Determination of Metal Particle Size in Partly Reduced Ni Catalysts by Hydrogen/Oxygen Chemisorption and EXAFS

Hydrogen chemisorption is commonly used to determine the degree of dispersion of Group VIII metal catalysts (e.g., (1–5)). In the determination of the metal surface area usually a hydrogen-to-metal stoichiometry of one has been used. However, increasingly more publications have appeared in which H/M values exceeding unity are reported (e.g., 3–6). Thus to overcome the apparent difficulties in determining the metal surface area in these highly dispersed systems by the hydrogen chemisorption technique we have recently presented a calibration of H/M values by EXAFS (extended X-ray absorption fine structure) for the Group VIII metals Rh, Ir, and Pt (7). Our results have clearly shown that the high H/M values are caused by high H/M$_{surface}$ stoichiometries (exceeding unity), with H/Pt < H/Rh < H/Ir. In this previous study we have used only fully reduced systems.

However, in practice often supported metal catalysts are studied which are only partly reduced. Therefore we present here hydrogen chemisorption and EXAFS measurements on Ni/SiO$_2$ systems with different degrees of reduction due to the application of different preparation methods (8).

The catalysts were prepared using SiO$_2$ (Degussa Aerosil 200) and Ni(NO$_3$)$_2$ · 6H$_2$O (p.a. Merck) according to the incipient wetness technique or the urea method (6). Nickel loadings were determined using atomic absorption spectroscopy.

Hydrogen chemisorption was carried out as described in (7): volumetric chemisorption measurements were performed in a conventional glass system at 298 K. Hydrogen was purified by passing through a palla-dium diffusion cell. The dried catalyst samples were first reduced in flowing H$_2$ at 723 K for 30 min (heating rate 5 K/min) and then evacuated (10^{-2} Pa) at the same temperature for 30 min. Hydrogen ($P(H_2)$ = 93 kPa) was admitted at 473 K, as hydrogen adsorption at room temperature is a slow process. Subsequently, the sample was cooled to 298 K under hydrogen and the amount of adsorbed hydrogen was measured ($P_{equilibrium}$ ~ 80 kPa). Thereafter a desorption isotherm was measured at room temperature by lowering the pressure step by step (ΔP ~ 13 kPa per step), while measuring the amount of desorbed hydrogen. The total amount of chemisorbed H atoms was obtained by extrapolating the linear high-pressure part (20 kPa < P < 80 kPa) of the isotherm to zero pressure (1). Correction for chemisorption on the bare support was not necessary, because extrapolation of the desorption isotherm for the bare support, pretreated in the same way as the catalysts, yielded zero within the uncertainty of the measurements.

Oxygen chemisorption experiments were carried out immediately after hydrogen chemisorption. The sample was evacuated at 298 K and then heated to 473 K (heating rate 5 K/min). At this temperature evacuation was prolonged for 30 min (10^{-2} Pa), to remove all adsorbed hydrogen from the metal particles. The sample was cooled to 298 K under vacuum, a certain amount of oxygen was admitted (P ~ 40 kPa), and the sample was again heated to 473 K (heating rate 5 K/min). At this temperature the sample was held for 1 h, after which all reduced Ni had been converted to NiO, and then cooled to 298 K. Subsequently a de-

TABLE 1

Preparation Characteristics and Chemisorption Results for the
Ni/SiO$_2$ Catalysts

Catalyst[a]	H/M	H/M$_{corr}$	Degree of reduction	
			O/M	1 − f (EXAFS)
1.9% Ni/SiO$_2$, I	0.29	0.32	0.90	1
2.4% Ni/SiO$_2$, U	0.17	0.36	0.47	0.42
5.2% Ni/SiO$_2$, U	0.30	0.43	0.69	0.53

[a] Prepared by the incipient wetness technique (I) or the urea method (U).
Accuracies: H/M, ±5%; O/M, ±10%; 1 − f (EXAFS), ±15%.

sorption isotherm was measured in the same way as in the case of hydrogen. The O/Ni values thus obtained were used to correct the hydrogen chemisorption results for the amount of unreduced Ni in the sample:

$$H/M_{corr} = \frac{1}{O/M_{meas}} H/M_{meas}.$$

The preparation details and chemisorption results are presented in Table 1. It is clear that the sample prepared according to the incipient wetness technique is more easily reduced than those prepared according to the urea method.

