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Chemisorption of Methane on Silica-Supported Nickel Catalysts: A Magnetic and Infrared Study

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The adsorption of methane on silica-supported nickel catalysts was studied at various constant temperatures (30°C $< T <$ 100°C) and at increasing temperatures (30°C $< T <$ 300°C) using a low-field magnetic method and infrared spectroscopy. In the entire temperature range the chemisorption of CH_4 was found to be dissociative according to the reaction

$$CH_4 + 7Ni \rightarrow Ni_3C \text{ ("surface nickel-carbide")} + 4Ni\text{-}H.$$

It was observed that, per unit surface area, small nickel crystallites were more reactive toward methane than were large crystallites.

INTRODUCTION

In a previous paper we reported on the decomposition of methane on a nickel-on-silica catalyst during continuous flow and pulse flow experiments (*1*). It was found that at temperatures above 175°C methane reacted with the catalyst to yield adsorbed carbon and gaseous hydrogen. At lower temperatures it was impossible to discriminate between completely dissociative and partly dissociative chemisorption owing to the adsorption of hydrogen. Moreover, little detailed information on the nature of the deposited carbon was obtained. We therefore decided to study the chemisorption of CH_4 on Ni catalysts magnetically as well as by infrared spectroscopy. A low-field magnetic method was used and adsorption experiments were carried out in the temperature range from 30 to 300°C.

EXPERIMENTAL

The catalysts were prepared by precipitation of Ni(II) ions from an aqueous solution onto a suspended silica (Aerosil, Degussa). Homogeneous precipitation was effected by means of urea decomposition at 90°C (catalysts denoted by U), or by injection of hydroxyl ions also at 90°C (catalyst denoted by I). Both preparation procedures have been described in detail by Hermans and Geus (*2*) and by Van Dillen *et al.* (*3*).

The precipitates dried at 120°C were pressed (800 kg cm^{-2}) and cut to small bodies of dimensions between 1.5 and 2.5 mm. Reduction was carried out in a flow of 10% hydrogen in argon for at least 80 h. The temperature of reduction and other characteristics of the catalysts investigated are summarized in Table 1. The degree of reduction was determined thermogravimetrically or magnetically: in the thermogravimetric experiments it was calculated from the increase in weight during the reoxidation at 400°C of a catalyst sample (U_{42}, U_{42} (ir)), which previously had been calcined in N_2 at 600°C and subsequently reduced in a flow of 10% H_2 and 90% N_2 at 450°C. In the magnetic experiments the degree of reduction was determined by measuring the saturation magnetization of a reduced catalyst sample of known weight at 77 K and at a magnetic field strength of 14 kOe (1 Oe = 79.58 A m^{-1}). The specific surface area of the nickel was calculated from the extent of hydrogen chemisorption at a H_2 pressure of about 300 Torr at 30°C (1 Torr = 133.3 N

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TABLE 1

CATALYST CHARACTERISTICS

Catalyst	Surface area of Aerosil ($m^2\ g^{-1}$)	wt% Ni in the precipitate	Reduction temperature (°C)	Degree of reduction (%)	Surface area of Ni ($m^2\ g^{-1}$)
U_{20}	200	10	470	99	177
I_{42}	380	50	550	99	81
U_{42}	380	50	450	70	90
U_{42} (ir)	380	40	450	70	—

m^{-2}); a surface area of 3.58 m^2/ml of hydrogen adsorbed was assumed.

After reduction, the catalyst was evacuated for at least 4 h at a temperature 25°C below the reduction temperature to prevent desorption of water from the support. Evacuation and subsequent adsorption experiments were performed in a Pyrex high-vacuum system.

During the adsorption experiments the magnetization of the catalyst sample was measured in a low-field apparatus analogous to that described by Selwood (*4*) and Geus *et al.* (*5*). Technical data of the equipment used are given by Erkelens and Wösten (*6*). The alternating (260 Hz) magnetic field strength was 66 Oe. The signal was detected by a lock-in amplifier (Princeton Applied Research, model 5101).

