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RESEARCH NOTE

Particle Size Distribution of an Ni/SiO$_2$ Catalyst Determined by ASAXS

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Anomalous small-angle X-ray scattering (ASAXS) was used to determine the Ni particle size distribution of an Ni/SiO$_2$ catalyst. In the analysis of the data no assumptions were made regarding the form of the size distribution. Parameters calculated from the distribution were in good agreement with the mean crystallite size estimated from the line broadening of X-ray diffraction peaks. Our results indicate that ASAXS will become a very useful tool for the determination of particle size distributions in catalysis research.

Key Words: **ASAXS; particle size distribution; Ni catalyst.**

The determination of particle sizes and particle size distributions of metal-supported catalysts is of principal importance in catalysis research. The surface area and hence the attainable number of active sites are given by the shape and size of the metal particles and frequently the electronic properties of the metal depend on the particle size. A number of different methods may be used to measure particle sizes, e.g., volumetric gas chemisorption, X-ray diffraction, electron microscopy, magnetic resonance or various spectroscopies (1) but also EXAFS, e.g., in combination with molecular dynamics simulations (2). Catalysts with similar mean particle sizes may have widely different particle size distributions and accordingly very different properties. Compared to measuring mean particle sizes, determination of particle size distributions is much more difficult and most of the above-mentioned methods either fail or have severe limitations.

Small-angle X-ray scattering (SAXS) is a versatile technique that has found widespread use in materials research (1, 3). For two-phase systems (material and void) it allows the determination of particle size distributions with a high statistical significance and without the need for special sample preparation procedures. Supported metal catalysts are three-phase systems (metal, substrate, and void) and in general it is very difficult to subtract the intense background scattering of the porous substrate. This is overcome by anomalous small-angle X-ray scattering (ASAXS) which exploits the fact that the scattering factor of, e.g., a metal atom varies close to its absorption edges whereas the scattering factor of the substrate remains constant. Hence, by taking the difference of two SAXS measurements close to an absorption edge of the metal, one obtains the small-angle scattering curve of the metal particles without the contribution from the substrate (4).

ASAXS was recently used to study Au and Pd catalysts supported by active carbon (5) and Pt electrocatalysts supported by porous carbon (6) but the general applicability of the method to other standard catalytic systems still needs to be verified. The purpose of this study was to investigate whether the metal particle size distribution of an Ni/SiO$_2$ catalyst could be determined using the ASAXS technique.

A commercial silica carrier (surface area, 406.2 m^2/g; pore volume, 1.22 ml/g) was used as support. The sample was prepared by pore volume filling with a 0.589 M aqueous solution of Ni(NO$_3$)$_2$, followed by calcination at 450 °C (2 h) resulting in a metal load of 4 wt% of NiO. Then the pellets were crushed to powder and reduced in H$_2$(g) (2 h) at 400 °C. Finally, the sample was passivated with a gas mixture (2% O$_2$ in N$_2$) at room temperature before exposure to air. Measurements were performed both on powder and on thin tablets made from a mixture of powder and a small amount of polyethene (PE, from Merck).

The sample was characterised by X-ray powder diffraction (XRD) using a Philips PW1820 goniometer with Bragg–Brentano geometry, a variable divergence slit, and a graphite monochromator. A mean crystallite size of 62 ± 1 Å was estimated from the width of the (200) diffraction peak using the Scherrer equation after correction for instrumental broadening. Furthermore, H$_2$ chemisorption measurements were performed using a Quantachrome Autosorb system. The monolayer uptake was found to be 5.42 μmol/g (sample) corresponding to a specific surface area of 10.1 m^2/g (Ni) assuming a loading of 4 wt%.

