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Support Structure and Particle Size Influences on the Effect of Adsorbed Hydrogen on the Magnetization of Catalytically Active Nickel

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Saturation magnetizations have been obtained for small particles of catalytically active nickel supported on silica gel and on gamma-alumina. The measurements were made in fields up to 17 koe, and in the temperature range 2° to 300°K.

The saturation magnetization of nickel under these conditions appears to be independent of particle size over the radius range 13 to 58 Å as determined from low and high field magnetizations. There is no obvious effect on the saturation magnetization of changing the support from silica to alumina, although the absolute accuracy is poor owing to problems found in the chemical reducibility of the samples on alumina.

The effect of adsorbed hydrogen in lowering the saturation moment of the nickel was determined for all samples. All samples on silica gave about the same effect, regardless of particle size. A possible influence of the alumina was shown in a diminished effect of hydrogen on the magnetization of alumina-supported samples. This is attributed to the change of metal particle size, shape, and size-distribution when the carrier is changed.

INTRODUCTION

It has been shown previously (*1*) that chemisorbed hydrogen diminishes the saturation magnetization of nickel. For nickel particles of average radius 64 Å [as found from the low field magnetization (*2*)], supported by silica gel, the value of ϵ was found to be 0.71 ± 0.04 Bohr magnetons where ϵ was defined as follows:

$$\epsilon = (\Delta M_0/M_0)(\mu_{\mathrm{Ni}}N_{\mathrm{Ni}}/N_{\mathrm{H}}) \qquad (1)$$

$\Delta M_0/M_0$ being the fractional change of magnetization at 0°K and infinite field, μ_{Ni} the atomic (saturation) moment of nickel, and $N_{\mathrm{Ni}}/N_{\mathrm{H}}$ the relative number of nickel and hydrogen atoms present in the samples. The value of ϵ was found to be independent of surface coverage and of change of temperature subsequent to adsorption of the hydrogen.

The purpose of the present investigation was to determine if μ_{Ni} and especially ϵ are dependent on (a) nickel particle size, (b) nickel size distribution, and (c) a change of carrier from silica to alumina. Because of certain experimental difficulties encountered in the precise determination of μ_{Ni} (as described below), it was found expedient to define ϵ in terms of purely experimental quantities as follows:

$$\epsilon = \Delta M_0/N_{\mathrm{H}}$$

EXPERIMENTAL

Magnetic Measurements

The method for obtaining saturation magnetizations before and after admission of a measured volume of hydrogen was essentially that previously described (*1*),

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modified by the use of a 12-inch magnet with appropriate controlled power supply (*3*). Measurements were made from 2° to 300°K, in magnetic fields up to 17 koe.

Preparation of Samples

Four different preparations were used. These were chosen to obtain a range of average nickel particle size, and a comparison of silica vs. alumina as support. The designation used refers to the preparative method.

Nickel-silica coprecipitate. Boiling solutions of sodium silicate, sodium carbonate, and nickel nitrate were mixed as described by van Voorthuysen and Franzen (*5*). The gelatinous precipitate was washed, then dried at 100°C, and heated for several hours at 400°C. The product prior to reduction contained 48.0% nickel, and had a specific surface (BET, N_2) of 275 m^2. For the purposes of the magnetic measurements this sample was mixed mechanically with Davison silica gel, to obtain a sample containing 25.5% nickel.

Nickel-alumina impregnate. Gamma-alumina was prepared by the usual procedure of precipitation from an aluminate solution with carbon dioxide. The alumina had a specific surface of 281 m^2. This was impregnated with nickel nitrate solution to yield calcined products containing 13.5% and 20.7% nickel in two preparations. The final specific surface areas were 216 and 200 m^2, respectively.

Nickel-alumina sintered impregnate. Preparation was similar to that described above except that the 13.5% sample was heated in flowing hydrogen at 600°C for 5 hr, for the purpose of increasing the nickel particle size. This procedure lowered the specific surface to 175 m^2.

Nickel-silica impregnate. Davison silica gel (grade 950) of specific surface 501 m^2 was calcined at 400°C, then impregnated with nickel nitrate solution to yield a dried product containing 13.5% nickel, with a specific surface of 483 m^2.