The background pressure in the vacuum system varied between 10^{-6} and 10^{-5} Torr. The pressure of the adsorbing gas was measured by a Bourdon-type Precision Pressure Gauge (Texas Instruments, model 145). Analysis of the gas phase was carried out by means of a high-frequency mass spectrometer (Leybold Heraeus, Topatron B). Hydrogen used in the adsorption experiments was purified by diffusion through palladium; methane (purity 99.995%) was supplied by Matheson.

Particle size distributions of the catalysts were obtained by means of a vibrating sample magnetometer. In this apparatus a magnetic field strength up to 14 kOe could be applied. The magnetization of the catalyst samples was measured as a function of the field strength at 77 and 295 K. More details on the determination of the particle size distribution, partly based on the method of Dreyer (*7*), as well as on the equipment used will be published by Vermeulen and Geus (*8*).

The infrared spectra were obtained in the apparatus described by de Jong *et al.* (*9*). Catalyst discs of approximately 0.1 mm thickness were reduced and evacuated *in situ*. The reduction procedure was the same as given above. Spectra (no coadding scans) were recorded at room temperature with a Perkin-Elmer 580 B infrared spectrophotometer. The spectrum of the gas phase was compensated for by means of a cell—identical to and in open connection with the sample cell—in the reference beam of the spectrophotometer, which was always used in the double-beam mode.

RESULTS

Magnetic Measurements

All catalysts were established to be superparamagnetic before the adsorption experiments were carried out. To that end the magnetization of the freshly reduced and degassed catalysts was determined as a function of H/T (H = magnetic field strength, T = absolute temperature). To obtain a sufficient heat conduction in the sample cell a He pressure of 50 Torr was applied. The measured values of the magnetization were corrected for the temperature dependence of the saturation magnetization of bulk nickel. This correction was effected by multiplying the measured value by $M_s^2(0)/M_s^2(T)$, where $M_s(0)$ is the saturation magnetization at 0 K and $M_s(T)$ the saturation magnetization at T K, the measuring temperature. The values for $M_s(0)$ and $M_s(T)$ were taken from the literature (*10*). According to Langevin's equation a plot of the magnetization versus H/T of a superparamagnetic sample yields a straight line, provided $\mu_p H$ (μ_p = magnetic moment of a nickel particle) is small as compared to kT. Figure 1 shows that this was found for catalyst U_{42} in the temperature range 124–392 K; the values measured at 77 K, however, were too small. The same result was obtained with catalyst I_{42}. Catalyst U_{20}, on the other hand, showed a linear relation in the entire temperature range 77–400 K. In the adsorption experiments the magnetization always was measured at temperatures between 30 and 100°C. All catalysts behaved superparamagnetically in this temperature range.

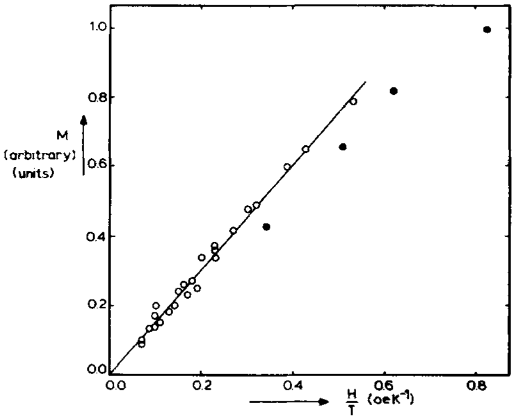

FIG. 1. The magnetization of catalyst U_{42} as a function of H/T; (○) measured in the temperature range 124–392 K; (●) measured at 77 K.

