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The Paramagnetic Susceptibility of Supported Nickel

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The magnetic susceptibility of silica-supported nickel was investigated at temperatures above the normal Curie temperature of nickel, i.e., at temperatures where nickel behaves as a paramagnetic rather than a ferromagnetic substance. The paramagnetic behavior of the supported nickel was found to be significantly different from that of bulk nickel and to depend on the concentration of nickel on the support. The results show that the paramagnetic Curie temperature and the paramagnetic magneton number of the nickel decrease as the degree of dispersion of the nickel is increased. It is concluded that the electronic structure of nickel is a function of its state of dispersion. The effect is observed when the metal particles become sufficiently small that significant fractions of the atoms are present in the surface.

INTRODUCTION

Supported metal catalysts are typically characterized by a high degree of dispersion of the metal. Frequently, the metal crystallite size is of the order of 50 Å or less (*1–4*). In considering the nature of such highly dispersed metals, we are confronted with the question of how well they can be characterized by the properties of the metal in the massive form. As the degree of dispersion of the metal is increased, a point is eventually reached at which the small crystallites have almost all their atoms present in the surface. One might expect that the properties of such extremely small metal crystallites would be significantly different from those of the bulk metal.

In the case of supported nickel catalysts, magnetic studies have been applied by several groups of workers (*5–7*) to obtain information on the properties of the nickel. Such studies have been conducted at temperatures lower than the normal Curie point of bulk nickel, i.e., at temperatures where bulk nickel is ferromagnetic. The results have shown that highly dispersed, supported nickel, in contrast with bulk nickel, does not exhibit typical ferromagnetic behavior. Rather, the magnetization depends on field and temperature in a manner similar to paramagnetic substances. The phenomenon has been termed "superparamagnetism" (*8, 9*) or "collective paramagnetism" (*10*), and is associated with ferromagnetic substances in a highly divided form. In view of this interesting behavior of very small ferromagnetic particles, the question arises of the possibility that properties such as the atomic magnetic moment and the Curie point may be different for a ferromagnetic metal in such a state of subdivision. With regard to the magnetic moment, there appears to be no very firm evidence that it is significantly different from that of the metal in the bulk state. On the matter of the possible variation of Curie point with crystallite size, the situation is also not clear (ref. *10*, p. 36).

In an attempt to obtain further information on the points considered in the previous paragraph, it was decided to investigate the magnetic properties of highly dispersed nickel at temperatures above the Curie point of bulk nickel. Supported nickel catalysts do not appear to have been investigated in the paramagnetic region, although such studies have been reported for bulk nickel (*11*). It was felt that a study of this type could supply useful complementary information to previous investigations on nickel catalysts conducted in the ferromagnetic region. The present paper describes the results of such paramagnetic susceptibility measurements on supported nickel catalysts of varying nickel concentration and dispersion, and includes a comparison with measurements on bulk nickel.

EXPERIMENTAL SECTION

Apparatus and procedure. The magnetic measurements were made using the Faraday method in apparatus which has been described previously (*1, 12*). The sample was suspended from a Cahn electrobalance in a quartz bucket located midway between the pole faces of a Varian 4-inch magnet. The quartz bucket weighed 59.2 mg. The sample weight varied from 2.3 mg for the bulk nickel sample to 25 or 30 mg for the supported nickel samples. The samples were reduced in flowing hydrogen and evacuated to 10^{-6} torr *in situ*. The electrobalance measures the force, f, exerted by the magnetic field, H, on the sample. The magnetic susceptibility, χ, is determined from the relation

$$f = m\chi H dH/ds \qquad (1)$$

where m is the mass of sample, dH/ds is the field gradient, and s is the vertical distance from a horizontal reference line between the pole faces. Specially designed pole caps obtained from Varian Associates, Palo Alto, California, gave a constant value of HdH/ds over the region within which the sample was suspended. The apparatus was calibrated using ferrous ammonium sulfate hydrate, commonly known as Mohr's salt. Magnetic fields up to 6500 oersteds were attainable in the apparatus.

Prior to measurements of the magnetic susceptibility of the various nickel catalysts, the samples were reduced in flowing hydrogen overnight at 370°C and then evacuated. Some samples were sintered in vacuo at elevated temperatures after reduction. To correct for the diamagnetism of the quartz bucket and the silica support, blank measurements were made on the bucket and on the bucket plus silica over the whole range of temperatures and fields employed for the nickel samples.

