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In situ anomalous small-angle X-ray scattering from metal particles in supported-metal catalysts. II. Results

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Information about the metal phase in a supported-metal catalyst can be obtained using anomalous small-angle X-ray scattering (ASAXS). The difference between the scattering profiles for SAXS at two different wavelengths near the metal's absorption edge is essentially the scattering of the metal alone. Novel *in situ* ASAXS measurements are made on mordenite impregnated with platinum metal while the temperature and composition of gas in the sample cell are changed. Measurements are made 62 times during treatment of the catalyst. The metal particles are assumed to be randomly distributed spheres with N(R)dR = number of spheres with radii between R and R + dR. It is found that N(R) is always a monotonically decreasing function of R, and that the average value of R, obtained from N(R), decreases by a factor of two over the time (approximately 6 h) for which the system is observed.

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1. Introduction

The activity and properties of a supported-metal catalyst depend not only on the chemical state of the support and the metal, but also on the interphase surface areas and particle sizes (Wachs, 1992; Stiles & Koch, 1995). Since these depend on the details of catalyst preparation, it is important to examine the correlation between catalyst morphology and processing parameters. Since they also probably change under reaction conditions, when the catalyst is exposed to changing atmospheres and temperatures, it is of interest to make measurements of catalyst properties *in situ*.

Because X-rays penetrate a bulk solid, such as a catalyst, non-destructively, X-ray scattering is useful for such measurements. Indeed, an early review (Somorjai et al., 1967) characterized small-angle X-ray scattering (SAXS) as 'the most versatile' technique for investigation of the state of the metal in supported-metal catalysts, and SAXS studies continue to appear (Li et al., 2003). Recently, it has been shown that, under the proper conditions, electron microscopy can also be used to investigate interphase surface areas, particle shapes, and particle sizes (Jacoby, 2002). Canton et al. (2003) measured the sizes of Pd nanoparticles supported on silica using high-resolution transmission electron microscopy and compared their results with those from adsorption measurements and line-broadening analysis of X-ray spectra. Other methods of characterizing supported-metal catalysts include gas adsorption and various spectroscopies; they have been reviewed by Meitzner (1992).

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In our previously reported (Brumberger, 1988; Brumberger *et al.*, 1996; Ramaya, 1997) SAXS measurements on supported-metal catalysts, we subtracted the scattering of the support alone from the scattering of the catalyst to obtain the scattering of the metal particles. The validity of this subtraction may not be completely justified. Other ways to remove the scattering of the support include crushing the catalyst to remove thes, and filling the holes with a liquid of electron density equal to that of the support framework (Somorjai *et al.*, 1967). A better means to remove support scattering is by making measurements at two different X-ray energies near the absorption edge of the metal in the catalyst (Naudon, 1995; Creagh, 1999). The difference in the scattering at the two wavelengths should consist essentially of the scattering of the metal (see below).

The catalysts we study here are zeolites impregnated with platinum. Assuming they consist of three homogeneous phases, namely zeolite (phase 1), void (phase 2), and metal (phase 3), their X-ray scattering arises from inhomogeneities in the electron density associated with phase boundaries. The scattering intensity is proportional to the Fourier transform of the correlation function $\gamma(r)$, which can be written (Goodisman & Brumberger, 1971; Ramaya, 1997) in terms of the 'stick probability functions' $P_{ii}(r)$; $P_{ii}(r)$ is the probability that a stick of length r, randomly located in the system, has one distinguishable end in phase i and the other in phase j. Consider two three-phase systems with the same P_{ij} , but having different electron densities for phase 3. Let their scattering intensities be I'(Q) and I(Q). In the preceding article (Brumberger et al., 2005), we showed that the difference, I'(Q) - I(Q), does not involve P_{12} and that, provided

[†] Deceased.

that P_{13}/P_{23} is equal to the ratio of volume fractions of support and void, I'(Q) - I(Q) has the form of the scattering of a twophase system. One phase is phase 3 and the other an average of phases 1 and 2.

The alteration of the electron density of phase 3 is accomplished by using X-rays with wavelengths near the absorption edge of the metal, and taking advantage of the anomalous scattering (Georgopoulos & Cohen, 1985; Epperson & Thiyagarajan, 1988; Creagh, 1999). Near the absorption edge, the index of refraction and hence the scattering power of the metal vary noticeably with wavelength, so measuring the scattering at two different wavelengths is equivalent to measuring the scattering from two systems with different values of n_3 , the electron density of phase 3. The source of monochromatic X-rays of appropriate wavelengths is the Cornell High Energy Synchrotron Source (CHESS). Synchrotron radiation has an additional advantage over radiation from conventional sources: the much higher intensity. This makes it possible to obtain the X-ray scattering profile I(Q) for each wavelength in seconds rather than many minutes. Thus I(Q) can be obtained for a system in which the correlation function or the particle size distribution changes with time. We also take advantage of a novel simultaneous dual-energy method of data collection.

The application of anomalous small-angle X-ray scattering to problems in materials science has recently been reviewed by Goerigk et al. (2003). ASAXS has now been used by a number of workers to study the size distribution of catalyst particles in porous supports, as we do in the present work. These systems include Pd particles on a silica support (Canton et al., 2003), Au and Pd supported on active carbon (Benedetti et al., 1999), Ni on an SiO₂ support (Rasmussen et al., 2000), a Raney nickel-type catalyst (Bota et al., 2002), platinum electrocatalysts on a carbon support (Haubold et al., 1996, 1997, aluminio-organic-stabilized 1999). platinum networks (Bönnemann et al., 2002; Vad et al., 2002), and colloidal Pt particles during their formation (Haubold et al., 2003). A discussion of problems connected with such measurements has appeared (Polizzi et al., 2002). Anomalous wide-angle X-ray scattering has been used to study a Sn/Zn system supported on alumina (Revel et al., 2002).