ASAXS measurements were performed at the JUSIFA ASAXS beamline at DESY-HASYLAB, Hamburg (7),

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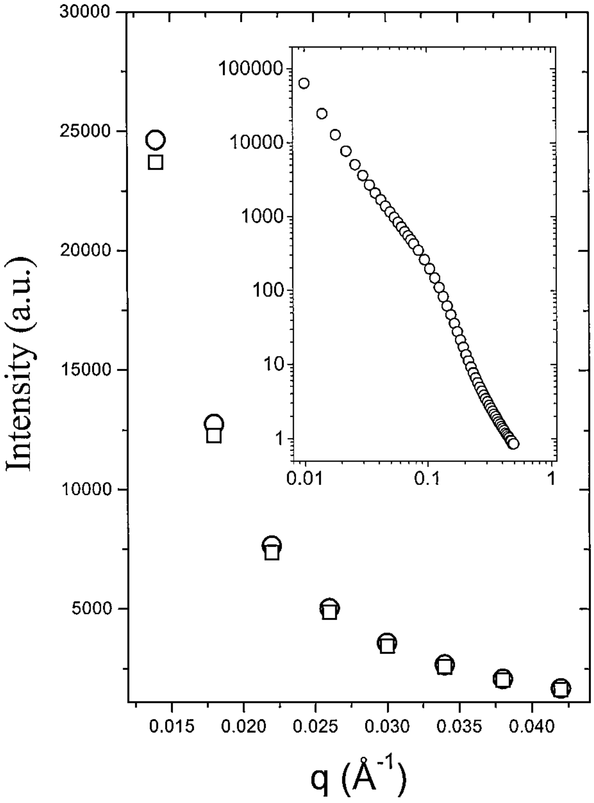

FIG. 1. A section of the small-angle X-ray scattering curve (linear scales) of an Ni/SiO$_2$ sample measured at 8290 eV (circles) and at 8326 eV (boxes). The inset shows the full small-angle scattering curve (log scales) measured at 8290 eV.

using three different energies below the Ni K-absorption edge at 8333 eV and two sample–detector distances (q-range, 0.01–0.50 Å^{-1}). Intensities were normalised to the primary beam intensity and corrected for sample absorption, background, and detector efficiency.

Figure 1 shows the normalised small-angle scattering of an Ni/SiO$_2$ tablet sample using an incident X-ray energy of 8290 eV (inset) and compares it to the scattering curve measured at 8326 eV. The abscissa of Fig. 1 is given in q-values, which are related to the scattering angle 2θ and the wavelength λ by

$$q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$

We observe that the total scattering intensity is much larger than the changes induced in the intensity by varying the X-ray energy. This is due to the very strong small-angle scattering of the highly porous SiO$_2$ carrier, and demonstrates that a very careful treatment of the data is needed in order to separate the scattering of the nickel particles.

Figure 2 shows the experimentally separated ASAXS intensity obtained as the difference between the normalised SAXS data measured at 8290 and 8326 eV on a tablet sample containing a small amount of PE. Separation using measurements performed at 8031 eV and one of the above energies resulted in similar scattering curves, as did measurements performed on pure powder samples.

As the Ni particles are highly dispersed on the porous silica we may consider the small-angle scattering as originating from independent particles. In this case, the intensity should depend linearly on q^2 for low q, if all particles have more or less the same size (3). As shown in Fig. 3 this is not the case, indicating that the Ni particles have a distribution of sizes.

Assuming only that the particles are solid spheres a free-form determination of the size distribution is possible (8). We used the linear least-squares method with smoothness and non-negativity constraints given recently by Pedersen (8). The number-density size distribution $N(R)$ was represented by a linear combination of 15 linear spline functions and the radius R was restricted to be between 5 and 250 Å. The best fit obtained is shown as the full line in Fig. 2, whereas the corresponding particle size distribution is shown in Fig. 4.

