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NOTE

ASAXS Investigation of a Au/C Catalyst

The determination of the active phase dispersion is of paramount importance for the understanding of metal supported catalysts properties. A certain number of characterisation techniques can be used, each with their pros and cons (1, 2); among them, wide angle X-ray scattering (WAXS), and small angle X-ray scattering (SAXS) are often used in a complementary way to characterise these systems. In fact, WAXS allows one to phase-specifically determine particle sizes by analysing the broadening of the relevant peaks, and, at the same time, monitoring possible structural changes, such as isomorphic phase transitions, crystal disorder or alloy formations, in cases where more than one metal is present. Yet, it is known that this technique determines the size of crystallites (coherently scattering domains) and not necessarily that of the catalytically active particles, which could be composed of more than one crystallite. On the other hand, SAXS is not sensitive to the structure or disorder of the scattering particles, but can yield, in principle, the dimensions of the real particles.

Both these techniques, anyway, undergo great difficulty when the support is an active carbon. In WAXS data, the presence of a slowly varying background, due to the amorphous carbon, does not allow one to reliably analyse the peak shape, which contains the information about the dimensions of the crystallites. In particular, the tendency to underestimate peak tails results in an overestimation of the particle sizes (3). In SAXS data, the porous structure of the carbon produces a scattering which is not easily separated from that due to the metal particles. In both cases, the scattering of a blank sample does not match correctly the catalyst scattering (4); this can be due to modifications of the support along the catalyst preparation when the metal is present and/or to the metal-support cross-scattering. In principle, anomalous scattering (5) is able to subtract the support scattering by exploiting the contrast variations encountered in the neighbourhood of an absorption edge. While the scattering factor of the absorbing element varies, all other scattering factors remain unchanged. Thus, by taking the difference of two measurements close to the absorption edge of the metal, the scattering of the support will be automatically subtracted. The only drawback of this technique is that a synchrotron source is necessary, and data has to be treated with extreme accuracy, in order to detect the small differences in the scattering curves.

About 10 years ago anomalous scattering was successfully applied to WAXS, in order to study some Pt catalysts supported on silica gels and alumina (6). Despite the large number of studies carried out using anomalous small angle scattering (ASAXS), to the best of our knowledge, the only paper which applied this technique to a catalytic system has just been published very recently on platinum electrocatalysts supported on porous carbon with a metal load in the range 5–85 wt% (7). The aim of the present study is to apply ASAXS to supported metal catalysts, where the metal load is typically smaller than a few percent. The investigated material is, in fact, an activated carbon, loaded with only 0.2 wt% of Au. The ASAXS results have been compared with those obtained using conventional WAXS and SAXS measurements.

A commercial active carbon, with an apparent surface area of 1200 m^2/g and a pore volume of 0.60 ml/g, was used as a support. The sample was prepared by impregnation with $HAuCl_4$ aqueous solution and was reduced by HCOOH at 80°C.

WAXS was carried out with a Philips vertical goniometer, connected to a highly stabilised generator. Cu-Kα Ni-filtered radiation, a graphite monochromator and a proportional counter with a pulse-height discriminator were used. The profile intensities were measured step by step (0.05° in 2θ) in several runs, for a whole fixed time of 100 s. Line broadening analysis was carried out according to a previously described procedure which combines best-fitting and Fourier analysis (8, 9). In order to describe the background a polynomial function, or the experimental scattering of a blank sample multiplied by an optimizable parameter, can be used.

SAXS data were collected with a Paar compact Kratky camera, using Ni-filtered CuKα radiation and a proportional counter with a fixed counting statistics of 10^5 pulses per point.

ASAXS measurements were performed at the JUSIFA small angle scattering beamline of the DORIS synchrotron radiation source in DESY (Hamburg) (10). The contrast variation was performed at different energies near the Au L(III) absorption edge ($E_L = 11916$ eV). Intensities

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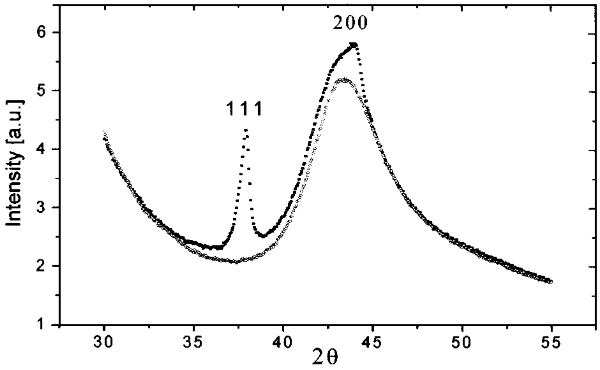

FIG. 1. Possible match of the WAXS data of the carbon support (open dots) to that of the Au/C sample (solid dots).

obtained at different energies were suitably interpolated at the same abscissas and were normalised to the primary beam intensity and corrected for absorption. Due to the asymptotic behaviour in the Porod plot, no fluorescence correction was carried out. Particle size distributions have been obtained by fitting the calculated scattering intensity of one or two Schultz distributions of spherical particles to the experimental data, using an optimisation procedure (11).