The EXAFS measurements were performed on the laboratory EXAFS spectrometer at Eindhoven University (9, 10), equipped with a Si(111) Johansson crystal. Measurements were done at the Ni K edge (8333 eV). The catalyst samples were pressed into self-supporting wafers with μx ~ 2.7. The wafers were mounted in an in situ EXAFS cell (11) and EXAFS spectra were taken at room temperature in H$_2$ after in situ reduction in flowing H$_2$ at 723 K (heating rate 5 K/min). EXAFS data analysis was performed using experimentally determined phases and backscattering amplitudes. Therefore, the reference compound Ni foil (12) was measured and the first Ni–Ni coordination shell was extracted from the EXAFS data in order to provide phase and backscattering amplitude information on Ni–Ni contributions. Likewise,

NiO (13) was measured to provide that information on Ni–O contributions.

In the partly reduced systems four contributions are expected with $R < 3.5$ Å: Ni–Ni of the reduced phase, and Ni–O, Ni–Ni, and Ni–Si of the hydrosilicate phase (14). Of these, the reduced Ni–Ni and the oxidic Ni–O coordination parameters (coordination number N, coordination distance R, and Debye–Waller factor $\Delta\sigma^2$ with respect to the appropriate reference compound) were determined using the difference file technique (15). In this technique, first an estimate for the parameters of the largest contribution (viz. Ni–Ni) is made, by fitting the right-hand side in the combined Ni–O + Ni–Ni peak at 1.6–2.8 Å after Fourier transformation in r space (Fig. 1a). This contribution is subsequently subtracted from the experimental data, and the difference spectrum is Fourier transformed. One then tries to estimate the coordination parameters of the Ni–O contribution at 1.6–2.6 Å in the same way (Fig. 1b). As a check both calculated contributions are added and compared with the experimental data in r and in k space. Usually it is repeatedly necessary to adjust the parameters of the Ni–Ni contribution and to calculate a new Ni–O contribution thereupon before good agreement between the experimental and the calculated spectrum is obtained (Figs. 1c and 1d). In Fig. 1d small differences are observed that are due to higher shell contributions (mainly Ni–Ni
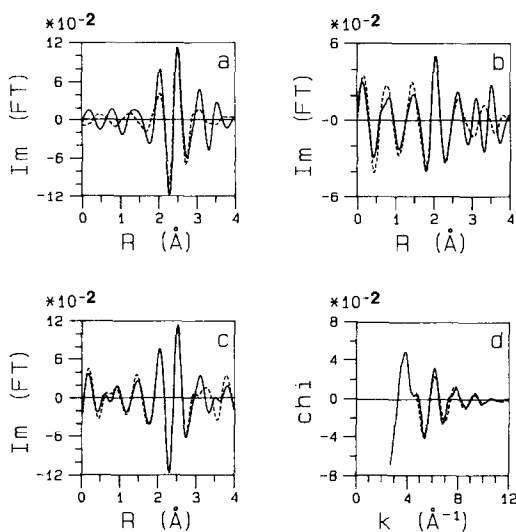
FIG. 1. (a) Imaginary part of k^1 Fourier transform (4.3–11.3 Å^{-1}, Ni–Ni phase corrected) of experimental EXAFS data for 5.2 wt% Ni/SiO$_2$ after reduction (—) and calculated Ni–Ni contribution (---); (b) imaginary part of k^1 Fourier transform (4.3–11.3 Å^{-1}, Ni–O phase corrected) of experimental data minus Ni–Ni contribution (—) and calculated Ni–O contribution (---); (c) imaginary part of k^1 Fourier transform (4.3–11.3 Å^{-1}, Ni–O phase corrected) of experimental data (—), and sum of the calculated Ni–O and Ni–Ni contributions (---); and (d) experimental data (—), and sum of the calculated Ni–O and Ni–Ni contributions (---) in k space.

and Ni–Si shells from the hydrosilicate phase). A full analysis of the EXAFS spectrum of the 5.2 wt% Ni/SiO$_2$ catalyst, including these higher shell contributions, will be presented elsewhere (16).