Materials. The bulk nickel used in this work was a sample of Type 255 carbonyl nickel powder obtained from the International Nickel Co., Inc., New York, N. Y. The nickel is typically 99.7% to 99.9% pure. The average particle size is 2.6 to 3.4 microns and the apparent density 0.5 to 0.6 g/cc. The nickel-silica catalysts were prepared by impregnation of silica with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The silica employed was Cabosil HS-5 (surface area 340 m^2/gm), obtained from the Cabot Corp., Boston, Massachusetts. After impregnation, the catalysts were dried overnight at 105°C.

RESULTS

The magnetic susceptibility measurements were for the most part made at temperatures above the normal Curie temperature of bulk nickel, i.e., above about 355°C. Measurements were obtained on a series of silica-supported nickel samples of varying concentration. This provides a way of studying the effect of the state of dispersion of the nickel, since the dispersion improves with decreasing nickel concentration. In addition, some samples, after reduction in flowing hydrogen, were heated in vacuum at different temperatures to vary the particle size of the nickel. Finally, measurements were also made on a sample of unsupported, bulk nickel for comparison with the results on the silica-supported nickel. The bulk nickel represents a case of very poorly dispersed nickel, and serves as a reference point.

In determining the magnetic susceptibility of the nickel in the various samples, it is necessary to take account of the diamagnetism of the quartz bucket and of the silica support. The magnetic susceptibilities of the bucket and the support were found to be, respectively, -0.38×10^{-6} and -0.21×10^{-6} per gram. Over the temperature range employed, these values were constant to within ±1% and ±2.5%, respectively. The small temperature dependence was, nevertheless, taken into account in the corrections for the diamagnetism of the bucket and support. In the case of the 0.8% nickel on silica catalyst,

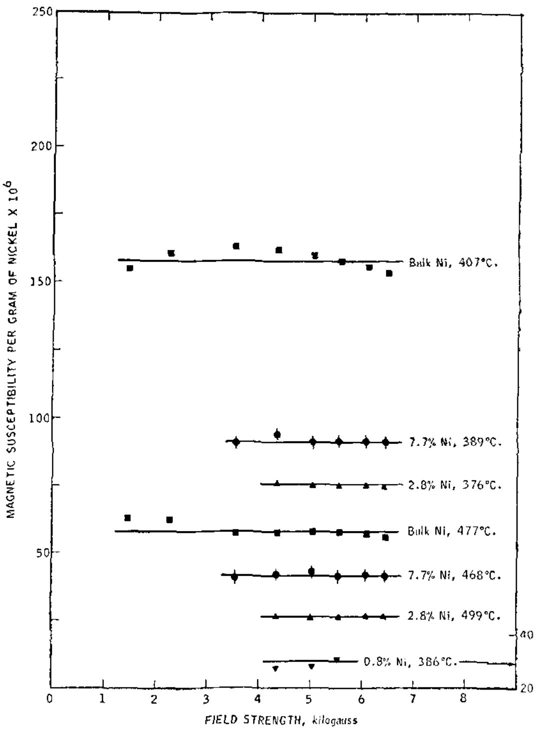

FIG. 1. Typical data on the magnetic susceptibility of silica-supported nickel and bulk nickel over a range of field strengths. Prior to magnetization measurements, the samples were evacuated at 500°C for 1 hr after overnight reduction in hydrogen at 370°C. The nickel concentrations of the silica-supported nickel samples, and the temperatures at which the susceptibilities were measured, are shown in the plot.