Figure 1 shows a possible arbitrary match between the WAXS intensity of the support and the scattering curve of the catalyst.[1] The match evidences that peak tails extend on a very large angular range and suggests that the sharper 111 reflection is superimposed on a second very broadened peak, which indicates a bimodal distribution of particles. Unfortunately, fitting such a profile with two functions and a scaleable background is a very ill-conditioned problem, so that ambiguous results are obtained. In order to obtain a rough estimate of the average crystallite size, a single peak with a polynomial background has been fitted to the 111 reflection, giving a value of 150 Å. As mentioned above, the latter method is likely to yield an overestimated value.

In Fig. 2 the SAXS intensities of the catalysts and the support are shown. Since the intensities have been normalised to absolute units, if the blank support was the real background, one would expect its scattering curve to directly match that of the catalysts. This is unfortunately not the case.[1]

By multiplying the intensity of the support by an arbitrary factor and by trying to make a compromise between the match in the lower and in the higher angular region, one can obtain an average match. When the so-obtained background is subtracted, the difference data suggest, once again, the presence of a bimodal distribution by showing two linear regions in the log J-log h plot. Nevertheless, quantitative results obtained in this way must be handled with kid gloves.

In conclusion, the use of conventional techniques suggests the presence of very small particles in the investigated catalyst, but it does not allow one to give a quantitative measure of their dimensions and of their relative amount in respect to the larger ones. However, these same particles could play an important role in the catalytical activity of the material, due to their high specific surface area. In an attempt to clarify this point, ASAXS measurements were carried out.

In Fig. 3 the experimental ASAXS intensity obtained as the difference between the two normalised patterns collected at $E_1 = 11560$ eV and at the edge energy $E_2 = 11916$ eV is reported. Intensity differences, which were determined by using other values of E_1, gave similar results. The presence of two well-defined linear regions in the angular ranges $0.3\ \text{nm}^{-1} < h < 0.7\ \text{nm}^{-1}$ and $2\ \text{nm}^{-1} < h < 7\ \text{nm}^{-1}$ of this log–log plot, evidences the contribution to the scattering of two well separated particle size distributions of the metal phase. The h^{-4} dependence of the intensity for the second range at larger h values (see Fig. 4A) reflects the so-called Porod law and points out the correctness of the subtraction procedure, notwithstanding the low metal load. The positive deviation from the Porod law for the first range of smaller h, shown in Fig. 4B, is

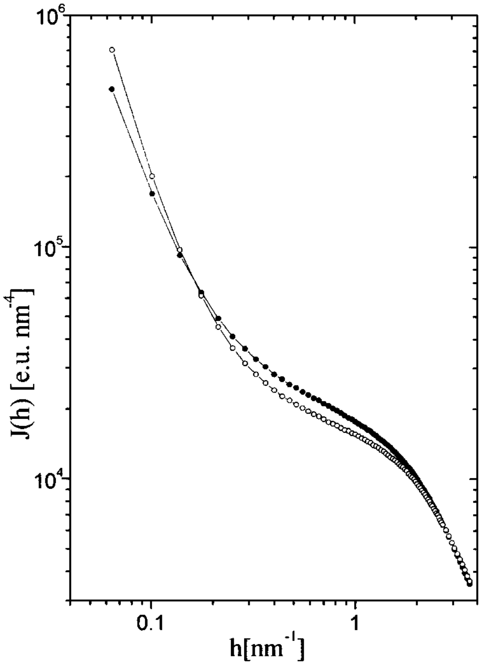

FIG. 2. SAXS intensities of the Au/C sample (solid dots) and the carbon support (open dots) in absolute units.

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[1] A mated support, prepared following the same preparation steps undergone by the catalyst, and a sample with very low metal load (0.001 wt%) produced a worse match.

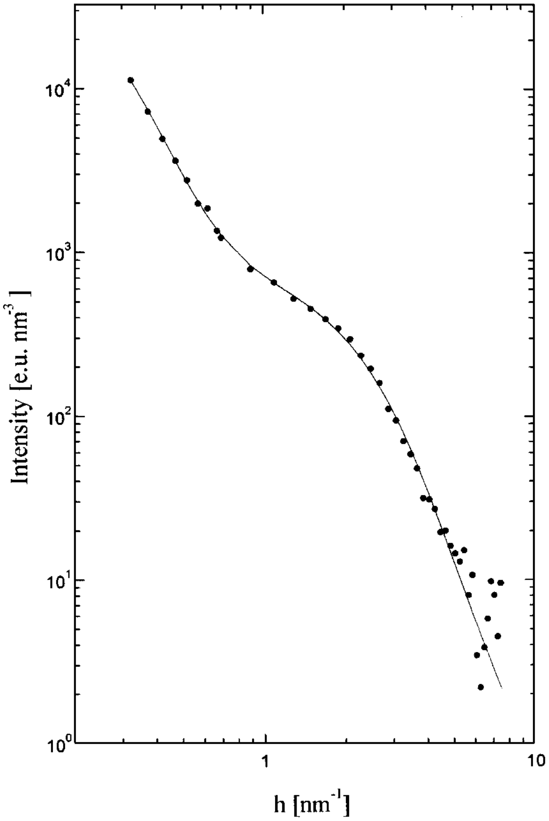

FIG. 3. Separated ASAXS data of the Au/C sample (solid dots) and fitting of a bimodal particle size Schulz distribution (line).