A number of parameters calculated from the size distribution are listed in Table 1. The low R part of the

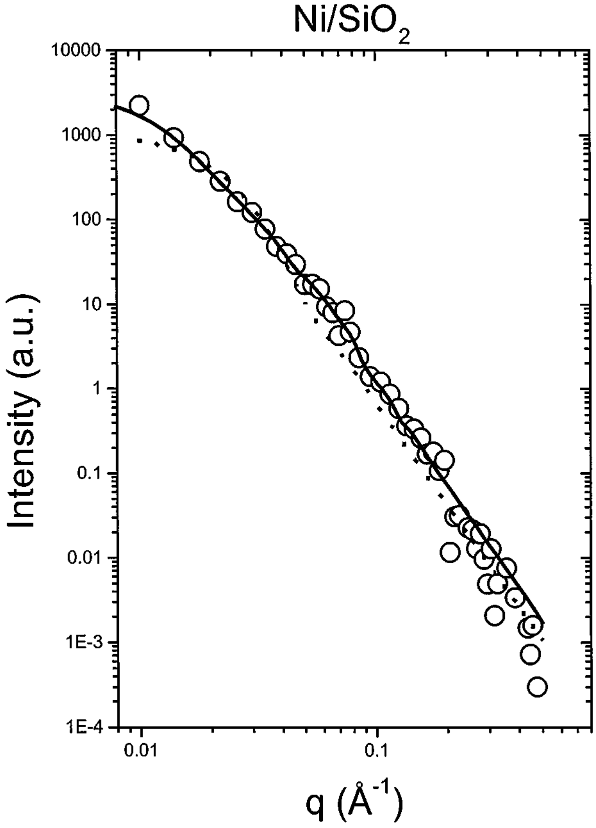

FIG. 2. Separated ASAXS data of an Ni/SiO$_2$ sample (open circles). The best fits obtained by a free-form distribution of spherical particles (full line) and by a log-normal distribution of spherical particles (dotted line) are also shown.

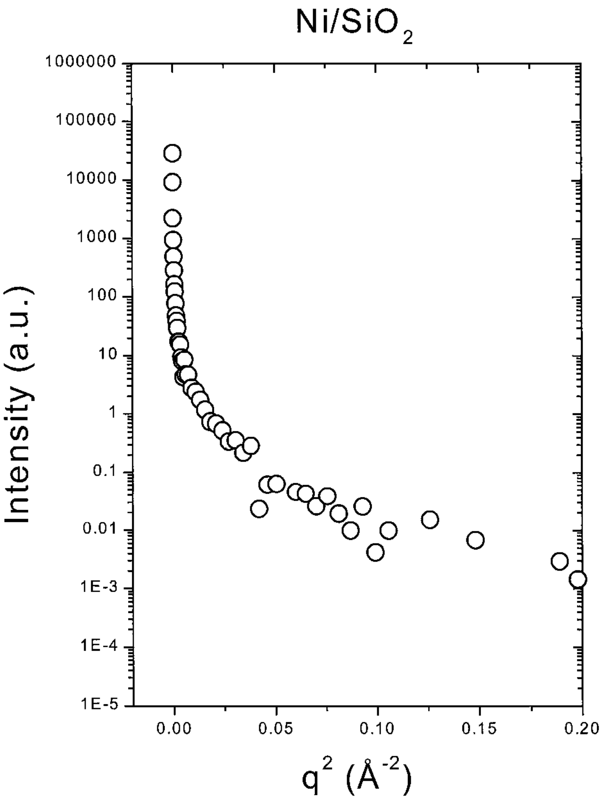

FIG. 3. Guinier (I vs q^2) plot of the separated scattering of the Ni particles.

distribution resembles a log-normal distribution, and indeed an acceptable fit to the data is obtained assuming such a distribution (see Fig. 2). The parameters obtained are $\xi = 31.8$ Å and $\sigma = 0.11$, where $\log_{10}(\xi)$ is the mean and σ^2 the variance of $\log_{10}(R)$. As shown in Fig. 4 the main difference between the two distributions is the tail of larger particles observed using the free-form determination. It is clear from the fits obtained that this tail is significant, and it shows the importance of not assuming a specific form of the size distribution.

The volume-weighted mean particle/crystallite radii determined by ASAXS and XRD are 96 and 62 Å, respectively. However, the small fraction of larger particles observed by ASAXS causes the calculated mean radius to be larger than the typical radius. Introducing a cutoff at $R = 100$ Å in the distribution of Fig. 4 we arrive at a volume-weighted mean radius of 57 Å, in good agreement with the XRD value. Without very good statistics and a detailed line shape analysis a small fraction of larger particles cannot be observed by XRD.

