

Sintering of Ni/Al₂O₃ catalysts studied by anomalous small angle X-ray scattering

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Abstract

Sintering is an important deactivation mechanism of nickel-based catalysts used for the production of synthesis gas and hydrogen in the steam reforming process. In this work sintering of nickel catalysts supported by aluminum oxide is studied by a combination of sulfur chemisorption, X-ray diffraction and anomalous small angle X-ray scattering (ASAXS). Size distributions of nickel particles are obtained by ASAXS without any assumption on the shape of the distribution, assuming only that the nickel particles are spherical. Specific nickel surface areas calculated from the measured size distributions agree with the surface areas measured directly by chemisorption. Combining the scattering and chemisorption results allows the sintering process to be studied in detail. This combined approach shows that sintering of a 9.5 wt.% Ni/Al₂O₃ catalyst at 650 °C is dominated by a nickel particle coalescence mechanism. At higher temperatures the nickel particle size distributions indicate that migration of nickel atoms begins to contribute to the sintering process.

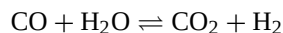
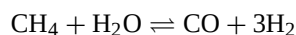
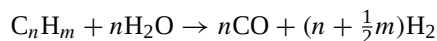
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1. Introduction

Hydrogen gas or mixtures of hydrogen, carbon monoxide and carbon dioxide (synthesis gas) are used extensively in a wide range of industrial processes. These include ammonia and methanol synthesis, as well as in the production of synthetic fuels and basic chemicals. Fuel cell technology, using hydrogen as fuel, is expected to become a major future source of electrical power.

Production of hydrogen by steam reforming of hydrocarbons is the technology of choice in most cases:



and the process usually proceeds over a supported nickel catalyst [1]. An important route for deactivation of modern

steam reforming catalysts is whisker carbon formation [2]. Many attempts have been made to overcome this problem by promotion of the catalyst or using alloy catalysts [3,4]. Another important concern is catalyst deactivation through sintering of the nickel particles and subsequent loss of nickel surface area [1,5–13]. Understanding the sintering mechanism is important for fundamental as well as technological reasons. Many parameters influence the sintering process, the two most important being the temperature and the atmosphere over the catalysts. Sintering rates increase strongly with temperature and are particularly large in the presence of water [9].

The sintering of nickel particles is influenced by the substrate pore structure that may determine the final attainable particle size of nickel particles [1,8,14–16]. Furthermore, the support itself may be affected and undergo morphological and structural changes during sintering. This could lead to sintering of the nickel particles mediated by the collapse of the substrate pore structure. Finally, substrate phase transitions including alloying with nickel may also influence the sintering of the nickel particles [17–19].

Ni particle sintering may be studied by direct measurement of the nickel surface area using chemisorption or

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from a determination of the mean nickel crystallite size by, e.g. X-ray powder diffraction (XRD). However, more information is obtained if the nickel particle size *distribution* is available. Several experimental techniques have been used to determine nickel particle size distributions of steam reforming catalysts including magnetization experiments, profile analysis of X-ray powder diagrams and small angle X-ray scattering (SAXS) [7,8,15,18]. Most widely used is transmission electron microscopy, which is a very powerful technique but it only gives a two-dimensional projection of the particles (see, e.g. [13]).

SAXS has found widespread use in materials science as a versatile technique complementing other characterization techniques very well. The statistical significance of SAXS data is very large and in situ experiments at realistic pressures are readily performed with any X-ray-based method. A disadvantage of SAXS is that it does not directly produce real space images, but curves in reciprocal space that must be fitted by a suitable model expression. In a traditional SAXS study of a supported metal catalyst the pores of the support are filled with a suitable liquid having the same scattering length density as the support [18]. Samples treated in this way only show the small angle scattering of the metal particles, which can then be studied. However, in practice this so-called pore-masking technique is both cumbersome and prone to error. A better way is to use anomalous scattering or ASAXS, where the energy dependence of the scattering is utilized to separate the contribution from the metal from the background pore scattering. ASAXS has recently been used to determine metal particle size distributions of a few selected supported catalysts [20–23] but is still a relatively new technique within this field.

In this paper we present ASAXS, XRD and sulfur chemisorption investigations of Ni/Al₂O₃ steam-reforming catalysts subjected to sintering treatments. The purpose is twofold, first to demonstrate the applicability of ASAXS for the determination of nickel particle size distributions and second to obtain information on the dominating sintering mechanism using size distributions determined by ASAXS.

2. Experimental

2.1. Catalysts preparation

The model catalysts studied here contained 9.5 wt.% Ni on Al₂O₃ prepared by impregnation of 200 g of support with a concentrated Ni(NO₃)₂ solution followed by a calcination to 450 °C in air. The Al₂O₃-support was calcined in air at 925 °C before impregnation after which it exhibited a surface area of 203.6 m²/g, a total pore volume of 591 ml/kg and a mean pore radius of 58 Å.