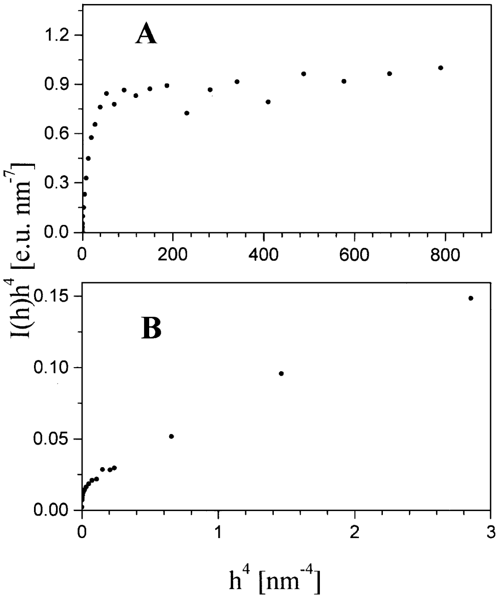

FIG. 4. Porod plot of the ASAXS data in Fig. 3 in two different angular ranges.

justified by the superimposition, in this range, of the Guinier region of the smaller particles.

The continuous line shows the best fit of the intensity, which is obtained by using two distributions of particle size. Using a single distribution it was not possible to reach a meaningful fit. The obtained values of volume-weighted average diameters of the two distributions are 17 Å and 140 Å, respectively. The larger value can be related to the average dimension found by WAXS and shows that, in this sample, the particles are single crystallites. The distribution of smaller particles represents the fraction of very small, possibly disordered particles, which are below the WAXS resolution limit for this particular sample. The ratio $\alpha = V_1/V_2$ of the total volume of the small particles to that of the larger ones was calculated using the best-fit parameters as $\alpha \approx 7$. This means that the largest part of the metal particles remains undetected when using a simple WAXS analysis. This very important result is confirmed by the increase of the WAXS peaks relevant to the metal, when a thermal treatment is carried out. During this treatment, sintering of the smaller particles into larger ones takes place, letting them enter the resolution range of the technique.

The reported results show the ability of ASAXS measurements in microstructural studies, also on a catalyst system loaded with a very low percentage of metal. A correct analysis of the ASAXS results can give basic information about the microstructural features of the metallic phase also in the size range 10–20 Å, which is very important from a catalytic point of view, and can be accessed with great difficulty using other conventional techniques. The use of this technique overcomes problems connected with the scattering of the support, which often makes the study of the active phase very difficult.

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REFERENCES

1. Lemaitre, J. L., Menon, P. G., and Delannay, F., *in* "Characterization of heterogeneous Catalysts" (F. Delannay, Ed.), pp. 299–365. Dekker, New York, 1984.
2. Matyi, R. J., Schwartz, L. H., and Butt, J. B., *Catal. Rev.-Sci. Eng.* **29**, 41 (1987).
3. Polizzi, S., Benedetti, A., Fagherazzi, G., Franceschin, S., Goatin, C., Talamini, G., and Toniolo, L., *J. Catal.* **106**, 483 (1987).
4. Benedetti, A., *J. Appl. Crystallogr.*, in press.
5. Materlik, G., Sparks, C. J., and Fischer, K. (Eds.), "Resonant Anomalous Scattering, Theory and Applications." Elsevier Science, Amsterdam, 1994.
6. Georgopoulos, P., and Cohen, J. B., *J. Catal.* **92**, 211 (1985).
7. Haubold, H. G., Wang, X. H., Jungbluth, H., Goerigk, G., and Schilling, W., *J. Mol. Struct.* **383**, 283 (1996).

8. Enzo, S., Polizzi, S., and Benedetti, A., *Z. Kristallogr.* **170**, 275 (1985).
9. Benedetti, A., Fagherazzi, G., Enzo, S., and Battagliarin, M., *J. Appl. Crystallogr.* **21**, 543 (1988).
10. Haubold, H.-G., Gruenhagen, K., Wagener, M., Jungbluth, H., Heer, H., Pfeil, A., Rongen, H., Branderberg, G., Moeller, R., Matzerath, J., Hiller, P., and Halling, H., *Rev. Sci. Instrum.* **60**, 1943 (1989).
11. Riello, P., and Benedetti, A., *J. Chem. Phys.*, **106**, 8660 (1997).

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