After reduction and evacuation, catalysts U_{20} and I_{42} were exposed to CH_4 at 30°C. The CH_4 dose admitted to the sample (weight about 2 g) was just sufficient to lead to a monolayer coverage, provided all admitted molecules are chemisorbed and one CH_4 molecule is bonded to seven nickel surface atoms. It was found that the catalyst with the small particles, U_{20}, took up more CH_4 than catalyst I_{42} with rather large particles: 1.05×10^{-2} ml STP m^{-2} Ni and 0.16×10^{-2} ml STP m^{-2} Ni, respectively (full coverage of hydrogen: 0.28 ml STP m^{-2}).

The temperature was then raised stepwise up to 300°C. At several intermediate temperatures the amount of CH_4 taken up after equilibration was determined. It was observed that at temperatures above 150°C hydrogen started to desorb from the catalyst surface. The calculation of the amount of CH_4 adsorbed, V_a, at these temperatures was carried out after determination of the ratio P_{CH_4}/P_{H_2} by means of the Topatron mass spectrometer. The decrease of the magnetization due to the adsorption V_a was determined after cooling the catalyst to 30°C. Figure 2 shows the results; in this figure M is the actual magnetization and M_0 is the magnetization when $V_a = 0$. It can be seen that the magnetization decreased linearly with V_a. At 300°C the surface coverage of catalyst I_{42} eventually was 6.20×10^{-2} ml STP m^{-2} Ni, while on catalyst U_{20} a surface coverage of 6.6×10^{-2} ml STP m^{-2} Ni was attained. A new dose of CH_4 admitted to the catalyst at 300°C caused a steep rise of V_a. On catalyst I_{42} this additional adsorption did not bring about a decrease in magnetization; with catalyst U_{20}, on the other hand, the adsorp-

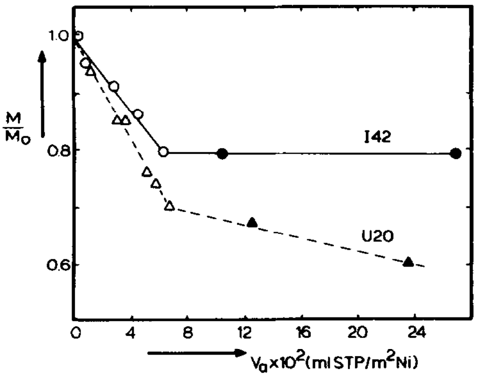

FIG. 2. The relative magnetization of catalysts U_{20} and I_{42} as a function of the amount of methane adsorbed: (○, △) adsorption during a temperature rise from 30 to 300°C (starting pressure of methane corresponding to a monolayer coverage); (●, ▲) additional adsorption at 300°C.

tion was accompanied by a slight drop in magnetization.

In the above experiments both the temperature and the pressure varied. Therefore we also studied the adsorption of methane isothermally. Catalyst U_{42} was used. Adsorption isotherms were measured at 30, 77, and 100°C. At these temperatures hydrogen set free from methane remains adsorbed on the catalyst surface. For each isotherm the time between two successive adsorption steps was about 1.5 h. In this period equilibrium was not established. The CH_4 pressures were between 0 and 300 Torr. In Fig. 3 the magnetization–volume isotherm for CH_4 adsorption at 100°C is shown. In the same figure the isotherm for hydrogen adsorption at 30°C is presented. The methane curve was measured twice, and the hydrogen isotherm was measured in three different experiments. The results reproduced well as can be seen in Fig. 3. Moreover, the time that had passed between the measurement of the first and the last hydrogen isotherm was about half a year, during which many adsorption experiments with subsequent reductions at 450°C were carried out: obviously the thermostability of catalyst U_{42} is rather high.