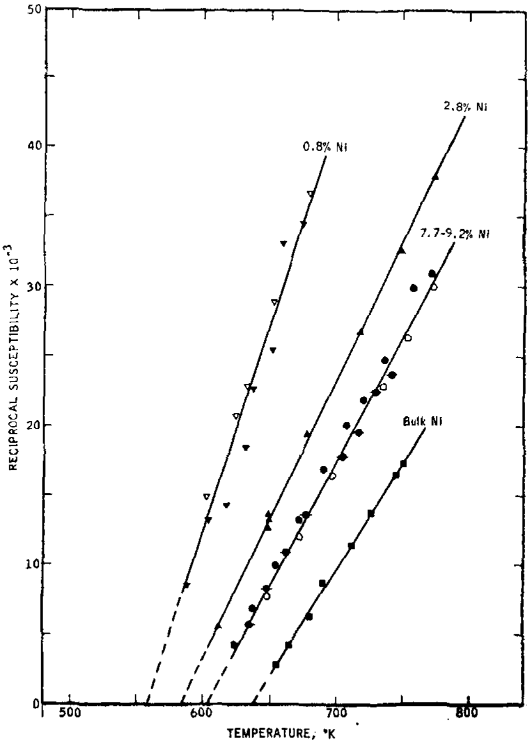

FIG. 2. Temperature dependence of the magnetic susceptibility of silica-supported nickel and bulk nickel. Prior to magnetization measurements, the samples were evacuated at 500°C for 1 hr after overnight reduction in hydrogen at 370°C: ■, bulk Ni; ▼, 0.8% Ni on SiO_2; ▲, 2.8% Ni on SiO_2; -♦-, 7.7% Ni on SiO_2; ●, 9.2% Ni on SiO_2. The points ▽ and ○ are, respectively, for 0.8% and 9.2% Ni on SiO_2 reduced for an additional hour at 500°C prior to evacuation.

the diamagnetism of the bucket and support was greater than the paramagnetism of the nickel, so that the overall response was diamagnetic. Nevertheless, even in this case the procedure of correcting for the diamagnetism of the bucket and support proved to be satisfactory for determining the paramagnetic susceptibility of the nickel. However, the data showed more scatter for the 0.8% nickel sample than for the higher nickel concentration samples.

The magnetic susceptibilities were determined over a range of field strengths. As expected, no significant variation with field strength was observed. Typical data for most of the samples are shown in Fig. 1. The data are representative of normal paramagnetic behavior in this respect. Figure 1 also shows the expected decrease in susceptibility with increasing temperature and indicates that the susceptibility of bulk nickel is different from that of silica-supported nickel. Furthermore, the data indicate that the susceptibility of the latter varies with nickel concentration. These points are shown more clearly in Fig. 2, in which the reciprocal of the magnetic susceptibility per gram of nickel is plotted as a function of the absolute temperature for a number of samples of silica-supported nickel and bulk nickel. The linear relation observed between the reciprocal of the susceptibility and the absolute temperature indicates that the data conform to the Curie-Weiss law,

$$\chi = C/(T - \theta) \tag{2}$$

where χ is the magnetic susceptibility, T is the absolute temperature, θ is the paramagnetic Curie temperature, and C is the Curie constant. The quantity θ is also known as the Weiss constant.

From Fig. 2 it is clear that significant differences exist between bulk nickel and the silica-supported nickel samples with regard to the magnitude of the magnetic susceptibility and the temperature dependence. The susceptibility of the silica-supported nickel is lower than that of bulk nickel and decreases with decreasing nickel concentration. Although the data on the 0.8% nickel sample in Fig. 2 have been treated on the basis that the relation between reciprocal susceptibility and temperature is linear, it is recognized that the evidence for a linear relation is less convincing than for the other samples. For the most part, the data in Fig. 2 are for samples reduced overnight in flowing hydrogen at 370°C, followed by evacuations for 1 hr at 500°C prior to the magnetization measurements. However, some data are also included for samples reduced in hydrogen for an additional hour at 500°C (after an initial overnight reduction at 370°C) prior to evacuation for 1 hr at 500°C. This difference in reduction procedure had no significant effect on the magnetic properties. The absence of an effect of increasing the reduction temperature to the level of the subsequent evacuation temperature indicates that the reduction is essentially complete at 370°C.

In Fig. 3 data are presented to show the effect of increasing the evacuation temperature for silica-supported nickel samples containing 0.8% and 7.7% nickel, all of which were reduced overnight in flowing hydrogen at 370°C prior to evacuation. Increasing the evacuation temperature provides a way of increasing the particle size of the nickel by sintering. The data show that increasing the evacuation temperature results in an increase in magnetic susceptibility and in a small change in the temperature dependence of the susceptibility. The effect of increasing the evacuation temperature, therefore, is to alter the nickel in a manner so that the magnetic properties approach more closely those of bulk nickel.