2.2. Sintering treatments

The sintering experiments were performed by exposing the catalysts to a 1:1 mixture of steam and hydrogen at

different temperatures at ambient pressure. Prior to sintering, the catalysts were activated by reduction in H₂ at 500 °C for 4 h. After sintering, the catalysts were passivated overnight at 50 °C in a mixture of 1% O₂ in N₂ before they were taken out of the reactor. The fresh catalysts were passivated immediately after the reduction with the same procedure.

2.3. Catalysts characterization

The total surface areas (BET) of the catalysts were determined by nitrogen adsorption using a Quantachrome MONOSORB apparatus. The measured values were normalized to standard temperature and pressure in accordance with the ASTM standard for single-point determination of BET surface areas [24].

Sulfur chemisorption capacity measurements (*S*_{cap}) were used to determine the specific nickel surface area. The sulfur chemisorption was performed according to Rostrup-Nielsen [1] using a flow of H₂S/H₂ over the catalysts until saturation. The sulfur uptake of the catalysts was determined by oxidation of the chemisorbed sulfur at high temperatures, using an infrared detector to measure the amount of SO₂ released. Under the experimental conditions used, the specific nickel surface area can be calculated from the sulfur capacity from the relationship that 440 ppm S is equivalent to a specific Ni surface area of 1 m²/g [1,25]. Ni surface areas determined by H₂S chemisorption in this way give values similar to surface areas determined by H₂ chemisorption. The absorption of H₂S on the alumina support is negligible [37].

X-ray powder diffraction measurements were performed using a Philips PW1820 goniometer with Bragg–Brentano geometry using Cu Kα radiation, a variable divergence slit and a graphite secondary monochromator. Phase compositions, lattice spacings and mean crystallite dimensions were obtained by Rietveld refinement on the diagrams using the program Powdercell 2.3 [26].

2.4. ASAXS experiments

Anomalous small angle X-ray scattering (ASAXS) experiments were performed at the dedicated ASAXS beamline (JUSIFA) at HASYLAB, DESY Hamburg [27]. All experiments were performed using thin pellets made from a mixture of catalyst powder and a small amount of polyethylene (PE from Merck) [22]. X-ray absorption fine structure (XAFS) measurements were performed on each sample prior to the ASAXS measurement to locate the edge position and obtain information on the oxidation state of the nickel phases. ASAXS measurements were made on all samples using the experimental setup and strategy described recently by Polizzi et al. [23]. Experiments were performed at two sample-detector distances (*q*-range: 0.005–0.6 Å^{−1}) using four energies (8033, 8292, 8308 and 8326 eV) below the Ni K-absorption edge at 8333 eV.

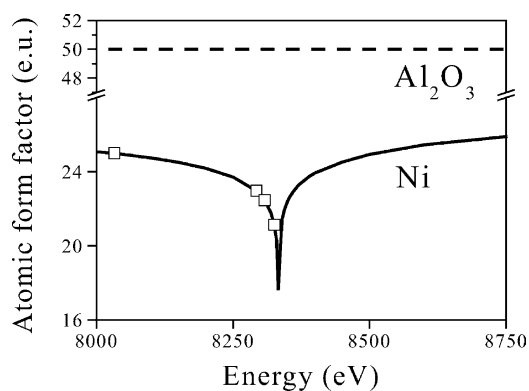


Fig. 1. The magnitude of the atomic form factors of Ni and Al_2O_3 in electron units [30]. The atomic form factor of Ni (full line) has a strong energy dependence close to the K-absorption edge of Ni (8333 eV), whereas the atomic form factor of Al_2O_3 (dashed line) is constant. The squares mark the four X-ray energies used in this study.

2.5. ASAXS data analysis

For a simple two-phase system consisting of homogeneous non-interacting spherical metal particles in a homogeneous matrix we write the differential small angle scattering cross-section as

$$\frac{d\sigma}{d\Omega}(q, E) = \Delta\rho^2(E) \frac{N}{V_s} \sigma_{\text{Thomson}} \int_0^\infty s P(r) V^2(r) S_{\text{sphere}}(r, q) dr$$

where q is the length of the scattering vector, E the X-ray energy, N the number of spherical particles, V_s the sample volume and σ_{Thomson} the Thomson cross-section ($7.94 \times 10^{-26} \text{ cm}^2$) [28]. $V(r)$ the volume of a sphere with radius r , $P(r)$ the number distribution of sphere radii and S_{sphere} the form factor of a sphere with radius r [29]

$$S_{\text{sphere}}(r, q) = \left[3 \frac{\sin(qr) - qr \cos(qr)}{(qr)^3} \right]^2$$

$\Delta\rho^2$ is the effective electron density contrast between the two phases and depends on the X-ray energy through the atomic form factors f_i

$$\Delta\rho^2(E) = |n_1 f_1(E) - n_2 f_2(E)|^2$$

where n_i is the average atomic density of phase i . Close to an atomic absorption edge the atomic form factor and hence $\Delta\rho^2$ has marked energy dependence as shown in Fig. 1.