2. Theoretical considerations

For an isotropic system, the scattering intensity I(Q), $Q = 4\pi\lambda^{-1}\sin(\theta/2)$ with λ the wavelength of the radiation and θ the scattering angle, is proportional to the Fourier transform of the correlation function, which is equal to

$$\gamma(r) = \frac{1}{\langle \eta^2 \rangle} \left[\sum_{i,j} P_{ij}(r) n_i n_j - \langle n \rangle^2 \right], \tag{1}$$

where $P_{ij}(r)$ is the stick probability function. Carrying out SAXS measurements at two wavelengths near an absorption edge is equivalent to performing them on two systems having the same structure (volume fractions, interphase surface areas, *etc.*) but different electron densities for one phase (phase 3,

the metal, in our systems). We showed (Brumberger *et al.*, 2005) that the difference in the SAXS for the two wavelengths is

$$I'(Q) - I(Q) = 8\pi V I_e(Q) (n_3 - n'_3) \int_0^\infty dr \, r^2 \frac{\sin(Qr)}{Qr} \times \Big[n_A (P_{AB} - \varphi_A \varphi_B) + n_B (P_{BB} - \varphi_B \varphi_B) \Big],$$
(2)

which is the scattering of a two-phase system. Phase B is phase 3 of the original three-phase system, and phase A the average of phases 1 and 2, so that phase A has volume fraction $\varphi_A = \varphi_1 + \varphi_2$ and average electron density

$$n_{\rm A} = \frac{\varphi_1 n_1 + \varphi_2 n_2}{\varphi_1 + \varphi_2}.$$

The stick probability P_{BB} is P_{33} and P_{AA} is $P_{11} + P_{12} + P_{21} + P_{22}$. The assumption that

$$\frac{P_{13}}{P_{\mathrm{AB}}} = \frac{\varphi_1}{\varphi_{\mathrm{A}}} = \frac{\varphi_1}{\varphi_1 + \varphi_2}$$

was made, *i.e.* that phases 1 and 2 are arranged randomly in the new combined phase A. The electron density difference $(n'_3 - n_3)$ is actually the difference in atomic form factors for the metal at two different X-ray wavelengths.

The metal is expected to be in the form of particles, embedded in the second phase. We suppose the particles are all of the same shape and randomly oriented, but of different sizes or radii, such that N(R)dR is the number of particles having characteristic radius between R and R + dR. Letting A(r; R) be the probability that a stick of length r, having one end located in a particle of radius R, has the other end in the same particle, we find (Brumberger *et al.*, 2005)

$$\frac{I'(Q) - I(Q)}{8\pi V I_{\rm c}(Q)(n_3 - n'_3)} = (\overline{n}_3 - n_{\rm A})\varphi_3(1 - \varphi_3) \int_0^\infty N(R)$$
$$\times \left[\int_0^\infty {\rm d}r \, r^2 \frac{\sin(Qr)}{Qr} A(r; R) \right] {\rm d}R,$$
(3)

where \overline{n}_3 is the average of n_3 and n'_3 . We assume that the particles are spheres, and write the distribution function as

$$N(R) = \exp(-\alpha R)(\beta + \gamma R + \delta R^2).$$
(4)

Then the difference scattering is given by

$$I_{t}(Q) = \int_{0}^{\infty} dR \exp(-\alpha R)(\beta + \gamma R + \delta R^{2})(4\pi\rho)^{2} \\ \times [\sin(QR) - QR\cos(QR)]^{2}/Q^{6},$$

which can be evaluated in closed form. The multiplicative constant in equation (3) is incorporated into β , γ and δ .

The values of the four parameters $(\alpha, \beta, \gamma, \delta)$ in N(R) are chosen to obtain the best fit of $I_t(Q)$ to the experimental I(Q).

Specifically, we minimize the sum of the squared relative deviations,

$$S = \sum_{j} \left[\frac{I(Q_j) - I_t(Q_j)}{I(Q_j)} \right]^2, \tag{5}$$

with respect to all four parameters. The sum in equation (5) is over the values of Q for which scattering intensity can be measured reliably. In our work, this corresponds to 517 values with $0.029 < Q < 0.149 \text{ Å}^{-1}$; intensities for larger Q are too small to measure and intensities for smaller Q are blocked by the apparatus. From the determined values of the parameters (α , β , γ , δ), we calculate properties of the distribution. Of particular interest are the two average values:

$$\langle R \rangle = \left(\frac{\beta}{\alpha^2} + \frac{2\gamma}{\alpha^3} + \frac{6\delta}{\alpha^4} \right) / \left(\frac{\beta}{\alpha} + \frac{\gamma}{\alpha^2} + \frac{2\delta}{\alpha^3} \right),$$

$$\langle R^2 \rangle = \left(\frac{2\beta}{\alpha^2} + \frac{6\gamma}{\alpha^3} + \frac{24\delta}{\alpha^4} \right) / \left(\frac{\beta}{\alpha} + \frac{\gamma}{\alpha^2} + \frac{2\delta}{\alpha^3} \right).$$

$$(6)$$

The difference, $\langle R^2 \rangle - \langle R \rangle^2$, is a measure of the width of the distribution N(R).

