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Effects of Particle Size and Degree of Reduction on the Magnetic Properties of Dispersed Nickel Catalysts

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Static magnetization and ferromagnetic resonance absorption measurements have been performed on a variety of supported Ni catalysts. Results obtained by these two techniques show good agreement. It is shown that the Curie temperature of Ni is almost independent of particle size for average particle diameters down to 2.5 nm. By contrast, a significant shift of the Curie temperature occurs in partially reduced samples or upon O_2 chemisorption. The consequences of these two observations are discussed with particular emphasis on their use for the chemical and electronic characterizations of highly dispersed Ni catalysts.

INTRODUCTION

Many properties (e.g., electronic, structural, magnetic, thermodynamic, and surface) have been claimed to depend on the state of dispersion of supported metal catalysts with possible consequences regarding their catalytic activity (*1*). For instance, this has been the case for the magnetic properties of Ni in highly dispersed Ni–silica catalysts. By comparison of the thermomagnetic curves (*2*) of the field dependence of the magnetization (*3*) and of the paramagnetic magneton number, β(Ni), and Curie temperature (*4*) for massive and highly dispersed Ni on silica, Carter and Sinfelt concluded that the "electronic structure of supported nickel is different from that of bulk nickel." It was observed that, with decreasing particle size (down from massive to 1.2-nm Ni), the paramagnetic Curie temperature shifts from 638 to 547 K while β(Ni) decreases from 1.73 to 1.1. These data supplemented some parallel work concerning the important question of how the degree of dispersion of a metal influences its catalytic activity (*5*). However, no trial was made by these authors to discriminate between a carrier effect or a true electronic effect arising from differences between surface and bulk atoms although a slight preference was given to the latter. In addition, the observed decrease in Curie temperature and its explanation still remain an open point since results on comparable or different systems have been reported which are at variance with the former studies (*6*). Apart from practical considerations which make difficult the determination of T_c in a superparamagnetic sample (*7*) one must note for example that small Co particles, about 1.4 nm in size, have been found to show normal thermomagnetic curves (*8–10*). Similarly,

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thin Ni films of various grain sizes deposited in ultrahigh vacuum conditions showed no T_c shifts (*11*). Finally, if the effective paramagnetic magneton number is affected by particle size, the saturation magnetization and the internal Weiss field of the ferromagnetic material should also depend on the state of dispersion.

Selwood (*6*) has provided evidence that the saturation magnetization in small Ni particles is within ±1% that of bulk Ni, and Mössbauer data (*12*) on small particles of ferro- or ferrimagnetic iron compounds showed no particle size variation of the internal field. Hence, particle size here seems to have little effect on magnetization, at least for particles larger than 2 nm.

The present paper throws some light on the following two questions arising from the problems described above. First, does the Curie temperature (and consequently the internal field and the saturation magnetization) depend on the particle size of Ni in dispersed catalysts? Second, should it be taken as evidence for an electronic or a chemical effect and, in the latter case, of what type? Previous knowledge of the morphology of most samples was available (*15*) and two complementary techniques have been used, namely, static magnetization and ferromagnetic resonance absorption (FMR) measurements.

EXPERIMENTAL

Catalyst samples. Highly dispersed Ni catalysts were prepared by adding Aerosil silica into a solution of hexoammine–nickel–nitrate (*13a*). The suspension was then filtered.

Upon evaporation of ammonia decomposition of the adsorbed complex occurred, with formation of $Ni(OH)_2$. The solid was then washed, dried, and pelleted under 2 ton cm^{-2}.

A precursor containing 15.8 wt% Ni was reduced for 15 h at 923 K in a 3-liter·h^{-1} H_2 stream and further outgassed at 673 K for 2 h. Then, inert He was introduced to ensure good thermal equilibrium during the static magnetic measurements. This sample is denoted as SiO_2–53. Saturation of this sample with chemisorbed oxygen and evacuation at room temperature followed by further heating at 673 K to ensure the sample's chemical stability during the thermomagnetic measurements led to sample SiO_2–53–O.