The samples studied here contain in addition to the nickel- and alumina-phases a third phase, namely the pores of the substrate. In this case we write the total differential cross-section as [31,32]

$$\frac{d\sigma}{d\Omega}^{\text{total}}(q, E) = \frac{d\sigma}{d\Omega}(q, E) + |\bar{f}(E)|^2 F(q) + \text{cross term}$$

where $F(q)$ is the form factor of the pore structure describing the shapes and sizes of the pores. The average form factor ($\bar{f} = c f_1 + (1 - c) f_2$) is given in terms of the molar fraction of phase one (c) and may be calculated from atomic form

Table 1
Atomic form factors^a

E (eV)	f_{Ni}^0	f'_{Ni}	f''_{Ni}	$f_{\text{Al}_2\text{O}_3}^0$	$ \bar{f} ^2$
8326	28	−6.89	0.48	50	2151.9
8308	28	−5.55	0.48	50	2167.5
8292	28	−5.03	0.48	50	2267.8
8033	28	−3.01	0.51	50	2291.9

^a The atomic form factors used in this study are calculated using the Cromer and Liberman method and are taken from the tables by Sasaki [30]. The molar fraction of nickel in the samples is $c = 0.125$ and $\bar{f} = c f_{\text{Ni}} + (1 - c) f_{\text{Al}_2\text{O}_3}^0$, with $f_{\text{Ni}} = f_{\text{Ni}}^0 + f'_{\text{Ni}} + i f''_{\text{Ni}}$.

factors (Table 1) when the energy is below the absorption edge [31].

If we neglect the cross term (see, e.g. Ref. [23]) then measurements at two energies are sufficient to remove the $F(q)$ contribution

$$\begin{aligned} & \frac{1}{|\bar{f}(E_1)|^2} \frac{d\sigma^{\text{total}}}{d\Omega}(q, E_1) - \frac{1}{|\bar{f}(E_2)|^2} \frac{d\sigma^{\text{total}}}{d\Omega}(q, E_2) \\ &= K \int_0^\infty P(r) V^2(r) S_{\text{sphere}}(r, q) dr = KI(q) \end{aligned}$$

the scale factor K can in principle be calculated from the sample composition and the atomic form factor values. However, in practice this is very difficult for technological samples and we will only consider the separated scattering curves ($KI(q)$) in the following analysis [23].²

Particle size distributions $P(r)$ were determined from the separated scattering curves using the linear least-squares method with smoothness and non-negativity constraints given by Pedersen [33]. This method allows the determination of $P(r)$ on a free form, i.e. without any assumption on the shape of the distribution. This allows conclusions to be drawn that depend on the shape of the size distribution. Typically $P(r)$ was represented by a linear combination of 20 linear spline functions with r restricted to be smaller than 150 or 250 Å. It is possible to include an effective particle–particle interaction into the determination of $P(r)$ [33], however, such an interaction turned out to be very small and was not included in the final analysis. The apparent absence of interaction effects is believed to be caused by a combination of the high degree of dispersion of the nickel particles on the porous Al_2O_3 substrate, the broad size distribution of nickel particles and the limited q -range of the separated scattering curves.

² As an example it is unavoidable that part of the nickel is oxidized under the experimental conditions used here. This implies that the composition of the nickel phase is not fully known and hence impairs the exact calculation of the scale factor K . The $\bar{f}$ -values used in the separation depends on the atomic form factor of the nickel phase and hence on the degree of oxidation of the nickel. However, for the samples used in this study (9.5 wt.% Ni) this effect only contributes a q -independent factor that enters into the scale factor K . The difference in the q -dependence of $I(q)$ depending on whether the nickel phase is assumed to be either metallic Ni or NiO can be neglected.