In the magnetization–volume isotherm for CH_4 two distinct regions can be distinguished; when V_a is less than 5.2 ml STP g^{-1} Ni, or 6.66×10^{-2} ml STP m^{-2} Ni, the chemisorption led to a large decrease in magnetization, whereas at higher coverages adsorption hardly affected the magnetization. In the first region the slope of the methane isotherm is considerably larger than that of the hydrogen isotherm. It is often found in the literature (e.g. Ref (*4*)) that the bond number of any particular gas is determined by comparing the initial slope of its magnetization–volume isotherm with the slope of the hydrogen isotherm. This procedure is justified only if all nickel particles have the same size and if the gas molecules and the hydrogen molecules are uniformly distributed over the metal particles. As will be shown in the following section, however, catalyst U_{42} is far from monodisperse (Fig. 5). The smaller nickel particles are contributing considerably less to the magnetization than the larger crystallites. This is due to the poor alignment of small

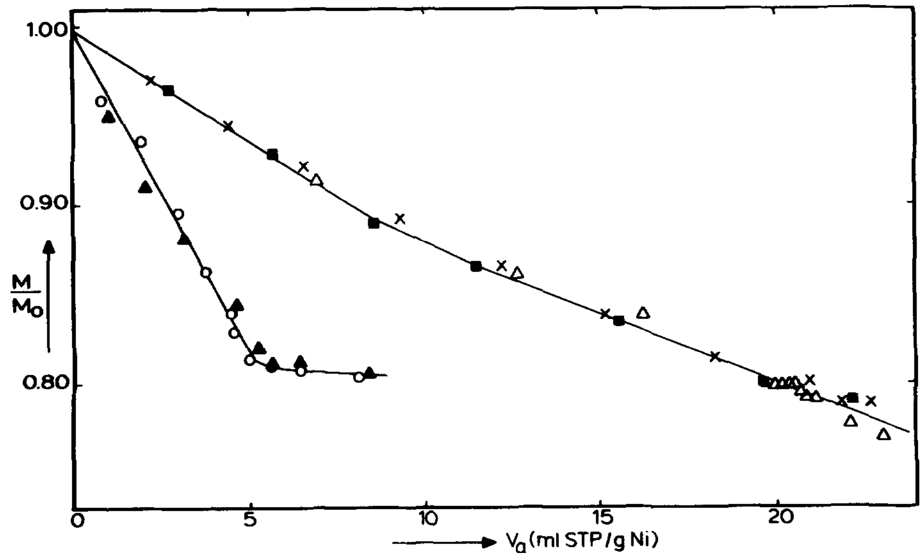

FIG. 3. The relative magnetization of catalyst U_{42} as a function of V_a: (×, ■, △) hydrogen adsorption at 30°C; (▲, ○) methane adsorption at 100°C.

magnetic moments in the direction of a weak magnetic field (H = 66 Oe), as compared to larger moments. When adsorption preferably proceeds on large particles, the initial slope of the magnetization isotherm is consequently larger than with preferential adsorption on small crystallites. When hydrogen and methane are differently distributed over the particles of varying size, comparison of the initial slopes of the two isotherms therefore gives a wrong bond number. It is hence preferable to consider the overall magnetic effect, ΔM, at high surface coverage. According to Fig. 3 the maximum decrease in magnetization, 19%, is observed after adsorption of 5.2 ml STP CH_4 g^{-1} Ni. Adsorption of 17.8 ml STP H_2 g^{-1} Ni caused the same decrease in magnetization. Assuming that a hydrogen molecule is dissociatively chemisorbed and "decouples" the magnetic moment of two nickel surface atoms, the bond number of a CH_4 molecule can be calculated according to

$$\text{bond number} = \frac{17.8 \times 2}{5.2} = 6.9.$$

Each chemisorbed methane molecule annihilates the contribution to the magnetization of 6.9 nickel surface atoms.

When V_a exceeded the value of 5.2 ml STP g^{-1} Ni the magnetization no longer decreased. Apparently further adsorption did not affect the magnetism of more Ni atoms.