The Ni–Ni coordination number obtained from the EXAFS data analysis is averaged over all Ni atoms in the sample, i.e., those in the metallic phase as well as those in the oxidic hydrosilicate phase. However, the real coordination number of the Ni atoms in the metallic phase only is sought, in order to determine the mean metal particle size in the catalysts. If a fraction f of the Ni atoms in the sample is unreduced, then, assuming that the real Ni–O coordination number is 6 (14), f is equal to (17)

$$f = \frac{N_{meas}(\text{Ni–O})}{N_{real}(\text{Ni–O})} = \frac{N_{meas}(\text{Ni–O})}{6}.$$

As a consequence, the fraction of reduced Ni atoms in the sample is equal to $1 - f$. The real Ni–Ni coordination number in the metallic phase can now be determined as

$$N_{real}(\text{Ni–Ni}) = \frac{N_{meas}(\text{Ni–Ni})}{(1 - f)}.$$

The results of the EXAFS analysis are presented in Table 2 and Fig. 1. With respect to the accuracies given in Table 2, it should be mentioned that, although the absolute accuracy for, e.g., EXAFS coordination numbers is ±0.5, the relative accuracy is much higher. We feel confident that the Ni–O coordination number obtained for the 2.4 wt% Ni/SiO$_2$ system is significantly higher than that obtained for the 5.2 wt% Ni/SiO$_2$ catalyst.

TABLE 2

Coordination Parameters for the Reduced Ni/SiO$_2$ Catalysts

Sample	Ni–O			Ni–Ni			
	N	R (Å)	$\Delta\sigma^2$ (Å^2)	N	N_{corr}	R (Å)	$\Delta\sigma^2$ (Å^2)
Ni foil[a]	—	—	—	12.0	12.0	2.488	0
NiO[a]	6.0	2.098	0	—	—	—	—
1.9% Ni/SiO$_2$	n.d.	n.d.	n.d.	9.8	9.8	2.487	0
2.4% Ni/SiO$_2$	3.5	2.078	−0.0026	3.2	7.7	2.466	0.0020
5.2% Ni/SiO$_2$	2.8	2.063	−0.0009	4.3	8.1	2.470	0.0013

[a] XRD data (12, 13). Absolute accuracies: N, ±0.5; R, ±0.02 Å; $\Delta\sigma^2$, ±0.001 Å^2.

In the literature, the hydrogen chemisorption technique is described in many different ways. Small differences in the experimental details and in the interpretation of the measurements often yield different results. It must therefore be kept in mind that the numerical results presented here and in (7) depend on the method of hydrogen chemisorption. However, we think that our method yields representative results (7):

—Often, the chemisorption process takes place at room temperature instead of at a higher temperature (we used 473 K). Both methods were found to differ only 7% in the H/M value determined for an Ir/γ-Al₂O₃ catalyst (7).

—Hydrogen adsorption isotherms for supported Pt and Rh catalysts are reported to be Temkin-like (showing a linear relation between $\log(P)$ and H/M over a wide pressure range) (18, 19). Measuring H/M values at too high a pressure may thus result in values representing a situation in which more than a monolayer has been adsorbed. However, in our procedure we extrapolate to zero pressure.

—H/M values are reported to depend on the measurement temperature (20), being larger at lower temperatures. We used the most convenient temperature of 298 K.

—Often, a distinction is made between "reversibly" and "irreversibly" adsorbed hydrogen (e.g., (5)). Only the irreversibly adsorbed hydrogen is then taken into account in the determination of the H/M value. We think it is very difficult to determine the amount of irreversibly adsorbed hydrogen objectively, because the amount of weakly adsorbed hydrogen that can be removed by pumping depends very much on the experimental conditions. Moreover, it has been shown that the NMR chemical shifts of hydrogen atoms adsorbed on Pt/Al₂O₃ (21) and Rh/TiO₂ (22) catalysts still decrease with increasing H₂ pressure at $P >$ 40 kPa, and thus the hydrogen atoms which adsorb at these pressures must still be asso-

ciated with the metal. Therefore our H/M values are based upon the total amount, rather than the 'irreversibly' adsorbed amount of H₂.

The degrees of reduction from chemisorption (O/M_{meas}) and from EXAFS (1 − (N_{meas}(Ni–O)/6)) are equal within the accuracy of the measurements (see Table 1). This shows that slow oxidation of the reduced Ni/SiO₂ samples, a well-known problem with this type of catalyst (23), does not influence our measurements beyond the accuracies given: chemisorption measurements (hydrogen and oxygen) typically take several hours, while for EXAFS measurements more than a day is needed. Both the chemisorption and EXAFS results show that the incipient wetness technique yields a highly reduced system containing rather large metal particles. The corrected metal–metal coordination number N versus corrected H/M value is presented in Fig. 2, together with the previously obtained results on Rh, Ir, and Pt (7).