Another precursor containing 4.5 wt% Ni was reduced according to two reduction procedures. The solid either was reduced at 793 K for 1 h in a 3-liter·h^{-1} H_2 stream (leading to SiO_2–24–O) or was first outgassed for 2 h at 793 K and then subsequently reduced at 813 K in a 30-liter·h^{-1} flow (resulting in the sample SiO_2–25). These two samples were similarly outgassed at 673 K and exposed to He. Exposure of SiO_2–25 to air, followed by evacuation at room temperature down to 10^{-6} Torr before FMR measurement, resulted in a new sample denoted as SiO_2–25–O.

The massive Ni reference catalyst, 12% Ni on $MgAl_2O_4$, was supplied by Haldor Topsøe A/S. It will be referred to as $MgAl_2O_4$–1400 and was activated as follows. After evacuation at room temperature, the prereduced supplied catalyst was heated at a rate of 13°C min^{-1} under H_2 flow (9 liters·h^{-1}) up to 1123 K where it was left for an additional 2 h. After evacuation to 10^{-6} Torr, the sample was sealed off.

The main features of these catalysts are summarized in Table 1.

Static magnetic measurements. Static magnetization measurements were performed by the Weiss extraction method using an electromagnet providing fields up to 21 kOe at 77, 300, and variable temperatures up to 700 K.

In the case of superparamagnetic behavior, the low field approximation to the

TABLE 1

Characteristics of Dispersed Ni Catalysts

Sample	Ni content[a] (wt%)	Average particle size (nm)	Degree of reduction R (%)	T_c(K)	
				FMR[b]	SM[b]
$MgAl_2O_4$-1400	12	140.8[c]	100[d]	631 ± 5	—
SiO_2-53	15.8	5.3[e]	106[f]	625 ± 5	625 ± 10
SiO_2-25	4.5	2.5[e]	100[f]	645 ± 10	640 ± 10
SiO_2-53-O	15.8	5.3[g]	78[f]	—	610 ± 10
SiO_2-25-O	4.5	2.5[g]	50[f]	505 ± 10	—
SiO_2-24-O	4.5	2.4	65[f]	—	570 ± 10

[a] Metallic Ni.

[b] FMR, Ferromagnetic resonance; SM, static magnetization.

[c] Number average from electron microscopy measurements after reduction as described in the text.

[d] Assumed value following high temperature reduction treatment.

[e] As evaluated from H_2 chemisorption in agreement with magnetic data assuming superparamagnetism after reduction as described in the text.

[f] Calculated from saturation magnetization measurements after reduction as described in the text.

[g] Assuming no particle size distribution modification upon O_2 adsorption.

volumic magnetization can be written as (*13b*):

$$M = M_S^2 \frac{vH}{3kT} \qquad (1)$$

and

$$\chi T = \frac{MT}{H} = M_S^2 \frac{v}{3k}, \qquad (2)$$

where M = volumic magnetization; M_S = saturation volumic magnetization, approximately equal to the spontaneous magnetization at low fields; v = volume of the particle; H = magnetic field strength; k = Boltzmann constant; T = absolute temperature; χ = volumic susceptibility. Equations (1) and (2) show that χT is proportional to M_S^2. Hence, Curie points were determined by plotting χT vs T, χ being calculated at each temperature by extrapolation at zero field of the ratio δ/H (δ = deflection; H = field strength) vs H.

Ferromagnetic resonance absorption (FMR). FMR measurements were performed up to 700 K using an EPR Brüker spectrometer B-ER-420 operating in the X band, using 100-kHz field modulation and 2-mW microwave power. Variable temperature was achieved by using the BST-10,000X (low temperature) and BER-400 XHT (high temperature) attachments.

Particular attention was paid to avoid Q-factor fluctuations during the recording of the resonance signal. Temperature calibration was achieved by double thermocouple detection over the sample length (*14*).

FMR intensities are normalized in relative units, i.e., I/I_0, where I is the FMR intensity at temperature T and I_0 is the FMR intensity at the lowest experimental temperature. Intensity values were computed using a specially designed computer program allowing for baseline adjustments (*14*).