The adsorption of methane was not only measured at 100°C, but also at 77 and 30°C. In Fig. 4 the magnetization–volume isotherms at these temperatures are represented. With an equilibration time of 1.5 h between successive doses of methane, the amount of CH_4 taken up was larger at higher temperatures. However, the slope of the magnetization isotherm was the same at all measuring temperatures, which implies that also at 30 and 77°C chemisorption of one CH_4 molecule annihilates the magnetism of 6.9 Ni atoms.

Infrared Spectroscopy

A small amount of catalyst U_{42} was pressed into a disc. After reduction and subsequent evacuation the disc was exposed to 51 Torr of methane at 95°C. In the infrared spectrum no CH_x absorption bands were observed. Due to the adsorption of CH_4 the transmittance of the disc was

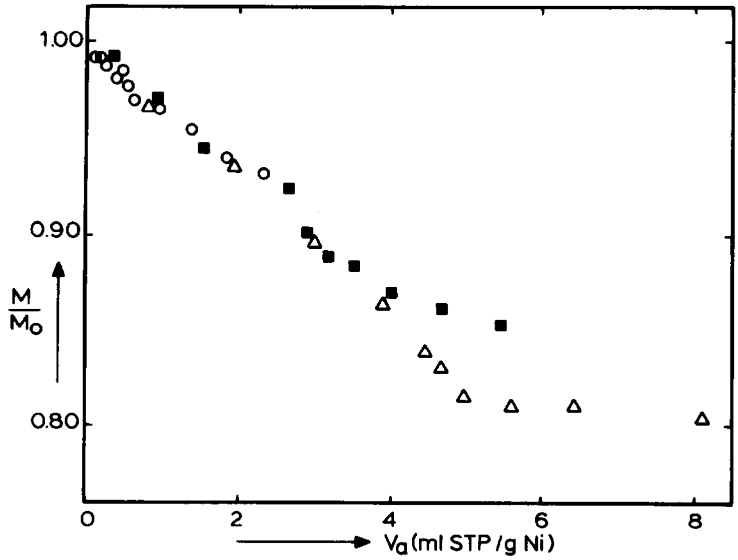

FIG. 4. Magnetization–volume isotherms for the adsorption of methane on catalyst U_{42}: (○) T = 30°C; (■) T = 77°C; (△) T = 100°C.

somewhat enhanced, especially between 1800 and 1400 cm^{-1}. Because of the poor transparency of catalyst U_{42}, the experiment was repeated with catalyst U_{42} (ir), for which the Ni to SiO_2 ratio is smaller. After exposure to 200 Torr of methane at 25°C for 1 h, again no CH_x absorption bands were observed in the spectrum. The transmittance was increased in the same way as for catalyst U_{42}. Also after chemisorption of CH_4 (p = 196 Torr) at 100°C no CH_x bands were found.

DISCUSSION

It was found that at 77 K the magnetization of catalysts I_{42} and U_{42} was smaller than the value predicted by the Langevin theory of superparamagnetism (Fig. 1). This deviation can be ascribed to the magnetic anisotropy energy, $K'v$ (K' = anisotropy constant, v = volume of a nickel particle) (*11*).

In Fig. 5 for catalysts U_{20}, U_{42}, and I_{42} the increment of the nickel volume V in intervals $d(\log r)$ is represented as a function of r, where r is the particle radius. As can be seen in this figure, catalyst U_{20} only contained particles with radii below 40 Å, whereas an appreciable volume fraction of the nickel in catalysts I_{42} and U_{42} was present as particles with radii exceeding 40 Å. For the small crystallites of catalyst U_{20} a linear plot of M versus H/T, including T = 77 K, was obtained; for the larger particles (r > 40 Å) of catalysts I_{42} and U_{42} $K'v/kT$ apparently was too large at 77 K to obey the Langevin function, which holds true for small values of $K'v/kT$ only.

