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Taking "Nothing" into Consideration: Supported Metal Catalysts by SAXS

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Abstract: The analysis of the X-ray diffraction patterns scattered at small-angles (SAXS) by porous materials is a powerful analytical tool providing relevant structural information on supported metals used as heterogeneous catalysts. In particular, the technique offers valuable structural insights on the interphases which govern the chemical behaviour of these materials. Using a series of silica-supported palladium catalysts we show how SAXS experiments address the crucial importance of porosity (or "nothing") in affecting the structure of these catalysts.

Keywords: heterogeneous catalysis; nanoarchitecture; palladium; SAXS; silica; supported catalysts

Heterogeneous catalysis is an inherently nanoscopic phenomenon of fundamental societal relevance as it is applied for the production of most chemicals used today.[1] In a recent seminal paper[2] Rolison emphasized how: "Nothing (i.e., porosity) is an important part of any nanostructured system that does chemistry"; and that, "new opportunities for improved performance arise when the multifunctionality inherent in catalytic processes, including molecular transport of reactants and products, is rethought... including the use of 'nothing' (void space) and deliberate disorder as design components".[2] Similar arguments on the relevance of disorder and amorphousness to surface catalytic processes were introduced in the 1980s by Avnir.[3]

As novel synthetic catalysts approaching the performance of biocatalysts (in which size and shape selectivity are achieved in the absence of periodicity) will increasingly be made of amorphous porous structures,[2] the study of these multifunctional chemical systems will require analytical tools able to resolve the various surface interphases.[4]

Using a series of silica-supported Pd catalysts as a simple model of a randomly ordered catalytic system, we show how the SAXS analysis of disordered porous materials, being ideally suited to study colloidal inhomogeneities,[5] may offer a structural insight into this complexity.

Supported metal catalysts are widely used by the chemical industry to achieve fundamental transformations, including hydrogenation, oxidation and nitrogen fixation.[1] Until the introduction of homogeneous sol-gel processes,[6] all the methods employed for the fabrication of solid catalysts invariably made use of the heterogeneous reaction between a solid surface (inorganic or organic) and a precursor of the metal, typically followed by a reduction step affording the metal nanoparticles well dispersed at the surface of the matrix support.[7]

Large surface area materials are commonly (but not always) employed as catalyst support to ensure high dispersion of the noble metal and maximise activity. In general, the shape, nature and size of the *i*) porosity, *ii*) metal nanoparticles, and *iii*) support all play a major role in affecting the catalyst's activity. We show below how in practice an SAXS analysis can address the contribution of these structural aspects to the behaviour of these materials.

Figure 1 shows the fit to the experimental diffraction pattern reported according to the Porod equation for the asymptotic value of I(h):[9]

$$\lim_{h \to \infty} I(h)h^4 = k = 2\pi \sum (\rho_i - \rho_j)^2 S_{ij} \quad (1)$$

where ϱ_i is the i-phase electron density and S_{ij} the value of the interphase area; the height of the *plateau* [Figure 1, h^3 replaces h^4 in Eq. (1) when a collimated X-ray beam is used in place of the ideal punctiform beam] directly depends on the value of the interface surface.

The scattered intensity is given by the squared value of the Fourier transform of the correlation function, and the latter can be expressed in terms of the electron density fluctuation η:[5]

$$\gamma(\mathbf{r}) = [(V<\eta^2>)(2\pi)^3]^{-1} \int_0^\infty I(\mathbf{h}) e^{i\mathbf{hr}} d\mathbf{h} \quad (2)$$

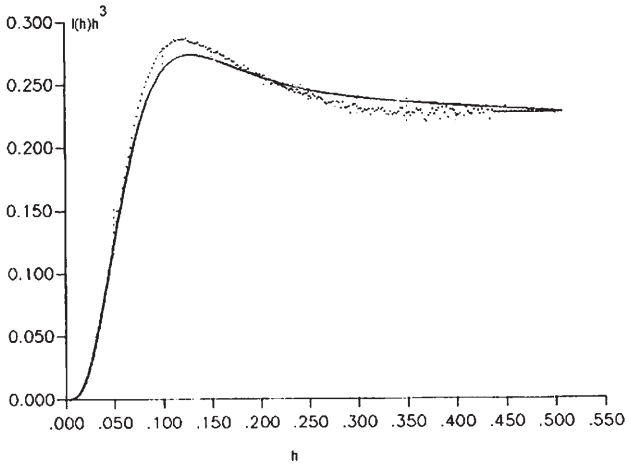

Figure 1. Theoretical fit to the experimental $I(h)h^3$ *vs.* h SAXS profile [for the 2.2% (w/w) Pd/SiO_2 catalyst, in this case] yields the specific surface area.