3. SAXS measurements

The measurements of X-ray scattering patterns were made on the C1 station of the Cornell High-Energy Synchrotron Source (CHESS), with an available energy range from 6 to 30 keV. A horizontal focusing side-bounce monochromator disperses energy with angle at the sample, permitting simultaneous dualenergy measurement. The two X-ray energies used were 11.546 ± 0.0152 keV and 11.305 ± 0.0083 keV. The former is just below the Pt L_3 edge (at 11.564 keV): as close as possible without exciting substantial background fluorescence. The coherent scattering factor for X-rays of energy $E (E = hc/\lambda)$ is given by (Haubold *et al.*, 1994; Naudon, 1995; Cross *et al.*, 1998)

$$f(Q, E) = f_0(Q) + f'(q, E) + if''(q, E),$$

where f_0 is the Fourier transform of the electron density and f'' is proportional to the absorption coefficient. The real part of the scattering factor, $f_0 + f'(E)$, varies markedly near the absorption edge, so that $f_0 + f'$ is equal to 52.4 at the cusp minimum and about 68 at the lower energy, giving a theoretical difference of more than 15 electrons. Smearing due to finite energy resolution diminishes this somewhat.

A system of slits was arranged to select two rays, corresponding to two X-ray energies, that passed through the sample, diverged and formed spots on two beamstops about 1 m downstream. These were just in front of a CCD area detector, placed perpendicular to the beam axis, which recorded the superposition of two SAXS patterns. Because the scattering intensity decreases rapidly with Q, the intensity falling on any point of the detector is dominated by the SAXS intensity from the closer of the two rays. Therefore, the intensity in each pixel (see below) is assigned to the scattering pattern of the closer ray, with Q calculated from the in-plane distance of the pixel from that ray. The working area of the detector, a Quantum-1 X-ray CCD camera (Area Detector Systems Corp.), contained 1152 × 1152 pixels. Scattering intensities were derived from pixel intensities in a manner which used information from as many pixels as possible. Let *L* be the distance from the sample to the detector along the beam axis (*z* direction). Let {*x_j*, *y_k*} be the coordinates of the *j*, *k* pixel (*j* = 1...1152, *k* = 1...1152), and let the coordinates of the two beams be {*x_A*, *y_A*} and {*x_B*, *y_B*}. The polar coordinates of the *j*, *k* pixel with respect to beam A are

$$r_{jk}^{A} = \left[(x_j - x_A)^2 + (y_k - y_A)^2 \right]^{1/2}$$
 and $\varphi_{jk}^{A} = \tan^{-1} \frac{y_k - y_A}{x_j - x_A}$,

and similarly for beam B. Q_{jk}^{A} , the value of Q for this pixel relative to beam A, depends on the scattering angle θ_{jk}^{A} , where $\sin(\theta_{jk}^{A}) = r_{jk}^{A}/L$. Since Q_{jk}^{A} does not depend on φ_{jk}^{A} , all the pixels on a circle of radius r_{jk}^{A} have the same value of Q relative to beam A.

The two beams were centered at about the 400th pixel in the y direction. The maximum value of r_{ik}^{A} that could be observed was thus about 600 pixel lengths. The lengths nD, $n = 1 \dots N$ with $ND \simeq 600$ pixel lengths, define N intervals, with the nth having Q^{A} corresponding to $r^{A} = (n - \frac{1}{2})D$. The scattering intensity $I(Q^A)$ was calculated as the average of the intensities of pixels for which Q_{ik}^{A} was between (n - 1)D and nD. As noted above, these pixels lie on an arc of a circle, the length of the arc depending on Q^A . For small Q^A , few pixels contribute because the circle radius is small. For large Q^A , the number of usable pixel intensities again becomes small for two reasons: much of the arc may not fall on the detector, and some of the pixels are closer to beam B than to beam A so are dominated by scattering intensity from beam B. Since we chose $D = \frac{1}{2}$ pixel length, intensities were obtained for about 1100 equally spaced values of Q^A , but those for small and large Q^A were not reliable and were not used.

Collection of the SAXS pattern required slightly more than 2 min, and data downloading required about a further 15 s. It was thus possible to start a new run about every 2.5 min. From the downloaded data, intensity as a function of scattering angle was calculated for both X-ray energies and subtracted. 62 measurements were made, each of which produced 10^6 data points which were subsequently used to calculate intensities for 1100 values of Q^A and Q^B . The measurements are numbered consecutively, from 158 to 225, as shown in Fig. 1. The heating program (measured temperature as a function of time) is also shown in Fig. 1.

The prepared catalyst (see below), originally at room temperature, was heated while being purged with He (ultrapure from Empire Gas Corp.) at 1 atm until the temperature reached 673 K (run number 171). The temperature was maintained close to 673 K from run 172 (time $\simeq 40$ min) to the end of measurement (time $\simeq 340$ min). At time $\simeq 40$ min, the gas flowing through the catalyst cell was changed to 10% oxygen, 90% helium (ultrapure from Empire Gas Corp.), an oxidizing atmosphere, which was expected to produce sintering. At run 200 (time $\simeq 160$ min) the gas was changed to pure hydrogen (ultrapure from Empire Gas Corp.), a reducing



Figure 1

Measured temperature of the catalyst system as a function of time. Each circle represents a measurement of scattering intensity for two wavelengths and about 1100 values of Q. The numbering of the runs shown in this figure is used to refer to particular measurements throughout. The gas flowing over the sample is He until run 170, 10% O_2 from 171 to 200, and H₂ thereafter.

atmosphere, which was maintained until the end of the measurements.