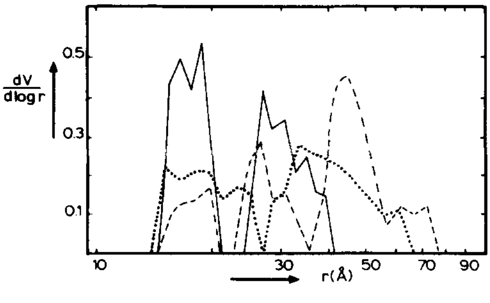

FIG. 5. Particle size distributions of the catalysts used: (——) U_{20}; (– – –) I_{42}; (· · · · ·) U_{42}.

When catalyst U_{42} adsorbed methane isothermally at 100°C, the magnetic moment of the nickel particles decreased by the contribution of 6.9 Ni atoms for each CH_4 molecule chemisorbed. From this number we infer that CH_4 dissociates completely into a "surface nickel carbide" and adsorbed hydrogen: $CH_4\ (g) \rightarrow Ni_3C + 4H$ (ads). This leads to the "decoupling" of 7 surface nickel atoms, which is very close to the number of 6.9 measured. Martin and Imelik (*12*), using high-field magnetic methods, also reported a value of 6.9, but only at temperatures above 300°C.

We calculated the bond number of methane from the decrease in magnetization at a surface coverage of about 0.8. There is still an error in the calculation when even at this high coverage H_2 and CH_4 are not equally distributed over the differently sized particles (only at full coverage, $\theta = 1$, would an equal distribution be ensured). We feel, however, that our method of calculating the bond number is far less inaccurate than simply comparing the initial slopes (at low values of θ) of the isotherms of CH_4 and H_2. The results with infrared spectroscopy also indicate complete dissociation of CH_4 on the surface of the catalyst. After adsorption of CH_4 at 95°C on catalyst U_{42}, which leads to a surface coverage of about 0.8, no CH_x absorption bands appeared in the spectrum. After exposure to CH_4 of catalyst U_{42} (ir) these bands were not observed, either at 25°C, or at 100°C. This is in agreement with the results obtained by Erkelens and Wösten (*6*) on a Ni/SiO_2 catalyst at 25°C. According to these authors the absence of CH_x absorption bands is due to a concentration of CH_x surface radicals too small to be detected by their apparatus. Because of the higher surface coverage obtained at 95°C (or 100°C) and due to the use of a very sensitive infrared spectrophotometer, however, we believe that the absence of CH_x absorption bands provides evidence, additional to the magnetic results, for the completely dissociative chemisorption of methane.

Erkelens and Wösten (*6*) also studied CH_4 adsorption on a Ni/SiO_2 catalyst using a low-field "permeameter." Comparing the initial slopes of the CH_4 and H_2 isotherms, both measured at 25°C, they derived that four to five surface bonds were formed by each CH_4 molecule chemisorbed. When we calculate the number of surface bonds in a similar (and, as argued above, erroneous) way from our measurements, we find a value of 4.6. Again our experimental results nicely agree with those of Erkelens and Wösten.

The magnetization of catalyst U_{42} no longer decreased with further adsorption after V_a had reached the value of 5.2 ml STP CH_4 g^{-1} Ni (Fig. 3), corresponding with 6.7×10^{-2} ml STP m^{-2} Ni. The same effect has been observed on catalyst I_{42} after adsorption of 6.2×10^{-2} ml STP m^{-2} Ni (Fig. 2). Above a surface coverage between 0.7 and 0.8, CH_4 is apparently no longer adsorbed on "free" surface nickel atoms. We performed additional experiments to elucidate the nature of the carbon deposited without magnetic effect; the results will be discussed in our next paper.