RESULTS AND DISCUSSION

The morphological characteristics of the various catalysts which have been examined are summarized in Table 1. Most of them were reported in greater detail in a

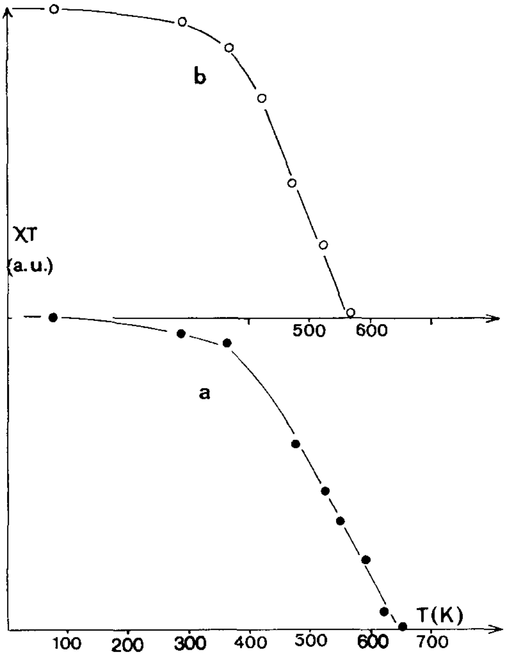

FIG. 1. Plot of χT vs T for the SiO_2-25 (a) and SiO_2–24–O (b) catalysts.

previous paper (*15*). It can be recalled that surface average diameters [see definition in Ref. (*15*)] were obtained by magnetic methods. After showing that most samples were superparamagnetic (excepted $MgAl_2O_4$–1400) by plotting the magnetization M against the reduced parameter H/T, average diameters were calculated by the Langevin low field (LLF) and Langevin high field (LHF) methods (*6*). In addition, the complete particle size distribution of sample SiO_2–25 was obtained from the analysis of the curve $M(H)$ according to the procedure described in Ref. (*13b*); it shows a maximum near 2.4 nm and ranges from 1.0 to 5.5 nm.

Average particle sizes for the samples SiO_2–25 and SiO_2–53, thus obtained, agree well with those calculated from H_2 chemisorption data, assuming that H_2 saturation of the Ni surface occurs at 300 K under a pressure of 750 Torr, that H/Ni is equal to unity, and that (111) and (100) planes are present on the metallic surface.

Some samples were also examined by electron microscopy. $MgAl_2O_4$–1400 has a size distribution spanning the range 30–200 nm. Particle diameters for the SiO_2–53 sample range from 3.0 to 9.5 nm with a maximum at about 5.8 nm, these particles being almost spherical in shape.

The degree of reduction, R, expressed as the ratio of metallic nickel to initial divalent nickel, i.e., Ni^o/Ni^{2+}, was calculated from saturation magnetization measurements, assuming that saturation magnetization in small metal particles remains equal to the bulk one, a point which will be discussed in another paper (*16*) and seems reasonable in view of other and previous data (*6*, *12*). An example of a magnetization curve is given in Fig. 1 of Ref. (*15*). The uncertainty in the value of the saturation magnetization and then in the Ni^o concentration is estimated to be a few percent.

Variations of χT with T for the samples SiO_2–25 and SiO_2–24–O are shown in Fig. 1. In the low temperature region, χT is

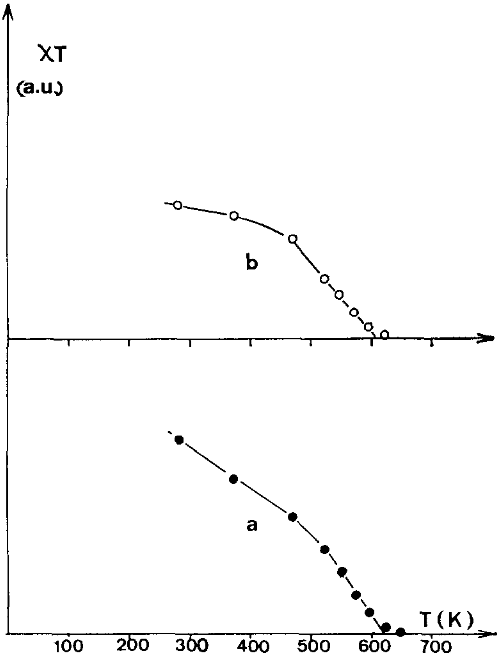

FIG. 2. Plot of χT vs T for the SiO_2–53 (a) and SiO_2–53–O (b) catalysts.

nearly constant, thus confirming the superparamagnetic character of these systems. For temperatures higher than 400 K, χT decreases linearly, affording Curie point determination at $\chi T = 0$. Figure 2 shows χT vs T plots for the SiO_2-53 catalyst either fully reduced (curve a) or after chemisorption of oxygen (sample SiO_2-53-O; curve b).