Each symbol in Fig. 1 indicates the time and temperature at which scattering intensity was measured as a function of angle at two X-ray wavelengths. In each measurement set, the data eventually used were for scattering angles corresponding to $0.029 < Q < 0.149 \text{ Å}^{-1}$, where $Q = 4\pi\lambda^{-1}\sin(\theta/2)$ with λ the radiation wavelength and θ the scattering angle. For $Q > 0.149 \text{ Å}^{-1}$, intensities were so low that the uncertainty in the difference was a sizable fraction of the measured intensity. The number of data points used in the fitting [by minimization of the relative standard deviation, equation (5)] was 617. In the fitting process, several different starting guesses at the parameter values were used; the fitting algorithm always found the same values to minimize the relative standard deviation.

4. Preparation of catalysts

The zeolite LZ-M-5, manufactured by the Linde division of Union Carbide, is a synthetic analog of the naturally occurring zeolite mordenite. The composition, as reported by the supplier, is 78.7 wt% SiO₂, 12.5 wt% Al₂O₃, and 7.33 wt% Na₂O. The crystallographic unit formula is Na₈[(AlO₂)₈-(SiO₂)₄₀]·*z*H₂O. LZ-M-5 is very stable to dehydration (water loss at 1273 K is 13.1 wt%), has high acid stability, and resists thermal degradation to over 1173 K. The void volume is 28%. Since it has a straight one-dimensional channel system characterized by a pore opening of 6.7×7.0 Å, it is easily loaded with metal by ion exchange.

In preparing a zeolite-supported metal catalyst, the catalyst metal is ion-exchanged into the zeolite, and then, after preliminary drying, the system is subjected to two heat treatments: (a) calcination, heating in an oxidizing atmosphere (usually air); and (b) reduction, heating in a reducing atmosphere (usually hydrogen). The result is a free-flowing powder. The

solution used to impregnate the zeolite support with platinum metal via ion exchange was tetraamineplatinum(II) chloride monohydrate. A solution of 5 g of this platinum salt in 500 ml of deionized water, which contained a total of 2.77 g of platinum, was prepared (55.4 wt% Pt). To obtain a nominal loading of 5 wt% on 20 g of zeolite, 20 g of the zeolite support was mixed with 320 ml of deionized water, and 180.5 ml of the Pt solution was added dropwise with stirring. The temperature was then raised to 353 K and kept there for 1 h while the mixture was slowly stirred. After cooling, filtration and washing with deionized water to remove Cl⁻ ions, the catalyst was allowed to dry at room temperature, placed in a vacuum system, and dried under vacuum overnight. The following morning the catalyst, under vacuum, was heated slowly to 371 K, kept there for 3 h to remove water, and cooled to room temperature. In spite of these procedures, it is likely that some water remained in the catalyst, or re-entered during transfer steps.

To determine the platinum concentration in the catalyst, a weighed sample of the finished catalyst was reacted with hydrofluoric acid in a bomb. After rinsing and drying, the remaining metal was weighed. In all cases, the wt% Pt was within 10% of the nominal 5 wt% Pt.

5. Results and analysis

Measurements were made during the heating of the catalyst from room temperature to 673 K, which required about 35 min, and for several hours thereafter, during which the catalyst was held at 673 K. As mentioned in §3, the gas flowing through the sample cell was He until the temperature reached 673 K, after which it was changed to 10% O₂ (oxidizing atmosphere), and subsequently to pure hydrogen (reducing atmosphere).

Fig. 2 shows some of the SAXS difference profiles. Each curve gives I_d , the difference of scattering intensities for the two X-ray wavelengths, as a function of Q. In Fig. 3, the same profiles are shown as Porod plots, *i.e.* Q^4I_d is plotted *versus* Q^4 . Fig. 4 shows four of these profiles with the experimental errors. Since $I_d(Q)$ is a difference between two intensities, I(Q) - I'(Q), the experimental error in $I_d(Q)$ is calculated as the square root of the sum of the squares of the errors in I(Q) and I'(Q). Each of these is taken equal to the square root of the number of counts.

The plots for the 62 measurements, of which the plots of Figs. 2 and 3 are representative, fall into three groups. In the first, corresponding to temperatures below 673 K and He atmosphere, the Porod plots are featureless, although the slopes, which are initially negative, increase through zero to positive values (runs 158, 160 and 168). In the second, corresponding to a temperature of 673 K, but with the atmosphere changed to 10% oxygen, a maximum develops in the Porod plot at $Q^4 \simeq 10^{-4} \text{ Å}^{-4}$, with a slight minimum at $Q^4 \simeq 2 \times 10^{-4} \text{ Å}^{-4}$; for larger Q the Porod plot is linear with increasing slope (runs 173, 187, and 199). The maximum results from the rapid increase in I_d as Q decreases below $2^{1/4} \times 10^{-1} \text{ Å}^{-1}$ (see Fig. 2); multiplied by the rapid decrease in the Q^4 factor in this

region. The maximum is maintained in the third group of Porod plots, with the slope for $Q^4 > 2 \times 10^{-4} \text{ Å}^{-4}$ increasing more rapidly (runs 201, 204, 212 and 221). The slope increase is largest between runs 199 and 200, which is the point at which the oxidizing atmosphere (10% O₂, 90% He) is replaced by



Figure 2

Difference of scattering intensities (intensity $I_{\rm d}$ versus Q) from results of ten representative measurements. Units of intensity are arbitrary. See caption to Fig. 1 for numbering scheme used. Data for $0.029 \le Q \le 0.149$ Å were used in fitting to the model according to equation (5). Data for Q < 0.105 Å are not shown in the figure for reasons of clarity.