Just as for the other Group VIII elements studied, a linear relationship between H/M and N is observed for Ni. The H/M surface stoichiometry observed is approximately equal to one, as had been expected from literature reports on combined magnetization/chemisorption experiments (24). Thus we may conclude that there are no systematic errors inherent in our experimental methods; viz. also for the other metals (Pt, Rh, Ir) presented in Fig. 2 we may have a high degree of confidence in the numerical
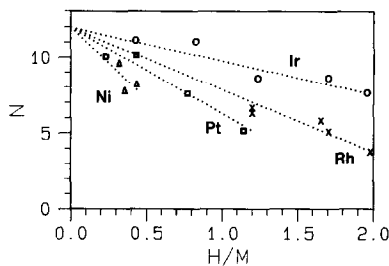
FIG. 2. Metal–metal coordination number N from EXAFS versus H/M from chemisorption for Ni (△), Pt (□), Rh (×), and Ir (○) (7).

values emanating from the H/M vs N curves.

For all metals presented in Fig. 2 there are 12 first shell neighbors in the bulk due to the fcc structure. Therefore at $H/M = 0$, a fixed $N = 12$ is chosen. Also, at $N \sim 3$, the measured H/M should be virtually equal to the $H/M_{surface}$ stoichiometry for the metal under study, assuming a half-spherical metal particle shape. We therefore conclude that in highly dispersed systems $H/Ni \sim 1$, $H/Pt \sim 1.5-2$, $H/Rh \sim 2-2.5$, and $H/Ir \sim 4$.

In order to relate the measured H/M values to particle sizes, assumptions must be made concerning the particle shape. Usually, it is assumed that the supported metal particles are half-spherical in shape. In that case straightforward calculations yield a relationship between the particle diameter and the first shell metal–metal coordination number as determined with EXAFS (7, 15). This is shown in Fig. 3. Using the correlation between N and H/M values, as determined in this study and in (7) for Ni, Pt, Rh, and Ir, we can now
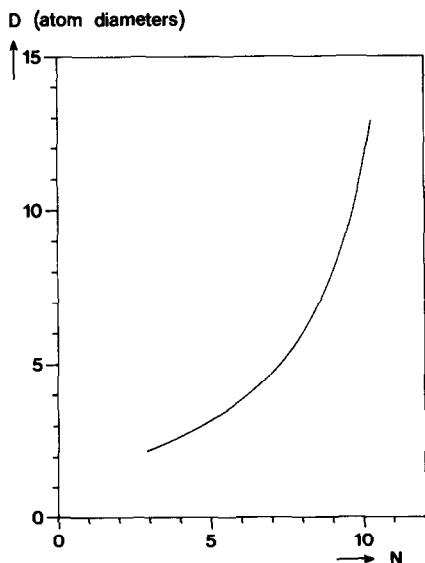

FIG. 4. Metal particle diameter D (expressed in atom diameters) based upon the metal–metal coordination number N versus H/M from chemisorption for Ni ($\triangle$), Pt ($\square$), Rh ($\times$), and Ir ($\bigcirc$) (7). The lines are calculated from the straight lines shown in Fig. 2.

relate hydrogen chemisorption results directly to particle sizes (see Fig. 4), without assuming a value for the H/M surface stoichiometry.

In summary, the EXAFS technique can be used as a method for determining the metal particle size even if the catalysts are not fully reduced. Caution must be taken that the degree of reduction is known when the EXAFS calibration of chemisorption values is used, to avoid assigning a too large mean metal particle size to the sample under study.

FIG. 3. Particle diameter D (expressed in atom diameters) calculated from the first shell metal–metal coordination number N from EXAFS, assuming half-spherical metal particles, versus N (7, 15).
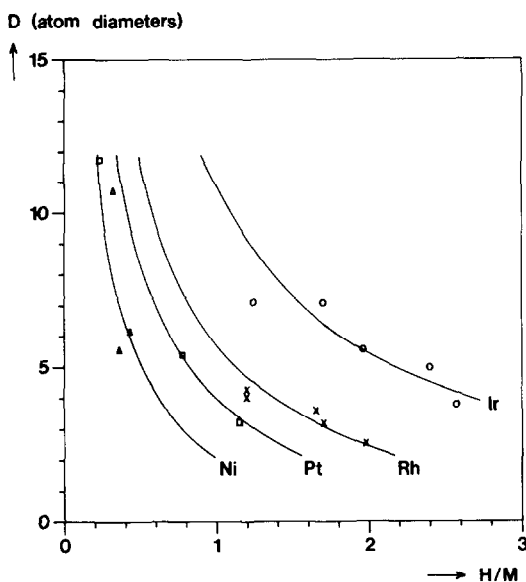
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