These data show that the Curie temperature of completely reduced nickel particles does not depend on particle size down to about 2.5 nm (probably even lower, as 2.5 nm is an average diameter) while the presence of divalent nickel ions strongly lowers the Curie point.

Similar conclusions are immediately arrived at by examining the thermomagnetic curves derived from FMR measurements.

Figure 3 shows plots of the relative intensity of the FMR signal, I/I_o, as a function of the reduced temperature $\theta = T/T_c$ (T_c = 631 K for bulk Ni^o) for the completely reduced $MgAl_2O_4$-1400, SiO_2-53, and SiO_2-25 catalysts. Such plots are, in principle, analogous to reduced magnetization vs reduced temperature graphs and hence it is not surprising that the variation observed for the large Ni particles ($MgAl_2O_4$-1400) follows rather nicely that predicted by the Brillouin formula valid for ferromagnets.

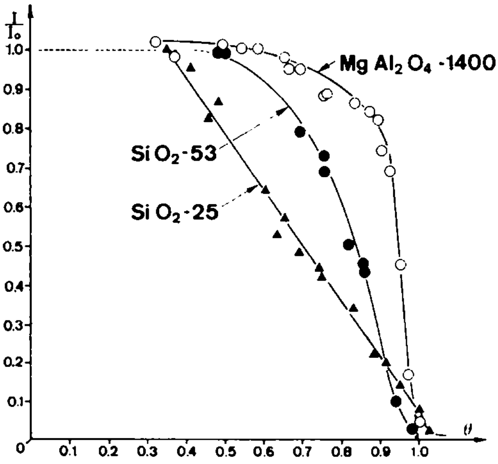

FIG. 3. Variation of the reduced FMR signal intensity (I/I_o) as a function of the reduced temperature ($\theta = T/631$) for the $MgAl_2O_4$-1400 (○), SiO_2-53 (●), and SiO_2-25 (▲) catalysts.

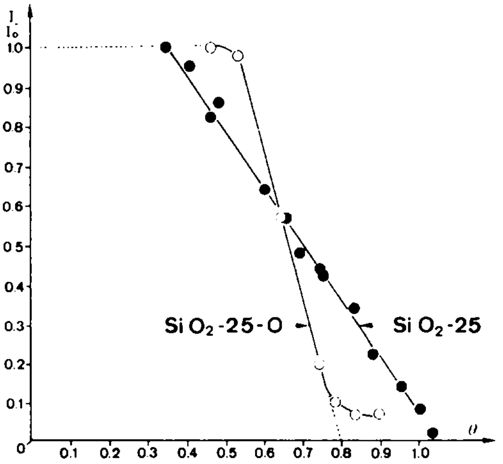

FIG. 4. Reduced FMR signal intensity (I/I_o) vs reduced temperature ($\theta = T/631$) for the SiO_2-25 (●) and SiO_2-25-O (○) catalysts.

Decreasing the particle size leads to superparamagnetism as is evidenced by the progressive modification of the intensity vs temperature graph. This point certainly deserves more attention and it will be dealt with in detail in another paper (*14*) in which other intrinsic features of the FMR signals (such as anisotropy, linewidth, etc.) will be used to derive more information on particle size, particle shape, and carrier effects.

Figure 4 shows the consequence of oxygen adsorption on the SiO_2-25 sample. It results most clearly in an important shift of T_c toward lower values.

Hence, both FMR and static magnetic measurements agree qualitatively and quantitatively on the following points which need to be discussed further.

First, and most important, Curie point shifts toward lower temperature are not observed to occur with decreasing Ni particle size (down to 2.5 nm) provided the catalysts are completely and carefully reduced.