Porod plots $(Q^4 \times \text{intensity versus } Q^4)$ of the difference of scattering intensities for two wavelengths, for the ten measurements for which intensity differences were plotted in Fig. 2. See caption to Fig. 1 for numbering scheme used. Units of intensity are arbitrary. The range of data used in fitting to the theoretical model is $7.1 \times 10^{-7} \le Q^4 \le 0.00049 \text{ Å}^{-4}$. Data for $Q^4 < 0.00015 \text{ Å}^{-4}$ are not shown in the figure for reasons of clarity.

the reducing atmosphere (pure H_2). The increase in I_d at large Q must correspond to smaller particles being formed.

Fig. 5 shows the theoretical fits to the independent-sphere model discussed above, along with the experimental data, for three of the plots of Figs. 2 and 3. The sum of the squares of the relative deviations S [equation (5)] was between 2 and 5 for all the runs except numbers 172 and 200 (which correspond to the



Figure 4

Four of the Porod plots of Fig. 3 (bottom to top, numbers 160, 173, 201 and 214) with experimental errors. The experimental error in $I_d(Q) = I(Q) - I'(Q)$ is taken as the square root of the sum of the squared errors in I(Q) and I'(Q), *i.e.* as $[I(Q) + I'(Q)]^{1/2}$.



Figure 5

Four-parameter best fits, according to equation (4), for three of the intensity plots of Figs. 2 and 3, compared with experimental data. Lines are calculated intensities, symbols are measured intensity differences. Every seventh experimental point is shown. The inset shows the normalized radius distribution function N(R) for the same three runs, using equation (4) with the parameters giving the best fits.

points at which atmospheres were changed). In these two cases, a few experimental points which are significantly out of line account for the increase in *S* over 5. Since there were 506 data points, a value of 5 for *S* corresponds to a root-mean-square relative deviation of less than 0.1, *i.e.* < 10% deviation between the experimental and fitted scattering plots. This is well within the statistical errors shown in Fig. 4.

The inset to Fig. 5 shows the normalized radius distribution function N(R) for the measurements shown, calculated using the four parameters yielding the best fit in each case. Clearly, the functions for later time shift to smaller values of R, a general trend over all the runs (Fig. 6 shows the average values of R for all runs). It is also noteworthy that, even though the function, equation (4), is capable of giving extrema, the values of the parameters determined to give minimum S, equation (5), always make N(R) a monotonically decreasing function. Of course, the distribution cannot be monotonic down to R =0, as predicted by this function. It must be remembered that N(R) is determined to give the best fit of I(Q) for the range of



Figure 6

Calculated $\langle R \rangle$ = average value of *R* (filled circles), and root-mean square deviation from the mean, $[\langle R^2 \rangle - \langle R \rangle^2]^{1/2}$ (squares), for all runs. These were calculated using *N*(*R*) of equation (4) with best-fit values of the four parameters.



Figure 7

Best-fit values of the exponential parameter α in the radius distribution function N(R), equation (4). This parameter is the most important in determining $\langle R \rangle$.

Q for which intensities were measured, and need not be correct for values of *R* which do not affect the measured scattering. Since $0.029 < Q < 0.149 \text{ Å}^{-1}$, the range of *R* is roughly from 7 to 34 Å.

The average value of *R* and the value of $T = [\langle R^2 \rangle - \langle R \rangle^2]^{1/2}$ are shown in Fig. 6. In general, *T* is about the same size as, but somewhat greater than, $\langle R \rangle$. That the two quantities are about the same size is expected since N(R) is approximately an exponential. If N(R) were proportional to $\exp(-\kappa R)$, $\langle R \rangle$ would be $1/\kappa$ and $\langle R^2 \rangle$ would be $2/\kappa^2$ so that *T* would be $1/\kappa$, exactly equal to $\langle R \rangle$. Generally, we find that *T* remains slightly above $\langle R \rangle$.

However, in runs 159–165, $\langle R \rangle$ decreases systematically, from 19.8 to 16.2 Å, while T increases systematically and appreciably, from 21.6 to 24.0 Å. This behavior may signal important changes in N(R) as the temperature increases to 673 K. There are also several exceptions to $T \ge \langle R \rangle$. For runs 166 and 167, $\langle R \rangle$ suddenly becomes significantly larger, making T significantly smaller than $\langle R \rangle$. This unphysical behavior casts doubt on these two runs. Other exceptions to $T \ge \langle R \rangle$ occur for runs 190–192, for which $\langle R \rangle$ is about twice as large as for nearby runs, but T is not much increased. This is also suspected to indicate experimental problems.

The most important parameter in determining $\langle R \rangle$ is the exponential parameter α . The values of α for all runs are shown in Fig. 7. Consistent with the overall decrease in $\langle R \rangle$, α increases overall by a factor of two. Exceptions occur where they were noted for $\langle R \rangle$: α increases from 0.046 to 0.078 between 167 and 169, α increases from 0.076 to 0.093 between 188 and 190 (there are no data for run 189), etc. The other parameters in N(R) behave differently. Thus, β is relatively constant at about 10 through run 169, jumps to over 100 and remains there through run 188, drops to negative values for a few runs, and then increases more and more rapidly (the fastest increase is after run 200), ending up over 1200. The parameter γ is small and negative (size less than 1 Å^{-1}) through run 188, is positive and several $Å^{-1}$ in size through run 195, and then decreases more and more rapidly, ending up below -70 Å^{-1} . Finally, δ remains very small (size several hundredths of $Å^{-2}$) until run 200, then increases rapidly and monotonically to ~ 1.2 Å⁻².

Because of the possibility that individual runs are invalid, one should look only at overall trends. We conclude that the average value of R decreases with time. The decrease is at first rapid (through run 170), then almost zero (through run 200), and then becomes more rapid again. It appears that, instead of sintering, which would increase the average size of the particles, disintegration is taking place. This is at variance with the conclusions of previous work (Brumberger *et al.*, 1996; Ramaya, 1997; Cicariello *et al.*, 1999) on Pt-NaY zeolite catalysts that sintering occurred during calcination.