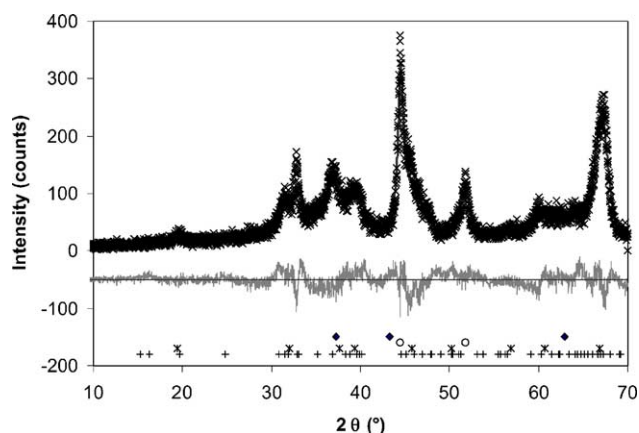


Fig. 2. XRD powder pattern obtained after heating for 50 h at 750 °C. Observed (x), calculated (full curve), and difference profile (lower trace) from Rietveld refinement. The markers show the positions calculated for the Bragg reflections of NiO (◆), Ni (○), η -Al₂O₃ (*) and θ -Al₂O₃ (+) ($R_p = 15.8$, $R_{wp} = 20.6$, $R_{exp} = 13.6$).

3. Results

Fig. 2 shows the X-ray powder diffraction diagram obtained on a sample sintered for 50 h at 750 °C. The diagram is dominated by the diffraction of the substrate but weak lines due to metallic Ni are also observed.

Table 2 shows some of the results of Rietveld refinements carried on the data. The carrier of the fresh catalysts contains both η -Al₂O₃ and θ -Al₂O₃ phases in about equal amounts (wt.%). As sintering proceeds the η -Al₂O₃ phase gradually transforms into θ -Al₂O₃. The powder diagrams indicate that small amounts of more or less crystalline phases of Ni and NiO are present in the fresh sample and after moderate sinter-

Table 2
Structural parameters from Rietveld refinements^a

	Fresh	25 h, 650 °C	100 h, 650 °C	50 h, 750 °C
θ -Al ₂ O ₃				
wt.%	45	50	55	64
<i>a</i> (Å)	12.19	11.84	11.88	11.86
<i>b</i> (Å)	2.93	2.91	2.91	2.90
<i>c</i> (Å)	5.63	5.63	5.63	5.60
β (°)	102.4	103.3	104.0	103.3
η -Al ₂ O ₃				
wt.%	46	41	35	28
<i>a</i> (Å)	7.92	7.92	7.92	7.93
Ni				
wt.%	4	6	6	7
<i>a</i> (Å)	3.48	3.47	3.50	3.52
<i>D</i> ₍₁₁₁₎	~47	>44	>47	130
NiO				
wt.%	~5	~4	~4	~1

^a Structural parameters (*a*, *b*, *c* and β) obtained by Rietveld refinement of X-ray diffraction powder diagrams using Powdercell 2.3 [26]. *D*₍₁₁₁₎ is the crystallite size in the (1 1 1) direction (Å). The NiO content was only estimated not refined assuming an amorphous-like background from a cubic crystal with *a* = 4.177 Å and a crystallite size *D*₍₂₀₀₎ ≈ 20 Å.

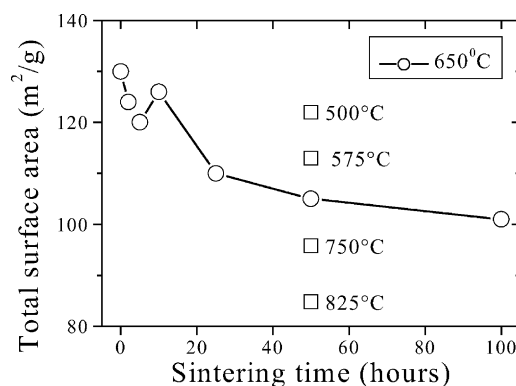


Fig. 3. BET total specific surface area as a function of sintering time and temperature. The measurements were performed on Al₂O₃-supported nickel catalysts after sintering in a 1:1 mixture of H₂ and H₂O at a total pressure of 1 bar.

ing treatments. After prolonged treatment at higher temperature larger Ni-crystallites are observed. The high *R*-values in the Rietveld refinement are due to the poor crystallinity of the alumina phases. Although no separate diffraction lines of NiAl₂O₄ could be observed in the XRD diagrams, the presence of Ni-aluminate cannot be excluded.

Fig. 3 and Table 3 show the total specific surface area obtained by nitrogen adsorption (BET) after sintering. Loss of surface area is observed already after 2 h at 650 °C or 50 h at 500 °C. After 100 h at 650 °C, 22% of the surface area has disappeared, only 65% of the original surface remains after 50 h at 825 °C. Clearly, both sintering of the nickel particles and structural and morphological changes of the carrier contribute to the observed decrease in total surface area.

Fig. 4 shows the sulfur adsorption capacity after sintering. The sulfur capacity and hence the specific nickel surface area follow the same trend as the total surface area in Fig. 3. Table 3 shows the specific nickel surface area (*S*_{Ni}) calculated from the sulfur adsorption capacity (*S*_{cap}). It can be seen that 57% of the nickel surface remains after 100 h at 650 °C, but only 27% is left after 50 h at 825 °C.