From the slopes of the lines in Figs. 2 and 3, values of the Curie constant in Eq. (2) can be evaluated, and from the intercepts on the temperature axis the paramagnetic Curie temperature can be obtained. From the Curie constant defined by Eq. (2), the magnetic moment μ can be calculated (*13*) from the relation,

$$C = N\mu^2/3k \tag{3}$$

where N is Avogadro's number and k is Boltzmann's constant. In calculating values of the moment from Eq. (3), the Curie constants derived from Figs. 2 and 3 must be multiplied by the atomic weight of nickel since the constant C in Eq. (3) refers to the value per mole. The magnetic moment

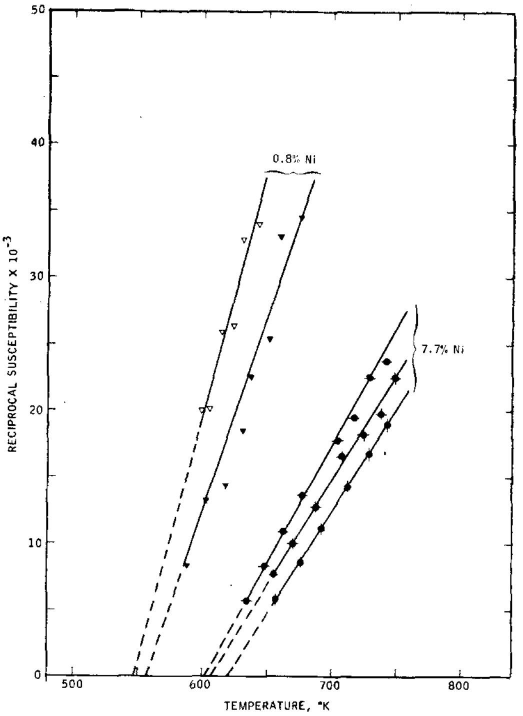

Fig. 3. Effect of sintering on the magnetic susceptibility of silica-supported nickel. The samples were first reduced in hydrogen overnight at 370°C and then evacuated for 1 hr at various temperatures prior to magnetization measurements: ▽, 0.8% Ni evacuated at 370°C; ▼, 0.8% Ni evacuated at 500°C; -●-, 7.7% Ni evacuated at 500°C; -ϕ-, 7.7% Ni evacuated at 800°C; ϕ, 7.7% Ni evacuated at 1000°C.

TABLE 1

Paramagnetic Curie Temperature and Magneton Number of Nickel as a Function of the State of Dispersion

Ni Conc. (wt %)	Evacuation temp.,[a] (°C)	Ni particle size,[b] (Å)	Paramagnetic Curie temp. (°K)	Paramagnetic magneton number
0.80	370	12	547	1.1
0.80	500	—	558	1.2
2.8	500	27	584	1.51
7.7, 9.2	500	—	603	1.60
7.7	800	65	608	1.69
7.7	1000	—	620	1.73
100 (bulk Ni)	500	2.6×10^4 [c]	638	1.73

[a] All samples evacuated for 1 hr at the temperature shown, subsequent to overnight reduction in hydrogen at 370°C.

[b] Determined from the field dependence of the magnetization at temperatures of 80° to 467°K.

[c] Estimated from gas adsorption data.

is conveniently expressed as the paramagnetic magneton number (in Bohr magnetons) by dividing by the quantity, 0.927×10^{-20}, which is the value of one Bohr magneton in erg/gauss. Values of the paramagnetic Curie temperature and paramagnetic magneton number for the various nickel samples investigated in this work are summarized in Table 1. It is important to note that the magnetic moment μ in Eq. (3) is different from the so-called "saturation moment." The latter is derived from magnetic measurements at very low temperature and high magnetic fields, at which conditions the magnetization approaches a saturation value.