6. Discussion and conclusions

In this paper, we analyze the small-angle X-ray scattering from a supported-metal catalyst, modeled as a system of three homogeneous phases with sharp phase boundaries. If the X-ray wavelength is close to, but below, the absorption edge for one of the phases, changing the wavelength is equivalent to changing the effective scattering power or electron density of that phase (phase 3). We have shown that, in this case, the difference in the SAXS at two such X-ray wavelengths is equivalent to the SAXS of a two-phase system. In the twophase system, one phase is phase 3 of the three-phase system (the metal in the present example) and the other phase is an average of phases 1 and 2 of the three-phase system.

We model the two-phase system as a random distribution of particles of the same shape (spheres) but different sizes. The sphere scattering function I^{sph} , multiplied by the distribution function N(R) [equation (4)] and integrated over R, gives the theoretical scattering intensity curve I_t [equation (3)]. The values of the four parameters in N(R) were chosen to minimize the sum of the relative squared deviations [S, equation (5)] between I_t and the experimental difference scattering curve. From the parameters in the distribution function, we determined average particle size according to equation (6).

The correct sphere scattering function was used in preference to the Guinier approximation because the latter does not give the correct Porod law behavior, $IQ^4 \rightarrow$ constant as $Q \rightarrow$ ∞ . In fact, our experimental scattering (see Figs. 3 and 4) does not obey Porod's law at our largest Q values. The reason for this may be that the interphase boundaries are not completely sharp, or that one needs to go to larger Q to see the Porod law behavior. If the former is the case, a constant term should be added to I_t . We carried out calculations using $I'_t = C' + I_t$ and chose the five parameters [four parameters in N(R) plus C'] to minimize the sum of the relative squared deviations between I'_{t} and the experimental scattering curve. The result was that C' increased markedly and fairly uniformly with time, and the parameters in N(R) took on unreasonable values. It is possible that the scattering data is not extensive enough (we did not have a sufficiently large range of Q) meaningfully to determine more than four parameters. However, the increase in C'with time is a necessary consequence of using $I'_t = C' + I_t$ to fit our data, and it makes no sense if C' represents inhomogeneities in phase boundaries, as there is no reason for the inhomogeneities to increase with time. We believe that the explanation for the non-Porod behavior is the limitation on O. Note that $Q = 0.149 \text{ Å}^{-1}$ corresponds to $\sim 7 \text{ Å}$, about the radius of the smaller particles found by other workers (see below).

The parameters for the distribution function N(R), determined by fitting calculated to observed scattering intensity, gave a monotonically decreasing N(R) in every case. This is in spite of the fact that the form of N(R), equation (4), is capable of yielding a maximum while still being positive for all R > 0. The monotonically decreasing N(R) is at variance with previously published results (see below). The discrepancy may be due to differences between the systems examined, or to use of an insufficiently flexible N(R) [equation (4) cannot give a bimodal distribution, for example]. Unfortunately, the accuracy of the data does not justify using more fitting parameters by, for example, writing N(R) as an exponential multiplied by a cubic in R. From N(R) we calculate the average value of R, $\langle R \rangle$, according to equation (6). Aside from some excursions which are probably artifacts of the experiment, $\langle R \rangle$ decreases during the course of the experiment (Fig. 6). The excursions correspond to data sets taken when the flowing gas was changed. The changeover from pure He to 10% O₂ was at $t \simeq 40$ min, and the changeover from 10% O₂ to pure H₂ was at $t \simeq 160$ min. Note that temperature control also became problematic when these changeovers occurred (see Fig. 1).

In our previous work on these systems (Brumberger *et al.*, 1996; Ramaya, 1997), we considered the catalyst as a threephase system and wrote the scattering intensity as C_1 times the scattering of the support alone (measured separately) plus the scattering of a distribution of particles. The Guinier approximation was used for the scattering of a single particle, and the distribution function was $N'(R) = \gamma R^{\beta} \exp(-\alpha R^2)$, the four parameters ($C_1, \alpha, \beta, \gamma$) being chosen to obtain the best fit of calculated to observed intensities. Although this P'(R) has a maximum at $R = [\beta/(2\alpha)]^{1/2}$, the values of β found by fitting (unpublished results) were so small as to make N'(R) essentially monotonic, like the present N(R).

Average Pt particle radii were calculated (Brumberger *et al.*, 1996) from N'(R) for three Pt/zeolite catalysts, differing in metal loading, each calcined at three different temperatures. It was found that, for each catalyst, raising the calcination temperature from 573 to 673 K led to an approximate doubling of the average radius, and raising it to 773 K more than doubled it again. The implication is that sintering occurred during calcination at high temperatures. We note that, although our present results indicate the dominant process is the break-up of large particles into smaller ones (Fig. 6), the decrease in $\langle R \rangle$ is rapid when pure He or pure H₂ is flowing over the system, but almost zero with 10% O₂. It is possible that sintering does occur in the oxidizing atmosphere, which compensates for the break-up of larger particles, so $\langle R \rangle$ is approximately constant.

Overall, the average Pt particle radius decreases continually (Fig. 6), from about 20 Å initially to about 5 Å at the end. Interestingly, our previous work (Brumberger *et al.*, 1996; Ramaya, 1997) gave $\langle R \rangle \simeq 5$ Å for systems calcined at 473 K and $\langle R \rangle > 20$ Å for systems calcined at 673 K. (A value of 20 Å for $\langle R \rangle$ implies that most of the particles are not in the zeolite cages but on internal surfaces, but a radius of 5 Å is small enough for particles to fit into the cages.)

