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ASAXS study of Au, Pd and Pd–Au catalysts supported on active carbon

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Abstract

Among the techniques commonly used, small angle X-ray scattering (SAXS) is, in principle, particularly suited for the analysis of nanostructured systems. However, catalysts supported on porous materials are three phase systems (support, voids and metal), so that the resulting spectrum contains more information than a single conventional SAXS measurement allows to extract. The use of synchrotron radiation source allows to circumvent this difficulty and to separate the scattering of the support from the one of metal by taking advantage of the so-called anomalous or resonant behavior of the atomic scattering amplitude of an element near its absorption edge. The results so far obtained on some Au, Pd and Pd–Au samples supported on active carbon are reported here. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

It is known that the activity of metal dispersed catalysts is directly dependent on the size and the spatial dispersion of the metal particles in the matrix [1–5]. For this reason, the determination of the particles size is very important to characterise this class of materials. When the metal is very finely dispersed and is present in small quantity, many techniques show their limit to detect the active particles. In particular, if carbon is the support, transmission electron microscopy (TEM) has serious difficulties to show particles smaller than say 4 nm and chemisorption has serious problems whenever gold is present. In wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) the separation of the background scatter-

ing due to the matrix makes a quantitative analysis very problematic. On the contrary anomalous scattering techniques (AWAXS and ASAXS) [6] are in principle able to make a direct background separation, allowing a quantitative analysis to be carried out. In a recent paper [7], we have demonstrated for an Au/C sample that particles sizes could be quantitatively determined with such a small load as 0.2 wt.% A large fraction of very finely dispersed particles were found, that remained undetected using other methods. However, for low metal load, the resonant scattering is a very small fraction of the total scattering, so that very accurate experimental measurements and data analyses must be carried out. As shown in the following, while the accuracy of the technique still needs to be improved, the ASAXS (and probably AWAXS too) is likely to play an important role in the field of catalysis. The aim of the present work was to check the ASAXS findings on a larger set of samples (Au/C, Pd/C and

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bimetallic Au–Pd/C) and compare them with other scattering techniques like WAXS. Furthermore, on the same samples, a thermal treatment has been carried out, with the aim of letting the smaller particles grow and possibly enter the WAXS resolution. A suitable modification of the Rietveld analysis [8,9] has been also applied and has shown to be a very promising tool in this area [10].

2. Experimental

2.1. Samples

A commercial active carbon with a surface area of $1200 \text{ m}^2/\text{g}$ and a pore volume of 0.60 ml/g has been used as support. Catalysts were obtained by impregnation with aqueous solution of HAuCl₄ or Na₂PdCl₄ or co-impregnation with a mixed solution of the two salts and were reduced by HCOOH at 353 K. The studied samples were: Au 0.20 wt.% (sample I), Pd 0.72 wt.% (sample II) and Au 0.20 wt.%–Pd 0.39 wt.% (sample III). The metal weight fractions were determined by atomic mass spectroscopy (Perkin Elmer mod.500). The samples, were studied as prepared (indicated as IA, IIA and IIIA) and after an ageing thermal treatment (in an H₂O/H₂ = 1 environment) at 673 K for 4 h (indicated as samples IB, IIB).

2.2. ASAXS

Measurements were performed at the JUSIFA small angle scattering beamline of the DORIS synchrotron radiation source in DESY (Hamburg) [11]. The contrast variation was performed at different energies near the Au L(III) ($E_L = 11916 \text{ eV}$) and the Pd K (E = 24350 eV) absorption edges.

Intensities 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 were obtained by fitting the calculated scattering intensities of one or two Schultz distributions of spherical particles to the experimental data, using an optimisation procedure [12].

2.3. WAXS

Data was collected with a Philips X'Pert vertical goniometer, connected to a highly stabilised generator. Cu K_{α} Ni-filtered radiation, a graphite monochromator and a proportional counter with a pulse-height discriminator were used. Data for line broadening analysis were measured over several runs for a total fixed time of 100 s with a step size of 0.05° in 2θ and analysed according to a previously described procedure which combines best-fitting and Fourier analysis [13,14]. Data for Rietveld analysis were collected for 10 s per 0.02° step on the 25–145° range. The analysis was carried out by a modified Rietveld program [8,9], which is able to evaluate the relative quantity of each phase (including noncrystalline ones) from the integrated intensities.

3. Results and discussion

3.1. Au/C

The analysis of the ASAXS data of sample I was able to distinguish between two different populations of particles: the larger ones with average diameters of 14 nm (see Table 1) and clusters smaller than 2 nm. The presence of such a population of very finely dispersed particles seems to be a common situation for these kind of catalysts, since it has been found in all the analysed samples. For this reason Table 1 only shows the average size values of the larger particles. The population of nanocluster appears to be even predominant in this sample: if one calculates the weight fraction of the two populations 0.025 wt.% for the large particles and 0.175 wt.% for the small ones is found, which is almost seven times larger. The

Table 1					
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werage size (iiii) of the population of larger particles					
Sample	ASAXS	WAXS			
I (Au)	14	15			

14	15
16	15
14	13
11	10
13*	8
14^{*}	9
	14 16 14 11 13 [*] 14 [*]

*Average of Au- and Pd-edge values.