$$\gamma(\mathbf{r}) = [V\eta^2]^{-1} \int_0^\infty \eta(\mathbf{r}1 + \mathbf{r})\eta(\mathbf{r}1)d\mathbf{r} \quad (3)$$

It may thus be demonstrated that the correlation function of a triphasic (support, metal and void) porous catalyst can be parameterised of in terms of Stick Probability Functions $P_{ij}(r)$ and these, in their turn, in terms of the interphase surface area and angularity values.[9]

Fitting of the experimental plots such as that in Figure 1 using the experimental density values (skeletal and bulk) of the various silica-supported Pd catalysts (Table 1) affords the theoretical values of the interphases parameters (Table 2), including the surface areas and angularities of the silica support, of the support/metal phase and of the metal.

The angularity of an interphase surface corresponds to the second derivative of the SPF function calculated at the origin ($\mathbf{r} = 0$), and its value can be taken as a measure of a surface irregularity and roughness, as the angularity of a surface is $\neq 0$ only if the surface is *not* a smoothly varying continuous function, i.e., if it is a rough surface presenting edges of facets, edges and corners.

Table 1. Densities (skeletal and bulk) of various silica-supported Pd catalysts and volume fractions of the relative phases (1, 2, 3 = silica, void and metal, respectively).

Sample	Pd (w/w)[a] [%]	d_B[b]	d_S[c]	ϕ_1	ϕ_2	ϕ_3 ($\times 10^2$)
1	0	0.60	2.19	0.27	0.73	–
2	0.44	0.74	2.20	0.33	0.66	0.26
3	0.63	0.55	2.20	0.25	0.75	0.33
4	2.20	0.63	2.24	0.28	0.719	0.37
5	2.8	0.63	2.244	0.28	0.7185	1.47

[a] Chemical colorimetric analysis (UV/vis).
[b] Mass/volume.
[c] From published values.

Table 2. Theoretical values of the relative interphase areas and angularities of various silica-supported Pd catalysts.

Surface areas, Sij* [m^2/g]					
Sample	χ^2	σ	Support/ void	Support/ metal	Metal/ void
1	0	0.60	0.27	0.73	–
2	0.44	0.74	0.33	0.66	0.26
3	0.63	0.55	0.25	0.75	0.33
4	2.20	0.63	0.28	0.719	0.37
5	2.8	0.63	0.28	0.7185	1.47
Angularities, Aij [m^{-2}/g]					
			1.9238	-3×10^{-3}	0.1806
			2.1964	-1×10^{-3}	0.0248
			2.1096	-7×10^{-4}	0.024
			2.1868	-9×10^{-4}	0.0464

The large silica/void angularity A_{12} in Table 2 shows therefore that the interconnected particles of the silica gel have an extremely irregular (rough) external surface which in its turn is in accord with such interphase is a surface fractal with large Haussdorf dimension (*ca.* 3).[10]

In practice, in silica as in other physical objects, this surface fractality is limited to a narrow (two orders of magnitude) range of resolution;[11] but for the silica gel powders generally used in catalytic applications[12] this result implies that particles of different diameters have similar surface areas as a high D value means that the surface area is only weakly dependent on particle diameter.

Interestingly, recalling that amorphous silica is obtained by fast sol-gel hydrolytic polycondensation of $Si(OH)_4$, the convoluted surface of the SiO_2 xerogel points to a large extent of polycondensation (and branching) of the intermediate sol particles, and thus that almost all the silicon is at the surface yielding a polymer of formula $[SiO_3H_2]_n$,[6a] that is in accord with a non-equilibrium growing mechanism recently invoked for the formation of physical fractals.[11]

The low metal/void angularities (A_{23}), in turn, confirm the common observation that metal nanocrystallites have an external smooth surface, in which layers of metal atoms are closely packed to minimise distance and potential energy.

Finally, the negative values of metal/support angularities, A_{13}, point to a metal/support configuration such as that in Figure 2. Indeed, the angularity A_{13} in the case of a contact line among three different phases is given by:[9]

$$P_{13}''(0) = -A_{13}/4V = -(1/6\pi V) \cdot \int dy\, [(\pi - \alpha_3)\cot(\pi-\alpha_2) - (\pi-\alpha_3)\cot(\pi-\alpha_3)] \quad (4)$$

Therefore, when the contact angle between the support (1) phase and the void (2) $\alpha_2 > \pi/2$ along the whole con-

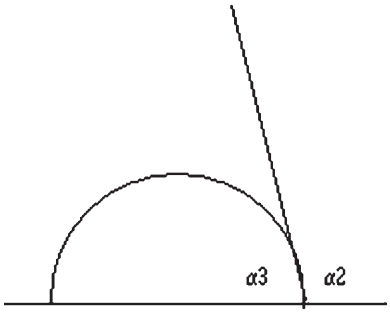

Figure 2. A possible configuration of the metal particles justifying negative angularities: hemispheres grown over a silica support.