Table 1 includes values of nickel particle size for some of the samples. In the case of bulk nickel the particle size was estimated from a room-temperature hydrogen chemisorption isotherm by a procedure described elsewhere (*12*). In the case of the silica-supported nickel samples, the nickel particle sizes were estimated from magnetic measurements at temperatures below the normal Curie temperature of nickel by a method involving data on the field dependence of the magnetization at low field strengths, as described in detail elsewhere (*1*). The average particle volume, $\bar{v}^2/\bar{v}$, is determined from the slope of a plot of magnetization M vs. field strength H at the origin. The slope is equal to $(\bar{v}^2/\bar{v})I_{SP}^2/3kT$, where I_{SP} is the spontaneous magnetization, k is Boltzmann's constant, and T is the absolute temperature. The average particle size is obtained simply as the cube root of the average particle volume.

Discussion

The results of the present work show that the paramagnetic behavior of highly dispersed, supported nickel is significantly different from that of bulk nickel. Furthermore, the magnetic properties vary with the concentration and dispersion of the nickel on the support. The differences in paramagnetic behavior are reflected in both the paramagnetic Curie temperature and the magneton number of the nickel.

As the degree of dispersion of the nickel is increased, the paramagnetic Curie temperature decreases. Previous workers (*6, 7*) have suggested that the Curie temperature depends on particle size, on the basis of the anomalous thermomagnetic curves observed for highly dispersed, supported nickel at temperatures below the normal Curie temperature of bulk nickel. The idea has a theoretical basis, in that the Heisenberg theory of ferromagnetism (ref. *13*, p. 475) leads to a relation in which the Curie temperature is proportional to the coordination number of the atoms in the metal lattice. It is clear that the atoms in the surface of a particle are incompletely coordinated, and if the particle size is decreased to a point where a significant fraction of the atoms is present in the surface, one can consider the atoms of such particles to have a lower average coordination number than the atoms of bulk metal. This in turn leads to the expectation that the Curie temperature depends on particle size. However, previous experimental studies of the ferromagnetic properties of small metal particles have led to varying conclusions on this point (*9*; *10*, pp. 36, 74). A distinguishing feature of the present study is that the conclusions regarding the effect of particle size were derived from an analysis of data on the paramagnetic susceptibility in terms of the Curie-Weiss law. The determination of the paramagnetic Curie temperature in this manner is a reasonable alternative to the determination of Curie temperatures from studies of the ferromagnetic behavior of small particles. There is the minor complication that studies on bulk ferromagnetic metals have indicated small differences in the Curie temperatures (15–20° for nickel) determined, on the one hand, from data on the temperature dependence of the spontaneous magnetization at temperatures below the Curie point, and, on the other hand, from data on the Curie-Weiss temperature dependence of the paramagnetic susceptibility above the Curie point. This has led to the adoption of two Curie temperatures, termed the "ferromagnetic" and "paramagnetic" Curie temperatures (ref. *13*, p. 471). However, this complication should present no major difficulty regarding conclusions on the effect of the degree of dispersion, since the Curie temperatures were determined consistently by the same method.

With regard to the magneton numbers derived from the susceptibility data, the lower values for the silica-supported nickel as compared to bulk nickel indicate differences in the electronic structures of the nickel atoms in these different forms. Directionally, the results indicate a lower number of unpaired electrons in atomic d orbitals (or in the d band) in the case of the silica-supported nickel. As the concentration of nickel on the silica is decreased, with the accompanying increase in the degree of dispersion of the nickel, the difference from bulk nickel becomes even more pronounced. It seems reasonable that this effect arises at least in part from differences in the electronic structures of surface atoms and atoms in the bulk. The effect would be expected to be significant when the particle size is decreased to a point where the surface atoms in the particle represent an appreciable fraction of the total, a situation which clearly exists for supported metal particles of the sizes employed in the present work. However, the possibility that the support itself influences the electronic structure of finely dispersed nickel, apart from particle size effects *per se,* can not be completely dismissed.

The indication that the electronic structure of supported nickel is different from that of bulk nickel, and in turn depends on the nickel concentration and state of dispersion, could have important implications in catalysis. It has previously been reported that the specific catalytic activity of supported nickel is a function of the chemical nature of the support and of nickel concentration on the support (*14*). Studies on sintered nickel catalysts also have presented striking evidence for the variation of specific activity with crystallite size (*12*). Although it is difficult to relate these catalytic phenomena in a detailed way to the results of the present work, there is at least an interesting parallel with respect to the effects of important catalyst variables such as the support, the metal concentration, and the degree of dispersion of the metal.

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