Fig. 1. ASAXS data of sample I A (Au(0.20 wt.%)/C) (●).

presence of such a high amount of smaller particles, even if it is difficult to explain correctly, could be due to the use of a very low reduction temperature that prevents the mobility of the metal atoms spread out on the support.

By looking at Fig. 1, where error bars have been added to the data published earlier [7], it can be seen that large statistical errors are present in the higher angular range, which is the region where the smallest particles give their scattering contribution. Thus, the present ASAXS results must be taken with care as the fraction of small particles is concerned, but are important as an indication whether a population of particles with sizes smaller than 2 nm is present or not. It was already shown [7] that the fitting of WAXS profiles qualitatively confirms this finding by evidencing a very broad scattering contribution underneath the diffraction peaks. On the other hand, the metal fractions can be quantitatively determined if Rietveld analysis is carried out by a suitably modified procedure [8–10]. Using this method the following values have been obtained: 0.056(3) wt.% for the larger particles and 0.15(3) wt.% for the smaller ones, i.e. about three times larger. As the particle size is concerned, WAXS line broadening analysis of the 111 reflection gives a value of 15 nm (see Table 1), which, however, could be affected by the very broad halo produced by the smaller particles. The size of the small particles can be only roughly estimated when



Fig. 2. WAXS data of sample I (Au(0.20 wt.%)/C) before (\bullet) and after thermal treatment (\bigcirc), together with the fitted carbon support (_____). The peak at $2\theta = \sim 44.4^{\circ}$ corresponds to the 200 Au reflection.

they are of the order of the WAXS resolution (2-3 nm).

The ASAXS analysis of the thermal treated sample shows only a small increase in the average size of the larger particles (see Table 1), while the size of the smaller particles does not seem to change much within the sensitivity of the present measurements. WAXS data confirm this result as sizes are concerned (see Table 1), but also evidence that large particles increased considerably in number during the thermal treatment. In fact, Fig. 2 shows an increase of the WAXS Au reflections, together with a depression of the halo below it, i.e. smaller particles grow to a size similar to the large particles already present, which on the contrary seem not to change during the thermal treatment. The relevant weight fraction of population of larger particles, as determined by Rietveld analysis, is now 0.103(4) wt.% meanwhile the fraction of the smaller particles resulted to be about 50% of the total gold present in the sample. Thus, the thermal treatment unequivocally demonstrates that the population of nanoclusters detected by ASAXS really exists inside the sample and is not an artefact.

3.2. Pd/C

Also in this case, ASAXS data indicate the presence of a population of small metal nanoclusters ((approxi-



Fig. 3. WAXS data of sample II (Pd(0.72 wt.%)/C) before (Δ) and after thermal treatment (\square), together with the scattering of the carbon support (\bullet). The peak at $2\theta = \sim 47^{\circ}$ corresponds to the 200 Pd reflection.

mately 1 nm), together with a population of larger particles (average 14 nm, see Table 1). Surprisingly, the results of the heat treated sample (IIB) show a decreasing of the size of the larger particles. This seemingly contradicting result can be explained as follows: the thermal treatment does not allow the larger particles to grow, so their average size remains almost the same. On the contrary, the smaller particles can easily migrate on the support with consequent little increase of their size.

These grown particles enter the population of larger ones and give rise to a decrease of the average value. Unfortunately, the present ASAXS data is not precise enough, at high angles, to follow the change in relative fraction of the two populations. As the size changes are concerned, WAXS data (see Fig. 3) confirm the same trend (see Table 1), but they give further information: as in sample I, a broad scattering halo is present underneath the diffraction peaks.

In the diffraction pattern (see Fig. 3) it is evidenced that the tails of the sample IIB fit much better the carbon pattern. In particular, in the range $2\theta = 35-38^{\circ}$, the intensity of sample IIA, shows a contribution due to a fraction of smaller particles. The comparison between the two 1 1 1 Pd reflections (of the samples IIA and IIB) shows a decreasing of the line broadening for the heat treated sample and an increasing intensity,



Fig. 4. WAXS data of sample III (Au(0.20 wt.%)–Pd(0.39 wt.%)/ C) before (Δ) and after thermal treatment (\square), together with the scattering of the carbon support (\bullet). The peak at $2\theta = \sim 46$ corresponds to the 200 Au–Pd reflection.

while the contribution of the smaller particles ($2\theta = 35-38^{\circ}$) almost disappears.