Table 3. Metal/void surface areas, particles diameter and dispersion of various silica-supported Pd catalysts obtained by SAXS analysis of the powders.

Sample	Pd (w/w)[a] [%]	S° m^2/g metal	D [Å]	FE
1	0.44	168.3	29.7	0.37
2	0.63	171.5	29.1	0.38
3	2.20	150	33.3	0.33
4	2.80	171.2	29.2	0.38

tact line between the phases, then P_{13}"(0) is positive and, as a consequence, the corresponding angularity is negative; an outcome which is consistent with an epitaxial growth model of the metal surfaces in the shape of hemispherical nanoparticles at the external surface of silica.

The values of the metal/support surface area in Table 1 directly afford the FE values of the metal dispersion in Table 3, that in the case of Pd can be written as follows:

$$FE = 11.12/D(Å) \quad (5)$$

The nearly constant values of FE in catalytic samples differing in metal load up to 6-fold can be ascribed to the large support/void interphase surface area offering a wide accessible space for metal particles separation that allows optimal separation of the metallites and high dispersion even at relatively high catalytic loads.

This finding indicates the crucial importance of the void phase (i.e., "nothing") mentioned above.[2] In practical applications, where such dispersion is of central importance, it is the task of the chemist to fabricate porous structures capable to retain high porosity, and thus elevate dispersions, while the reactants get chemically processed at the metal nanoparticles supported at the external surface. It is the large porosity of the silica gel – i.e. "nothing" – to determine the large metal dispersion of supported metal nanoparticles and thus ensure the high activity of supported metal catalysts. In order therefore to design catalytic nanoarchitectures of higher activity, one should plan the synthesis of large-surface area catalysts in which the support retains its stability during catalysis in order to avoid pore collapse and sinterisation of the metal particles.

Indeed, this is precisely what is needed in the development of high-performing porous sol-gel doped materials[13] in which progressive shrinkage and collapse of the large porosity and surface area are commonly observed.

While progress is in course, and solutions are to this problem are being found, such as the use of fluorinated silica matrices[14] or the employment of mechanical support,[15] the SAXS technique should be more widely considered as a rapid analytical tool able to provide a wealth of structural information in catalysis research, well beyond the catalytic textural properties commonly reported.

Experimental Section

The materials were obtained by a liquid-phase heterogeneous reaction.[8] A suspension of silica gel (10 g, Aldrich 23,675–6) in pentane (50 mL) thermostatted at $-10\,^{\circ}C$ was added with a pentane solution of $Pd(\eta^3\text{-}C_3H_5)_2$ under continuous stirring in an argon atmosphere. Catalysts of different loads were obtained using palladium-allyl solutions in various concentrations. After 3 h, the temperature was increased to $0\,^{\circ}C$ and the mixture left to stir to ensure complete anchoring of Pd. The suspension was then washed with pentane (20 mL, $\times 3$) and treated with H_2 (1 atm) at $-15\,^{\circ}C$ to reduce the anchored -$Pd(C_3H_5)$ moieties. The low temperature prevents sinterisation of the Pd particles thereby obtained. The solvent was finally evaporated and the catalyst stored under nitrogen. Catalytic Pd loads were determined by a colorimetric method at 525 nm. The SAXS experiments were carried out with a vertical powder diffractometer using a generator operating at 40 kV and 30 mA equipped with a Paar compact Kratky camera using Ni-filtered Kα radiation and a scintillator counter. Angularity, interphase surface area and Porod average diameter of the metal particles were calculated using a triphasic parameterisation of the material using the function minimisation Minuit programme developed at CERN (Geneva). The profile intensities were measured step by step (0.05° in 2θ) with a relatively long acquisition time for each point thereby set to ensure accuracy at all values of the scattering vector (typically, a single diffractogram was recorded in 12 h) corrected for absorption due to the sample holder by dividing the intensity values for the experimentally measured $\exp(-\mu t) = \langle I\rangle/\langle I_0\rangle$, in which $\langle I\rangle$ is the average of ten experimental intensities measured in the presence of the sample, μ is the absorption coefficient of the material and $\langle I_0\rangle$ the average over ten values measured at $2\theta = 0$ (using a beam attenuator to prevent detector's destruction). All measurements were conducted under infinite slit-height approximation and a scattering background was subtracted for each sample.

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[12] For instance, Grace's Davicat silica gels for catalysis are produced in particle sizes ranging from a few microns for granular and spray dried gels through to 4 mm for granular gels. See also at the URL: http://www.gracedavison.com/products/speccats/davicat/products.htm (last accessed August 10, 2005).

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