TABLE 1

Parameters Calculated from the Number Distribution $N(R)$ Shown in Fig. 4 (See Ref. 8)

$\langle R\rangle$	33.7 (1.2) Å
$\sigma(R)$	19.7 (0.3) Å
S/V	0.046 (0.002) Å^{-1}
$\langle R\rangle_{\text{vol}}$	95.9 (3.4) Å
$\langle R\rangle_{\text{vol}}$ ($R < 100$ Å)	56.5 (2.1) Å

Note. $\langle R\rangle$ is the mean and $\sigma^2(R)$ is the variance of $N(R)$, S/V is the specific surface area, and $\langle R\rangle_{\text{vol}}$ is the volume-weighted mean radius calculated from the full distribution or with an upper cutoff at 100 Å.

A small fraction of large particles does not contribute significantly to the specific surface area and it may therefore be of interest to compare the values determined by ASAXS and XRD. The specific surface area calculated from the distribution in Fig. 4 is 0.046 Å^{-1} or 52 m^2/g (Ni) assuming an Ni density of 8.9 g/cm^3. This is in good agreement with the specific surface area of a sphere with radius 62 Å equal to 0.049 Å^{-1} (55 m^2/g). The surface areas determined by ASAXS and XRD are larger than the value obtained by chemisorption (10 m^2/g). This may indicate that the individual particles (crystallites) observed by ASAXS (XRD) stick together, making only part of the Ni surface accessible to the chemisorbing hydrogen. Assuming a spherical shape of the Ni particles we estimate a composite particle size of 666 Å from chemisorption. Composite particles of this size

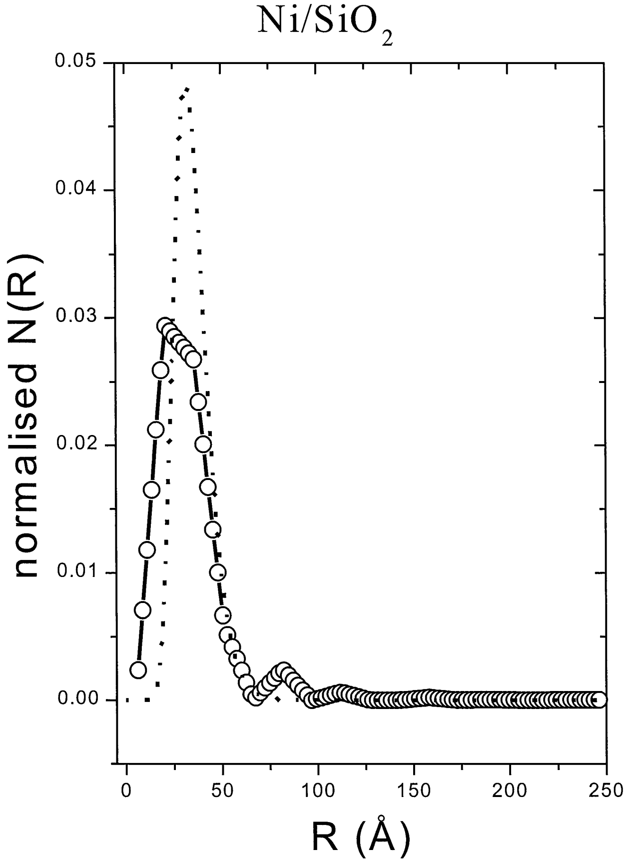

FIG. 4. Normalised number-density size distribution corresponding to the best fit of Fig. 2 (full line with circles). The dashed line is the log-normal distribution giving the best fit to the data.

will not be observed by ASAXS with the q-range available at the JUSIFA beamline.

In conclusion, ASAXS was used to determine the size distribution of Ni particles supported by a silica carrier without any assumption of the shape of the distribution. The results were in good agreement with XRD data but also indicated the importance of knowing the distribution of particle sizes. This experiment suggests that ASAXS could become an important tool for the characterisation of supported metal catalysts.

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