3.3. Au-Pd/C

For bimetallic samples, ASAXS gives a further advantage with respect to conventional SAXS: it allows one to distinguish between the scattering contribution of the two atomic species by measuring the scattering intensity at the two relevant absorption edges. So, if the two elements form different particles, their size and amount can be in principle determined separately. In the present case, both absorption edges gave similar results (see Table 1, where an average value is given). In fact, WAXS data (see Fig. 4) show a single 111 peak in a position intermediate ($a_0 =$ 3.956 ± 0.006) between the Au ($a_0 = 4.0786$) and the Pd one $(a_0 = 3.8898)$ [15], i.e. particles are made up of a solid solution of the two metals. The average size of this single peak determined by line broadening analysis gives a smaller value than the one obtained by ASAXS. This could be explained considering that we are comparing the average crystallite size (WAXS) and the particle size (SAXS); in catalysis, it is quite common to find particles formed by more than 1 crystallite. However also in this case, after the thermal treatment, the average size, determined both by ASAXS and by WAXS, does not change significantly

(see Table 1), while the WAXS intensity of the 111 peak does without changing its position.

4. Conclusions

ASAXS is shown to be a very promising technique for studying metal catalysts supported on porous materials. We have been able to detect small nanoclusters, which remained undetected until now. The presence of a large fraction of very finely dispersed particles with sizes smaller than 2 nm seems to be a common situation for this kind of samples. However, for the present sample with very low metal load, the precision of the experimental data still needs to be improved, in order to allow a reliable quantitative determination of the amount of these nanoclusters. In particular, for bimetallic catalysts ASAXS is able to separate the contribution of the two metals. A quantitative Rietveld analysis has been also shown to be a valid tool to complement ASAXS data.

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References

- A. Borodziński, M. Bonarowska, Relation between crystallite size and dispersion on supported metal catalysts, Langmuir 13 (1997) 5613.
- [2] F. Delannay, B. Delmon, in: F. Delannay (Ed.), Characterisation of Heterogeneous Catalysis, Marcel Dekker, New York, 1984, pp. 1–28.

- [3] J.L. Lemaitre, P.G. Menon, F. Delannay, in: F. Delannay (Ed.), Characterization of Heterogeneous Catalysts, Marcel Dekker, New York, 1984, pp. 299–365.
- [4] R.J. Matyi, L.H. Schwartz, J.B. Butt, Particle size, particle size distribution and related measurements of supported metal catalysts, Catal. Rev. Sci. Eng. 29 (1987) 41.
- [5] A. Benedetti, Small-Angle scattering of heterogeneous catalysts, J. Appl. Crystallogr. 30 (1997) 647.
- [6] G. Materlik, C.J. Sparks, K. Fischer (Eds.), Resonant Anomalous Scattering, Theory and Applications, Elsevier Science, Amsterdam, 1994.
- [7] A. Benedetti, S. Polizzi, P. Riello, F. Pinna, G. Goerigk, ASAXS Investigation of a Au/C catalyst, J. Catal. 171 (1997) 345.
- [8] P. Riello, P. Canton, G. Fagherazzi, Quantitative phase analysis in semicrystalline materials using the Rietveld method, J. Appl. Crystallogr. 31 (1998) 78.
- [9] P. Riello, G. Fagherazzi, P. Canton, Scale factor in powder diffraction, Acta Crystallogr. A54 (1998) 219.
- [10] P. Riello, P. Canton, A. Benedetti, Au/C Catalyst: an experimental evidence of coexistence of nanoclusters and nanoparticles, Langmuir 14 (1998) 6617.
- [11] H.-G. Haubold, K. Gruenhagen, M. Wagener, H. Jungbluth, H. Heer, A. Pfeil, H. Rongen, G. Branderberg, R. Moeller, J. Matzerath, P. Hiller, H. Halling, JUSIFA – A new userdedicated ASAXS beamline for material science, Rev. Sci. Instrum. 60 (1989) 1943.
- [12] P. Riello, A. Benedetti, Small angle scattering of a polydisperse system of interacting hard spheres: An analytical solution, J. Chem. Phys. 106(21) (1997) 8660.
- [13] S. Enzo, S. Polizzi, A. Benedetti, Application of fitting techniques to the Warren–Averbach method for X-ray line broadening analysis, Z. Kristallogr. 170 (1995) 275.
- [14] A. Benedetti, G. Fagherazzi, S. Enzo, M. Battagliarin, A Profile-fitting procedure for analysis of broadened X-ray diffraction peaks II. Application and Discussion of the methodology, J. Appl. Crystallogr. 21 (1988) 543.
- [15] Joint Committee on Powder Diffraction Standards, 1988, Powder Diffraction File. Swarthmore, Pennsylvania: International Centre for Diffraction Data, No. 4–784 and 5–681.