Fig. 5 shows the X-ray absorption spectra near the Ni K-edge of the fresh catalyst compared to the spectra of

Table 3
Total and nickel surface areas after sintering

Time (h)	Temperature (°C)	BET (m ² /g)	<i>S</i> _{cap} (ppm)	<i>S</i> _{Ni} (m ² /g)
0		130	3020	6.79
2	650	124	2740	6.16
5	650	120	2670	6.00
10	650	126	2460	5.53
25	650	110	2260	5.08
50	650	105	1970	4.43
100	650	101	1720	3.87
50	500	122	2880	6.47
50	575	113	2360	5.30
50	750	95.8	1040	2.34
50	825	84.8	820	1.84

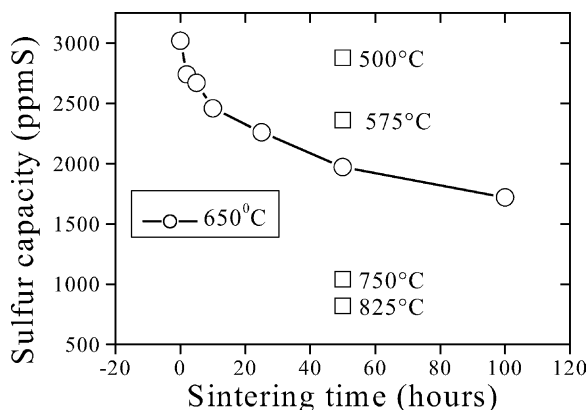


Fig. 4. Sulfur capacity as a function of sintering time and temperature. The sulfur capacity (S_{cap}) is related to the specific nickel surface area (S_{Ni}) through $S_{\text{Ni}} (\text{m}^2/\text{g}) = S_{\text{cap}} (\text{ppm S})/440$, see Ref. [1].

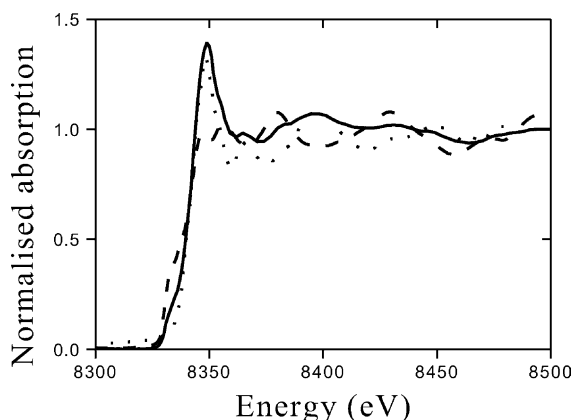


Fig. 5. Normalized absorption spectra of the fresh nickel catalyst (full line). The spectra of Ni (long dash) and NiO (short dash) references are also shown.

Ni-foil and NiO-bulk reference samples. If a substantial part of the nickel particles is oxidized we expect a shift in the position of the absorption edge and the presence of strong white line absorption in the near edge region (compare the Ni and NiO spectra of Fig. 5).

Fig. 6 shows the magnitude of the Fourier transformed data where the peaks correspond to inter-atomic distances.

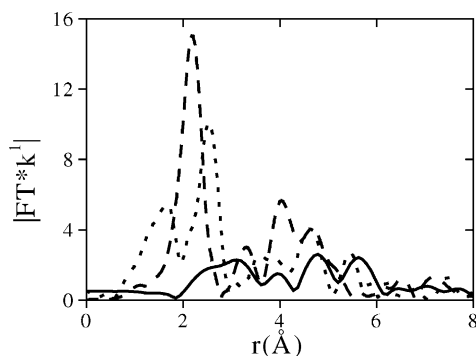


Fig. 6. Magnitude of the Fourier-transformed XAFS data (k^1 -weighted) measured on the fresh catalyst (full line) as well as Ni (long dash) and NiO (short dash) references (see Fig. 5).

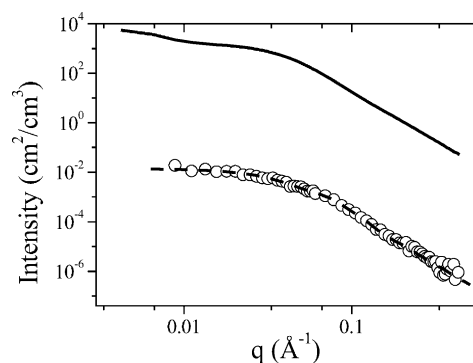


Fig. 7. ASAXS scattering curve measured at 8308 eV on the fresh catalyst (full line). The circles represent the separated scattering curve ($KI(q)$) obtained by subtracting the normalized scattering curves measured at 8308 and 8326 eV. The dashed line represents the best fit to the data using the approach described in the text.