Schouten *et al.* (*13, 14*) reported that the interaction of CH_4 with Ni single crystals was strongly affected by the atomic structure of the surface. At temperatures above 200°C and pressures up to 10^{-2} Torr the Ni(110) surface reacted rapidly with CH_4, whereas the reaction on the Ni(100) surface was rather slow. The Ni(111) surface did not react at all. From the extent of hydrogen adsorption at 30°C ($P_{H_2} = 300$ Torr) the monolayer capacity of catalyst U_{42} was calculated to be 25 ml of hydrogen. As can be seen in Fig. 4, at temperatures below 100°C the interaction of this catalyst with methane remained below the monolayer capacity of about 7 ml STP (final CH_4 pressure also about 300 Torr). The relatively limited interaction with methane indicates that our catalysts contained a marked fraction of less reactive surfaces like the Ni(111) surface described by Schouten *et al.* With smaller particles the fraction of surfaces of low reactivity decreased. This can be concluded from the continuing, although more gradual, decrease of the magnetization of catalyst U_{20} at values of V_a above 6.6×10^{-2} ml STP CH_4 m^{-2} Ni (Fig. 2). As seen above, at corresponding values of V_a the magnetization of catalysts I_{42} and U_{42} no longer decreased. Obviously, the small particles of catalyst U_{20} expose more active sites per unit surface area than large crystallites. This also explains the different extent of methane adsorption at 25°C on catalysts I_{42} and U_{20}: in the equilibrium state catalyst U_{20} adsorbed 1.05×10^{-2} ml STP m^{-2} Ni, whereas adsorption on catalyst I_{42} was limited to 0.16×10^{-2} ml STP m^{-2} Ni.

In a study on the reactivity of the carbon deposit toward hydrogen we obtained further magnetic evidence for the preferential adsorption of CH_4 on small particles (to be published).

It was evident in Fig. 4 that the slope of the magnetization–volume isotherm for CH_4 adsorption at 30 and 77°C was the same as at 100°C. Therefore we concluded that the chemisorption of methane was completely dissociative at all temperatures investigated. This conclusion is correct when it is assumed that the distribution of CH_4 over the catalyst particles is not influenced by the temperature. Stated otherwise, transport limitations should not occur and the surface reaction should be rate determining. In a previous publication (*1*) we reported experimental proof for this assumption: in pulse experiments it was established that a plot of ln (reaction rate) versus $1/T$ gave a straight line over a conversion range from 7% (30°C) to 93% (200°C). Because of the width of this range we may state that transport limitations did not occur.

REFERENCES

1. Kuijpers, E. G. M., Jansen, J. W., Van Dillen, A. J., and Geus, J. W., *J. Catal.*, in press.

2. Hermans, L. A. M., and Geus, J. W., *in* "Studies of Surface Science and Catalysis" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), Vol. 3, p. 113. Elsevier, Amsterdam, 1979.
3. Van Dillen, A. J., Geus, J. W., Hermans, L. A. M., and Van der Meijden, J., *in* "Proceedings of the Sixth International Congress on Catalysis (London, 1976)" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 2, p. 667. Chemical Society, London, 1977.
4. Selwood, P. W., "Chemisorption and Magnetization." Academic Press, New York, 1975.
5. Geus, J. W., Nobel, A. P. P., and Zwietering, P., *J. Catal.* **1**, 8 (1962).
6. Erkelens, J., and Wösten, W. J., *J. Catal.* **54**, 143 (1978).
7. Dreyer, H., *Z. Anorg. Chem.* **362**, 233 (1968).
8. Vermeulen, A. C., and Geus, J. W., to be published.
9. De Jong, K. P., Geus, J. W., and Joziasse, J., *J. Catal.* **65**, 437 (1980).
10. Landolt-Börnstein, "Magnetic Properties I," Vol. II/9, p. 1–17. Springer-Verlag, Berlin, 1962.
11. Bozorth, R. M., "Ferromagnetism," p. 568. Van Nostrand, Princeton, N.J., 1951.
12. Martin, G. A., and Imelik, B., *Surface Sci.* **42**, 157 (1974).
13. Schouten, F. C., Gijzeman, O. L. J., and Bootsma, G. A., *Surface Sci.* **87**, 1 (1979).
14. Schouten, F. C., Kaleveld, E. W., and Bootsma, G. A., *Surface Sci.* **63**, 460 (1977).