In subsequent work (Cicariello *et al.*, 1999) it was confirmed by SAXS that calcination at 523 K yielded very disperse Pt particles, whereas calcination at 573 K led to sintering. It was concluded that ammonia was eliminated without decomposition during calcination at the lower temperature, but that ammonia partially decomposed to nitrogen and hydrogen at the higher temperature.

Other workers have determined nonmonotonic N(R) for catalyst systems. By fitting SAXS intensities for Pt supported on porous carbon, Haubold *et al.* (1999) and Goerigk *et al.* (2003) determined a bimodal log-normal distribution for the Pt particles, with 88% of the Pt in the form of small particles (average radius $\simeq 9$ Å) and 12% in the form of larger particles

(average radius $\simeq 60$ Å). Furthermore, they concluded that, on passing from the reduced to the oxidized state, the average radius of the small particles increased to ~ 11 Å. They associated this with formation of an oxide shell on the Pt particles, which involved outward motion of the Pt atoms, rather than sintering.

Benedetti *et al.* (1999) investigated an Au catalyst supported on active carbon using ASAXS, to show that the technique could give information about metal particle size even for low metal loading (0.2 wt% metal). Like Haubold *et al.* (1999), they found a bimodal distribution: larger particles with average radius \sim 70 Å and smaller ones less than 10 Å in radius, the weight per cent of the latter being seven times that of the former. Two populations of different-size metal particles were also found (Benedetti *et al.*, 1999) in ASAXS measurements on Pd supported on C. The presence of the smaller particles explains the decrease in the average particle size with heat treatment.

ASAXS measurements on a Raney-type nickel catalyst were performed by Bóta *et al.* (2002). The difference between scattering curves for two different wavelengths was fit to various models for the Ni particles. It was not possible to determine the Guinier radius R_G because of the heterodispersivity, so a Maxwellian distribution [mass fraction of particles of radius R_G proportional to $R_G^n \exp(-R_G^2/r_0^2)$] was assumed, the parameters being determined to give the best fit. The resulting average Guinier radius was 20 Å (corresponding to sphere radii of 26 Å), with an error of about 5%.

Haubold *et al.* (1996, 1997) studied carbon-supported Pt catalysts using ASAXS. Using synchrotron radiation, they were able to make measurements *in situ*, while the catalysts were oxidized and reduced in an electrochemical cell. A lognormal distribution was used for N(R), with parameters chosen to give the best fit to the difference between scattering intensities for two X-ray wavelengths. Note that this distribution, like the Maxwellian distribution used by Bóta *et al.* (2002), is guaranteed to be peaked. Haubold *et al.* (1997) noted, however, that this distribution fit the measured scattering very accurately. The maximum in N(R) moved from $R \simeq 8$ Å to $R \simeq 11$ Å on oxidation for catalysts containing 80, 60 and 10 wt% Pt; for 5 wt% Pt, there was very little change in the position of the maximum.

Another study of metal particle sizes by ASAXS, on Ni supported on SiO₂, was performed by Rasmussen *et al.* (2000). The system was first characterized by H₂ adsorption and X-ray powder diffraction (XRD), the latter allowing an estimation of the mean crystallite size from the width of the diffraction peak. The ASAXS was analyzed assuming independently scattering spherical metal particles. The distribution function was represented by a linear combination of 15 linear spline functions, with parameters chosen to get the best fit to the experimental scattering. The resulting function shows a large peak near 20 Å and smaller peaks near 65 Å and 110 Å, with the average particle size 34 ± 1.2 Å. The volume-weighted mean particle radius was 96 Å, as compared with 62 Å determined by XRD, but it was noted that XRD cannot observe the larger particles.

Canton *et al.* (2003) investigated the shapes and sizes of Pd particles supported on SiO₂ using several techniques, including high-resolution TEM. They found a broad particle-size distribution in the system treated at low temperature (423 K), with many particles of diameters between 10 and 50 Å. When the same system was treated at 773 K, the particle sizes followed a log-normal distribution peaked at about 50 Å, indicating that appreciable sintering occurred. It was noted that X-ray line-broadening analysis gave appreciably smaller particle sizes, as found by Rasmussen *et al.* (2000).

Our results differ significantly from most of the studies discussed, which report a particle-size distribution function with one or more peaks, whereas we always calculate a monotonic N(R). It is possible that the discrepancy relates to differences in the systems studied, the temperatures used, and the gases flowing through the systems. It is also possible that the explanation is in the form chosen for N(R) [for example, the log-normal distribution is always peaked, while equation (4) may be peaked or monotonic]. It must be emphasized that the parameters in N(R) are determined to fit the scattering data over some finite range of Q, so that one is fitting N(R)over a correspondingly finite range of R (7–34 Å in our case). One cannot hope to find features of the true N(R) which occur outside this range, as do some of the most probable particle sizes found by other workers.

Another difference between our findings and those of others is that we find that the average particle size decreases over time. This conclusion is independent of the form used for N(R); it follows from the increase in the scattering at large Q. As noted, the rate of decrease of particle size is much lower when the atmosphere is oxidizing than when it is reducing. This suggests that, under an oxidizing atmosphere, sintering is occurring at the same time as break-up of particles, giving a small apparent rate of size decrease.