It is clear from the figure that the nickel particles are neither pure metallic Ni nor pure NiO. The Fourier transformed data of the fresh catalysts is much less distinct than the data collected on the Ni and NiO references, indicating that the nickel phase of the catalyst has less crystalline order or is present in a very dispersed phase. The presence of Ni-aluminate cannot be excluded. Similar XAFS data were obtained on all samples.

Fig. 7 shows the result of an ASAXS measurement on the fresh catalyst; the nickel particle size distribution obtained as described above is shown in Fig. 8. Performing the separation using different combinations of energies we obtain consistent results. A specific nickel surface area of $11.4 \text{ m}^2/\text{g}$ for the fresh catalysts is obtained from the size distribution using:

$$S_{\text{ASAXS}} = \frac{1}{\rho} \int \frac{3}{r} P(r) dr$$

where ρ is the skeletal density of Ni (8.907 g/cm^3). Similar calculations were performed for all the data and the result is given in Table 4 together with the average nickel

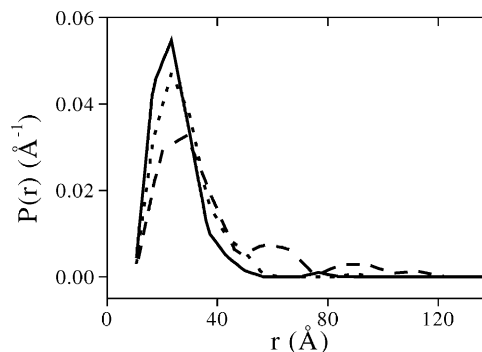


Fig. 8. Normalized nickel number particle size distributions of catalysts sintered at 650°C obtained by ASAXS as described in the text. The nickel particles are assumed to be spherical with radius r , but otherwise no assumption on the shape of the distribution is made. The full line is the distribution of the fresh catalyst. The short dash (long dash) is the distribution after sintering for 5 h (100 h).

Table 4
Parameters calculated from the nickel particle size distributions

Time (h)	Temperature (°C)	Radius (Å)	Variance (Å)	S_{ASAXS} (m ² /g)
0		25.1	9.0	11.4
2	650	25.4	8.9	9.8
5	650	27.8	10.3	8.8
10	650	27.4	12.6	7.9
50	650	29.2	15.0	6.9
100	650	37.9	21.5	5.0
50	500	29.3	10.5	8.4
50	575	26.9	12.7	7.9
50	750	36.9	21.7	4.6
50	825	36.1	33.6	3.1

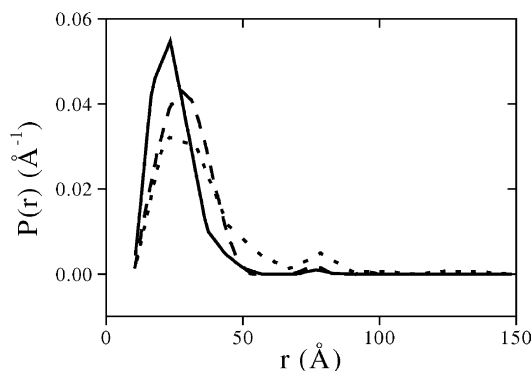


Fig. 9. Normalized number distribution of nickel particle radii of a fresh catalysts (full line) and after sintering for 50 h at 500 °C (long dash) or 750 °C (short dash) as observed by ASAXS.

particle radius and the variance of the nickel particle size distribution.

Figs. 8–10 and Table 4 show the effect of the sintering treatments on the nickel particle size distributions. It is seen that the sintering begins with an almost immediate reduction in the fraction of smaller particles and the appearance of larger and larger nickel particles as sintering proceeds. At 650 °C the average nickel particle size increases strongly within the first 10 h then the increase continues but at a slower rate (Fig. 10). The width (variance) of the nickel particle size distribution shows a similar behavior. The Ni surface area decreases much faster (with about a factor 4)

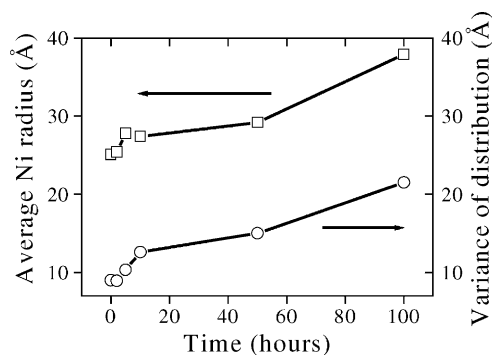


Fig. 10. Average nickel particle radius (squares) and variance (circles) of distribution determined by ASAXS after sintering at 650 °C.

than the average size increases (with only a factor 2), due to the fact that the average size is no good measure for the total size distribution (see Fig. 9) and the shift of the distribution to higher sizes.