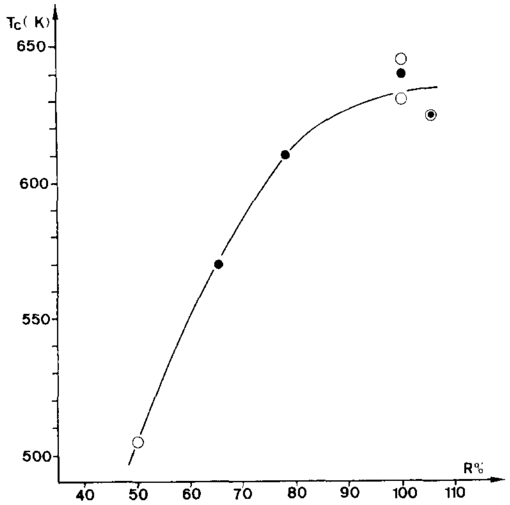

FIG. 5. Curie temperature T_c dependence on degree of reduction R. (●) Static magnetic measurements; (○) FMR data.

Second, Ni^{2+} ions (probably as NiO, resulting from incomplete reduction or from partial reoxidation following O_2 chemisorption) decrease very strongly the observed Curie temperature.

Third, very small (2.5 nm and below?) and completely reduced Ni particles seem to exhibit a Curie point slightly higher than the normal T_c of bulk Ni (631 K), as evidenced by the data shown in Table 1 and Figs. 1 and 3 (i.e., the high temperature "tail" for the SiO_2–25 catalyst). These statements will be discussed in the framework of the Weiss theory of ferromagnets.

If Z is the number of equivalent nearest neighbors, J is the Heisenberg exchange integral, β is the Bohr magneton, and N is the number of atoms per cubic centimeter, the Weiss molecular field is given by (*17*):

$$W = \frac{Z \cdot J}{4N\beta^2} \tag{3}$$

and

$$T_c = C \cdot W. \tag{4}$$

C being the classical Curie constant, one has $T_c \propto Z \cdot J$, which, for small particles, becomes

$$T_c \propto \langle Z \rangle \langle J \rangle \tag{5}$$

the brackets indicating average values calculated by taking into account surface effects which can alter both the coordination number and the exchange interaction.

Equation (5) clearly shows that T_c shifts should reflect changes in $\langle Z \rangle$ and $\langle J \rangle$. The coordination of surface atoms being lower than in the bulk, $\langle Z \rangle$ will decrease for smaller particles and hence T_c should normally decrease unless $\langle J \rangle$ increases, eventually because of structural reorganization in the smaller aggregates or geometrical relaxation of the surface layers.

Therefore, the increase of T_c with the degree of reduction R as shown in Fig. 5 could result from one or all of the following reasons.

First, magnetic coupling can certainly occur between the ferromagnetic Ni and the Ni^{2+}-containing antiferromagnetic phase. Such an effect has already been discussed for the system Co/CoO (*18*).

Second, the presence of Ni^{2+} ions will decouple or "individualize" neighboring Ni^0 atoms (*15*) of which the "metallic" coordination number will become smaller than the bulk value. Hence, this leads to a decrease in $\langle Z \rangle$. Similarly, surface oxidation leads to an effective metallic radius smaller than that of the unoxidized particle. As it will also prevent geometrical surface relaxation effects $\langle J \rangle$ remains constant and because of decreasing $\langle Z \rangle$, T_c should shift toward lower temperature. The surprising, but well-established, observation that well-reduced metal Ni particles down to about 2.5 nm in size exhibit no T_c shift toward low temperature (at least within experimental error) must be explained in this framework by a fortuitous compensation between $\langle Z \rangle$ (which decreases) and $\langle J \rangle$ (which then should increase) when the average particle diameter is decreasing.

As it is now rather well established that metallic particles only approximately 1 nm in size have electronic properties rather similar to those of bulk species (*19*), a pos-

TABLE 2

Comparison of Experimentally Observed and Calculated Curie Points

Sample	$\langle Z\rangle$	T_c	
		Experimental	Calculated[a]
MgAl$_2$O$_4$-1400	12	631	631
SiO$_2$-53	11.2	625	589
SiO$_2$-25	10.2	640-645	536
SiO$_2$-53-O	11.34[b]	610	596
SiO$_2$-24-O	10.95[c]	570	576
SiO$_2$-25-O	9.75[b]	505	513

[a] Assuming constant J value similar to bulk Ni.