The works cited show that ASAXS measurements are a valuable technique for studying supported-metal catalysts, since they yield information about the metal particles with no need to compensate for the support scattering. Previously (Brumberger *et al.*, 2005) we have shown explicitly the assumptions required to interpret the difference in scattering I_d as the scattering of a two-phase system. Another advantage of ASAXS, using synchrotron radiation, is that measurements can be performed *in situ* and under changing conditions, allowing observation of changes in particle sizes that accompany variations in temperature or atmosphere. In the present study, both the temperature and the gas flowing through the system were changed over time. In the future, we hope to present results of similar measurements on other Pt/zeolite catalysts.

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References

- Benedetti, A., Bertoldo, L., Canton, P., Goerigk, G., Pinna, F., Riello, P. & Polizzi, S. (1999). *Catal. Today*, **49**, 485–489.
- Bönneman, H., Waldoefner, N., Haubold, H.-G. & Vad, T. (2002). *Chem. Mater.* 14, 1115–11120.
- Bóta, A., Goerigk, G., Drucker, T., Haubold, H.-G. & Petro, J. (2002). *J. Catal.* **205**, 354–357.
- Brumberger, H. (1988). Makromol. Chem. Macromol. Symp. 15(Discuss. Conf.), 223–230.
- Brumberger, H., Goodisman, J., Ramaya, R. & Ciccariello, S. (1996). J. Appl. Cryst. 29, 526–530.
- Brumberger, H., Hagrman, D., Goodisman, J. & Finkelstein, K. D. (2005). J. Appl. Cryst. 38, 147–151.
- Canton, P., Menegazzo, F., Polizzi, S., Pinna, F., Pernicone, N., Riello, P., Fagherazzi, G. & Consorzio INSTM UdR Venezia (2003). *Catal. Lett.* 88, 141–146.
- Cicariello, S., Benedetti, A., Pinna, F., Strukul, G., Juszczyk, W. & Brumberger, H. (1999). *Phys. Chem. Chem. Phys.* **1**, 367–372.
- Creagh, D. C. (1999). *International Tables of Crystallography*, Vol. C., 2nd edition, edited by A. J. C. Wilson & E. Prince, §4.2.6. Dordrecht: Kluwer.
- Cross, J. O., Newville, M., Rehr, J. J., Sorensen, L. B., Bouldin, C., Watson, G., Gouder, T., Lander, G. H. & Bell, M. J. (1998). *Phys. Rev. B*, 58, 11215–11225.
- Epperson, J. E. & Thiyagarajan, P. (1988). J. Appl. Cryst. 21, 652.
- Georgopoulos, P. & Cohen, J. B. (1985). J. Catal. 92, 211.
- Goerigk, G., Haubold, H.-G., Lyon, O. & Simon, J.-P. (2003). J. Appl. Cryst. 36, 425–429.
- Goodisman, J. & Brumberger, H. (1971). J. Appl. Cryst. 4, 347-351.
- Haubold, H.-G., Gebhardt, R., Buth, G. & Goerigk, G. (1994). *Resonant Anomalous X-ray Scattering*, edited by G. Materlik, C. J. Sparks & K. Fischer, pp. 295–304. Oxford: Elsevier Science.
- Haubold, H.-G., Hiller, P., Jungbluth, H. & Vad, T. (1999). Jpn J. Appl. Phys. Part 1, **38**(Supp. 1), 36–39.

- Haubold, H.-G., Vad, T., Waldoefner, N. & Bönnemann, H. (2003). J. Appl. Cryst. 36, 617–620.
- Haubold, H.-G., Wang, X. H., Goerigk, G. & Schilling, W. (1997). J. Appl. Cryst. **30**, 653–658.
- Haubold, H.-G., Wang, X. H., Jungbluth, H., Goerigk, G. & Schilling, W. (1996). J. Mol. Struct. 383, 283–289.
- Jacoby, M. (2002). Chem. Eng. News, Aug. 5 issue, pp. 26-32.
- Li, Z.-H., Gong, Y.-J., Pu, M., Wu, D., Sun, Y.-H., Zhao, H. & Dong, B.-Z. (2003). *Wuji Huaxue Xuebao*, **19**, 252–256.
- Meitzner, G. (1992). *Characterization of Catalytic Materials*, edited by I. E. Wachs, ch. 2. Stoneham, MA: Butterworth–Heineman.
- Naudon, A. (1995). Modern Aspects of Small-Angle Scattering, edited by H. Brumberger, NATO ASI Series C: Mathematical and Physical Sciences, Vol. 451. Dordrecht: Kluwer.
- Polizzi, S., Riello, P., Goerigk G. & Benedetti, A. (2002). J. Synchrotron Rad. 9, 65–70.
- Ramaya, R. (1997). Study of Zeolite-Supported Platinum Catalysts Using Small Angle X-ray Scattering, PhD thesis, Syracuse University.
- Rasmussen, F. B., Molenbroek, A. M., Clausen, B. S. & Feidenhans, R. (2000). J. Catal. 190, 205–208.
- Revel, R., Bazin, D., Couchet-Fabre, B., Seigneurin, A. & Kihn, Y. (2002). J. Phys. IV Proc. 12, 309–322.
- Somorjai, G. A., Powell, R. E., Montgomery, P. W. & Jura, G. (1967). Small-Angle X-ray Study of Metallized Catalysts, in Small-Angle X-ray Scattering, Proceedings of the Conference Held at Syracuse University, edited by H. Brumberger. New York: Gordon and Breach.
- Stiles, A. B. & Koch, T. A. (1995). Catalyst Manufacture, 2nd ed. New York: Marcel Dekker.
- Vad, T., Haubold, H. G., Waldoefner, N. & Bönnemann, H. (2002). J. Appl. Cryst. 35, 459–470.
- Wachs, I. E. (1992). Editor. *Characterization of Catalytic Materials*. Stonehame, MA: Butterworth–Heineman.