4. Discussion

The sintering treatments carried out in this study clearly result in a reduction of the total surface area of the catalysts as shown in Fig. 3. The loss of surface is so large, that it cannot be explained by sintering of the nickel particles only. That the carrier is affected by the sintering treatments is also clear from the X-ray diffraction data.

The XAFS experiments were carried out on the same samples and in the same experimental setup immediately before the ASAXS experiments. The XAFS data clearly shows that the catalysts do not consist of pure and well crystalline Ni and NiO particles only. Instead a number of different atomic distances are observed reflecting partially oxidized nickel particles. Most likely, the smallest nickel-particles are completely oxidized whereas the majority of the nickel particles consist of a metallic Ni-core covered by a nickel-oxide surface layer. The X-ray diffraction results are consistent with this picture of partially oxidized nickel particles. Bartholomew and Pannell arrived at similar conclusions for a 9 wt.% Ni/Al₂O₃ catalysts prepared in a similar way [34].

Fig. 11 shows a comparison of the specific nickel surface areas obtained from sulfur chemisorption and ASAXS. The correlation between the two measures of surface area is very good, note that the apparent offset of the regression line (0.6 ± 0.8) cannot be distinguished from zero within the error. We do not expect the two measures of surface area to give numerically identical results. The ASAXS measurements were carried out on partially oxidized particles as explained above, whereas the nickel particles are completely reduced during sulfur chemisorption. If a metallic nickel particle reacts with oxygen and becomes partially oxidized this is expected to result in an increase in the particle size which is not fully compensated by the reduction in density.

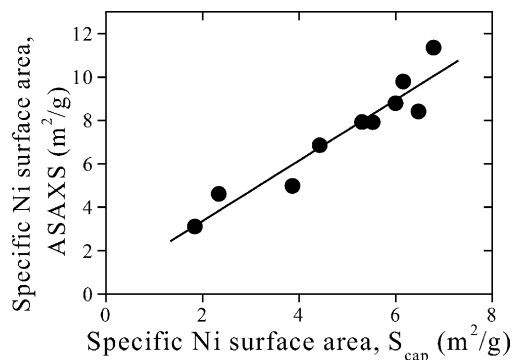


Fig. 11. Comparison of specific nickel surface areas derived from the sulfur chemisorption capacity (S_{cap}) and ASAXS (Tables 3 and 4). The line is the result of a linear regression ($S_{ASAXS} = 1.4(0.2)S_{cap} + 0.6(0.8)$), where the number in parentheses is the standard deviation of the fit.

Hence, the specific surface area is expected to decrease, although the effect is relatively small. More importantly, for any supported catalyst we expect part of the metal surface to be in contact with the substrate and hence, inaccessible for chemisorption. This will result in a surface area measured by chemisorption, which is smaller than that obtained by ASAXS. This is indeed observed as shown in Fig. 11. The ratio between the two measures of surface area in principle carries information on the nickel particle shape, particle packing and particle substrate interaction. Considering only the effect of metal–substrate contact the slope of Fig. 11 indicates that 29% of the nickel surface is inaccessible to chemisorption. A recent study on the sintering of nickel catalysts on MgAl_2O_4 -supports also found that the specific surface area measured by chemisorption corresponds to a larger particle size than observed by TEM on the same samples [13].

The surface areas measured by ASAXS and chemisorption agree in spite of the very different nature of the measurements and different assumptions involved in the analysis of the data. Combining the results of both methods allows the sintering process to be studied in detail.

An important goal of a sintering study is the assessment of the underlying mechanism. The surface energy of a metal particle is inversely proportional to its size and this constitutes the driving force for growth of the particles. Two mechanisms for the sintering of supported metal particle are generally proposed [16].

The first model (atomic migration model) involves emission of metal atoms from one metal particle, diffusion of the metal atoms on the substrate or in the gas phase and capture of the metal atoms by a (second) metal particle [16,35]. The atomic migration model predicts an initial increase in the number of small particles followed by growth of larger particles. If metal atoms can be trapped at reactive sites on the substrate or if the capture rates are small, then atomic migration may even lead to a decrease in the mean particle size.

The second model is a model of metal particle coalescence involving diffusion of particles on the substrate followed by collision and coalescence of the particles. The diffusion process is the rate-limiting step at typical sintering conditions. The coalescence model predicts an immediate increase in the average particle size and complete disappearance of small particles.

Both sintering mechanisms can be described by an empirical power law

$$\frac{dS}{dt} = -kS^n$$

where S is the specific surface area of the metal particles and k is a rate constant. The reaction order n assumes values between 2 and 5 in the case of atomic migration but is equal to or larger than 8 for particle coalescence [36,37]. Hence, the reaction order may in principle be used to determine the sintering mechanism. A complication is the fact that the coalescence mechanism often dominates at low tem-

peratures, whereas the atomic migration mechanism takes over at higher temperatures [5,8].

