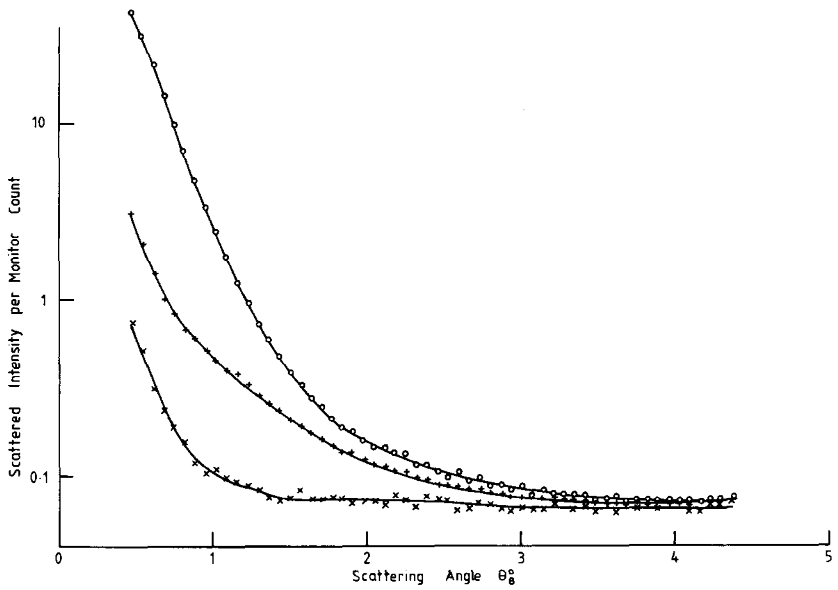

FIG. 1. Small-angle scattering data from α-Al_2O_3 (O), NiO + α-Al_2O_3 + CD_3OD (+), and α-Al_2O_3 + CD_3OD (×). In each experiment equal weights of alumina were examined.

able because of interference from the support. The volume-weighted distribution of the mean length perpendicular to the 220 planes was obtained by Fourier analysis of the X-ray diffraction lineshape (*3*). No account was taken of strain broadening. The essential features of the distribution were in good agreement with those obtained from neutron small-angle scattering, showing a bimodal distribution (Table 3). It is emphasised that related but not identical quantities are being compared in the two cases. The degree of agreement between these two results suggests that the neutron small-angle scattering technique can be used routinely to determine particle-size-distribution functions of impregnated catalysts.

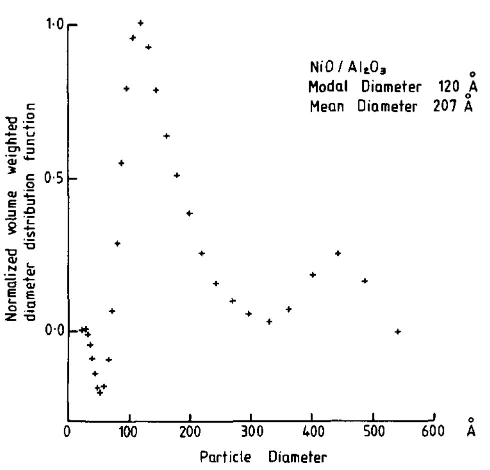

FIG. 2. The volume-weighted-diameter-distribution function of the nickel oxide particles in the NiO + α-Al_2O_3 catalyst determined by neutron small-angle scattering.

TABLE 3

Comparison of Results Obtained by Lineshape Analysis of 220 X-Ray Diffraction Peak, and Neutron Small-Angle Scattering for Nickel Oxide Supported on α-Alumina

	XRD (Å)	n.s.a.s. (Å)
Crystallite or particle size at mode 1	121	120
Crystallite or particle size at mode 2	303	440
Average size[a]	218	207

[a] Apparent crystallite size determined from the f.w.h.m. of the 220 line after deconvolution of the instrumental resolution function was 350 Å.

We investigated whether the residual scattering from the support containing CD_3OD was due to scattering-length-density differences between the alumina and the matching fluid by changing the neutron scattering length density of the impregnating fluid (from 0.092 to 0.097 by varying the CH_3OH/CD_3OD ratio). Little change in the scattering intensity occurred, showing that the residual scattering must be an intrinsic property of the alumina itself.

We conclude that neutron small-angle scattering shows considerable potential as an alternative to X-ray scattering for determining the particle-size distribution functions of supported catalysts. The advantages of using neutrons rather than X rays are the following:

(i) Unlike X rays they can be applied to catalysts dispersed on high-electron-density supports such as α-alumina;

(ii) The technique of "contrast matching" to mask-out one component of the scattering is much more versatile with neutrons than X rays, in part due to the ready availability of suitable deuteriated solvents.

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REFERENCES

1. Anderson, J. R., "Structure of Metallic Catalysts." Academic Press, New York/London, 1975.
2. Whyte, T. E., Kirklin, P. W., Gould, R. W., and Heinemann, H., *J. Catal.* **25**, 407 (1972); Renouprez, A., Hoang-Van, C., and Compagnon, P. A., *J. Catal.* **34**, 411 (1974).
3. Sashital, S. R., Cohen, J. B., Burwell, R. L., and Butt, J. B., *J. Catal.* **50**, 479 (1977); Warren, B. E., and Averbach, B. L., *J. Appl. Phys.* **21**, 595 (1950).
4. Gunn, E. L., *J. Phys. Chem.* **62**, 928 (1958).
5. Somorjai, G. A., Powell, R. E., Montgomery, P. W., and Jura, G., *in* "Small-Angle X-Ray Scattering" (H. Brumberger, Ed.) p. 449. Gordon & Breach, New York, 1967.
6. Vonk, C. G., *J. Appl. Crystallogr.* **9**, 433 (1976).

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