[b] Average diameter is decreased by 0.5 nm upon O$_2$ adsorption (about one layer of oxide is formed) surface coordination $Z = 9$.

[c] Calculated value assuming that the effect of oxygen in the bulk (incomplete reduction) is identical to that of adsorbed oxygen after heating.

sible reason which we propose for the increase in $\langle J\rangle$ is the contribution of surface atoms (which increases with dispersion) and the effect of surface relaxation. It is well known, indeed, from LEED measurements (*20*), that, although upon cleavage no atomic reorganization occurs in the newly created surface plane, some relaxation takes place in a direction normal to the surface. It is our feeling that, because of the dependence of J upon the interatomic distance as illustrated by the Slater–Néel empirical curve (*21*), this could well lead to an increase of J in the surface layer of Ni particles.

This interpretation also accounts for the rather constant value of the saturation magnetization of Ni over a wide range of particle sizes (*11*) and for the most surprising fact that the degree of reduction R for small particles, as calculated from saturation magnetization measurements, sometimes exceeds 100%.

The former conclusions are most probably and qualitatively correct. To ascertain them on a more quantitative basis (although this can eventually involve some crude assumptions), we have evaluated $\langle Z\rangle$ values using the data from Table 1. The general assumption is that, while bulk Ni^0 atoms have a coordination number of 12, Z for surface close-packed atoms is equal to 9. Second, one layer of oxide is formed upon oxygen chemisorption and it reduces the average particle diameter by about 0.5 nm. Third, the effect of incomplete bulk reduction is supposed to be equivalent to that of the corresponding partial reoxidation as achieved after O$_2$ chemisorption and heating.

Table 2 summarizes these values and

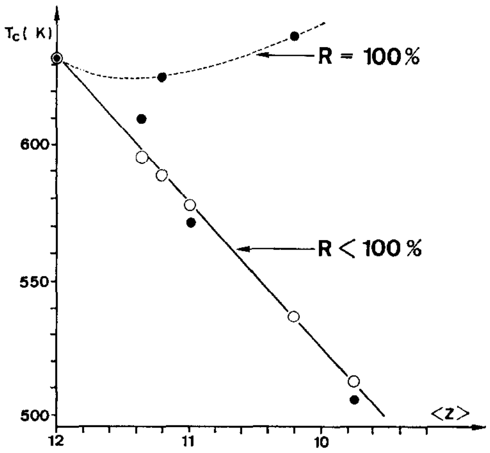

FIG. 6. Curie temperature T_c dependence as a function of the approximated average coordination number $\langle Z\rangle$. (○) Calculated values; (●) experimental values.

compares the calculated

$$T_c = (631/12)\langle Z\rangle$$

and experimentally observed Curie points. An unexpected good agreement (although, it still can be fortuitous in view of the approximations made) is observed for all the catalysts for which no surface relaxation, and therefore $\langle J\rangle$ value change, should occur. The fully reduced catalysts seem to fit a curve indicating an increase in J with smaller particle size, as evidenced by the difference between the calculated and experimental T_c values shown in Fig. 6. Hence, this would strongly support our previous qualitative conclusions regarding the relative effects of $\langle Z\rangle$ and $\langle J\rangle$.

In view of the former observations and suggestions, it is certainly possible to reconcile some of the contradictory facts presented in the Introduction. Namely, one should not expect any difference between the magnetic properties of Ni films evaporated under ultrahigh vacuum conditions and completely reduced Ni-supported particles, although there is the strong suggestion that contamination of the evaporated film will deeply affect the same properties. It is tempting to attribute the effects reported by Carter and Sinfelt (*2*, *3*) to incomplete reduction of their catalysts rather than to any particle size or direct carrier effect. Indeed, it has been reported recently (*22*) that the degree of reduction achieved under hydrogen for 12.6% Ni on silica catalysts is only about 40% at 643 K.