The nickel surface area of the catalysts sintered at 650 °C and measured by chemisorption follows the above power law with a reaction order $n = 8 \pm 1$. Alternatively, we may use the surface areas derived from the ASAXS particle size distributions. In this case we obtain a reaction order $n = 7 \pm 1$. The two experiments are consistent and point to the coalescence mechanism as the dominating at 650 °C.

The distribution of metal particle sizes also carries information on the sintering mechanism. The atomic migration model results in a metal particle size distribution with a tail towards small particles and a steep slope towards large particle sizes, whereas the coalescence model predicts a distribution with a tail towards larger particles such as a log-normal distribution [38–40]. Fig. 8 clearly demonstrates that sintering at 650 °C results in a nickel particle size distribution with a tail towards larger particles. The size distributions are fairly well approximated by log-normal distributions and an acceptable fit to the data can be obtained if such a distribution is assumed a priori [22]. Good descriptions of size distributions of sintered Ni catalysts on various supports by log-normal distributions were observed in many cases [13,39,41].

Several authors have criticized the use of either the sintering kinetics or the shape of the particle size distribution to determine the sintering mechanism [42,43]. Under special circumstances atomic migration may result in a log-normal particle size distribution indicating particle coalescence. However, in this case the sintering kinetics still reflects the true migration mechanism. Such problems can to a large extent be avoided using ASAXS where both the particle size distribution and the sintering kinetics can be measured independently. For sintering at 650 °C the shape of the particle size distribution and the loss of surface area as determined by ASAXS both indicate that the coalescence mechanism is the most important. Combining the ASAXS results with the chemisorption data we find strong evidence

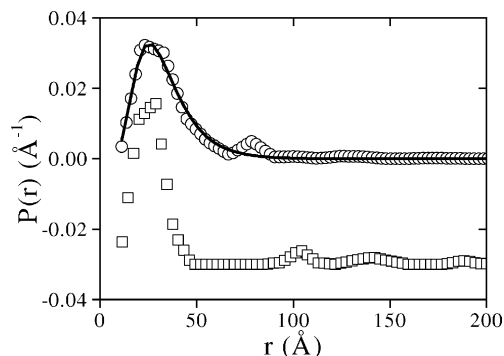


Fig. 12. Nickel particle size distributions obtained after sintering for 50 h at 750 °C (circles) or 825 °C (squares, displaced for clarity). Also shown is the best fit of a log-normal distribution ($P(r) = (1/\sqrt{2\pi r \ln \sigma}) e^{-(\ln(r/r_0)/2 \ln \sigma)^2}$) to the distribution obtained at 750 °C (full line). The best-fit parameters are $r_0 = 30.4$ Å and $\sigma = 1.53$.

for coalescence as the dominating mechanism, although the structural changes and loss of surface area of the carrier makes the actual process somewhat more complicated.

Sintering treatments at 500, 550, 650 and 750 °C for 50 h all result in size distributions with a tail towards larger particles indicating sintering by coalescence of nickel particles. This is shown in Fig. 12 where a log-normal fit to the data at 750 °C is also shown. The figure also shows the size distribution obtained after sintering at 825 °C. In this case we observe a relatively large amount of smaller particles ($r \approx 30$ Å) and some very large particles ($r \approx 100$ – 200 Å). Such a distribution indicates that particle migration is not the only mechanism but that atomic migration mechanism begins to contribute as well.

5. Conclusions

Sintering of Ni/Al₂O₃ catalysts were studied by sulfur chemisorption and anomalous small angle X-ray scattering. Sintering was performed at temperatures from 500 to 825 °C in a 1:1 mixture of H₂ and H₂O at a total pressure of 1 bar. Nickel particle size distributions were obtained from the ASAXS analysis, where the nickel particles were assumed to be spherical but otherwise no assumption on the type of the distributions was made. The ASAXS results were found to agree well with the chemisorption data.

Based on a combination of the form of the nickel particle size distributions and the reaction order of loss of nickel surface area a particle coalescence mechanism is proposed for sintering at 650 °C. The size distributions obtained indicate that the atomic migration mechanism begins to contribute to the sintering above approximately 800 °C. These conclusions are in agreement with those obtained in a number of related studies [1,6,9,10,13,15,37,41].

This study also demonstrates that valuable information on catalysts can be obtained by ASAXS. The ASAXS experiments complement the traditional methods of X-ray diffraction and chemisorption. From ASAXS measurements on supported catalysts, metal particle size distribution can be derived of a sufficient quality that, e.g. the metal particle surface area can be extracted. This allows both the size distribution and the surface area to be measured on the same sample under the same conditions. This is crucial and allowed us to infer the sintering mechanism for nickel particles on alumina at 650 °C.

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