CONCLUSIONS

This work demonstrates without ambiguity the complementary and most powerful use of static magnetization and ferromagnetic resonance absorption measurements for the characterization of dispersed particles of ferromagnetic materials. It also emphasizes the need for an extensive characterization of the samples (catalysts) before undertaking any definite magnetic experiments or drawing any conclusions. This applies not only to the knowledge of particle size (distribution) but also to that of the degree of reduction of the metallic species.

It is certainly correct to state that the Curie point of dispersed Ni particles, down to about 2.5 nm, does not depend extensively on particle size, although there seems to be evidence for a slight increase in the case of very small Ni particles. The degree of bulk reduction and/or the chemisorption of oxygen is found to shift the Curie point strongly toward lower temperatures. Hence, the experimental determination of T_c, if it is found to agree with that of bulk Ni, can be considered as good evidence for a clean and well-reduced metallic Ni (surface and bulk).

Whenever Curie points lower than that of bulk Ni (631 K) are observed, partial reduction is most probably present and this raises some doubts concerning the validity of the interpretation of the previously reported results by Carter and Sinfelt (*2*–*4*).

Further work is in progress to use quantitatively some other features of the FMR spectra (such as resonance field and linewidth) to establish a more quantitative and solid basis for the relationship existing between the Curie point shift and the degree of reduction, and to gain firm evidence for a possible increase of the Curie temperature in very small particles. It is hoped that this can lead to first-hand and rapid techniques for particle size (distribution) and reduction degree determinations, obviously two major parameters in the characterization of supported metal catalysts.

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REFERENCES

1. Examples of such effects can be found in Derouane, E. G., and Lucas, A. A. (Eds.) "Electronic Structure and Reactivity of Metallic Surfaces." Plenum Press, New York, 1976.

2. Carter, J. L., and Sinfelt, J. H., "Magnetic Studies of Supported Nickel Catalysts. The Effect of the Support." First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, February 3–4, 1966.

3. Carter, J. L., and Sinfelt, J. H., *J. Phys. Chem.* **70**, 3003 (1966).

4. Carter, J. L., and Sinfelt, J. H., *J. Catal.* **10**, 134 (1968).

5. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Phys. Chem.* **70**, 2257 (1966).

6. Selwood, P. W., "Chemisorption and Magnetization." Academic Press, New York, 1975.

7. Bean, C. P., and Livingston, J. D., *J. Appl. Phys.* **30**, 126S (1959).

8. Bean, C. P., Livingston, J. D., and Rodbell, D. S., *J. Phys. Radium* **20**, 298 (1959).

9. Bean, C. P., and Livingston, J. D., *J. Appl. Phys.* **30**, 120S (1959).

10. Knappwost, A., and Illenberger, A., *Naturwissenschaften* **45**, 238 (1958).

11. Neugebauer, C. A., *Phys. Rev.* **116**, 1441 (1959).

12. See, for example, Boudart, M., Delbouille, A., Dumesic, J. A., Khammouma, S., and Topsøe, H., *J. Catal.* **37**, 486 (1975).

13. (a) Martin, G. A., Imelik, B., and Prettre, M., *J. Chim. Phys.* **66**, 1682 (1969); (b) de Montgolfier, P., Martin, G. A., and Dalmon, J. A., *J. Phys. Chem. Solids* **34**, 801 (1973).

14. Derouane, E. G., Simoens, A., Védrine, J. C., to be published.

15. Primet, M., Dalmon, J. A., and Martin, G. A., *J. Catal.* **46**, 25 (1977).

16. Martin, G. A., and Dalmon, J. A., to be published.

17. Herpin, A., "Théorie du Magnétisme," p. 241. Presses Universitaires de France, Paris, 1968.

18. Meiklejohn, W. H., and Bean, C. P., *Phys. Rev.* **102**, 1413 (1956).

19. Fripiat, J. G., Chow, K. T., Boudart, M., Diamond, J. B., and Johnson, K. H., *J. Mol. Catal.* **1**, 59 (1975).

20. Demuth, J. E., Marcus, P. M., and Jepsen, D. W., *Phys. Rev.* **B11**, 1460 (1975); see also Ref. (*1*), pp. 231 and 320.

21. See Ref. (*17*), p. 281.

22. Martin, G. A., Ceaphalan, N., de Montgolfier, Ph., and Imelik, B., *J. Chim. Phys.* **70**, 1422 (1973).