General Procedure

Samples in the form of pressed pellets weighing about 1 g and being about ¼ inch in diameter were used for all measurements. The samples were reduced in flowing hydrogen at temperatures between 390° and 460°C for 15 to 120 hr. From time to time reduction was interrupted for evacuation. The samples were then allowed to cool to room temperature in a vacuum of about 10^{-6} mm mercury. A small quantity of helium was introduced to promote thermal equilibrium at lower temperatures. It was, however, found that the strong physical adsorption of helium on these high-area samples at liquid helium temperatures made it necessary to wait an extremely long time before the temperature of the sample became that of the bath. This difficulty, which is not often encountered in low temperature work, made it necessary to admit a considerably larger volume of helium than is normally necessary on samples of low specific surface. The difficulty became aggravated at temperatures below 4.2°K. As soon as the proper temperature had been reached, the magnetization of the sample was measured.

The sample was then warmed to room temperature, and a measured quantity of hydrogen was admitted. For all samples except the nickel-alumina sintered impregnate the volume of hydrogen adsorbed was 8 to 16 cc/g of nickel metal, corresponding to reasonably complete surface coverage. For the sintered sample the volume of hydrogen adsorbed was 3 to 6 cc/g nickel, also approaching complete coverage. The residual pressure in the dead-space was generally kept low to prevent anything more than a negligible physical sorption of hydrogen as the temperature was once more taken down to 4.2°K, after which the magnetization was measured again. But in some cases advantage was taken of the increased chemisorption which occurs down to about 77°K.

It was observed that a reduced sample could be kept in a 10^{-6} mm vacuum, with pumping, or alternatively in helium, at room temperature for 50 hr without showing any detectable decrease of magnetization. This freedom from progressive contamination is doubtless due to the very small external surface of the pellet which is directly exposed to the dead-space, as compared with the huge internal surface of the sample (*1*).

Chemical Reducibility and Magnetization of Small Nickel Particles

The volumes of the nickel particles in the several preparations described were such that all exhibited superparamagnetism (collective paramagnetism) over a wide range of H and T. The magnetization, M, of such an assembly is given by the Langevin function:

$$M = \int_0^\infty vI_{sp}\left[\coth\left(\frac{I_{sp}vH}{kT}\right) - \frac{kT}{I_{sp}vH}\right]n(v)dv \quad (2)$$

where I_{sp} is the spontaneous magnetization at temperature T, and v is the particle volume. The volume distribution is defined by

$$\int_0^\infty n(v)dv = N$$

where N is the total number of ferromagnetic particles in the sample. [This definition of the volume distribution is different from that previously used, and is presented in this way to facilitate the calculation of $\bar{v}$ from Eq. (4), below].

The low field approximation of Eq. (2) is given by:

$$\frac{M}{M_s} = \frac{\int_0^\infty I_{sp}{}^2v^2n(v)dv}{\int_0^\infty I_{sp}vn(v)dv}\cdot\frac{H}{3kT}$$

where M_s is the saturation magnetization at temperature T. If it is assumed that I_{sp} is independent of particle size, or that the particle-volume distribution is narrow, then:

$$\frac{M}{M_s} = \frac{I_{sp}H}{3kT}\cdot\frac{\overline{v^2}}{\bar{v}} \quad (3)$$

By using Eq. (3) it is possible to obtain an average value for the particle volume from the initial slope of the magnetization curve.

The high field approximation of Eq. (2) yields the analogous expression:

$$\frac{M}{M_s} = 1 - \frac{kT}{H}\frac{\int_0^\infty n(v)dv}{\int_0^\infty I_{sp}vn(v)dv}$$

which similarly reduces to:

$$\frac{M}{M_s} = 1 - \frac{kT}{I_{sp}H}\cdot\frac{1}{\bar{v}} \quad (4)$$

The several supported metal systems used all exhibit a range of particle volumes and, in such a case, some indication of volume distribution may be obtained through the use of Eqs. (3) and (4) because the initial magnetization is determined more by the larger (more easily magnetized) particles present, while the approach to saturation is determined chiefly by the smaller particles. If, for instance, the volume distribution is wide and may be considered to consist of two different particle sizes v_1 and v_2 such that $v_1 \gg v_2$, and with the total volume equally divided between the two size categories, then from the low field magnetization, [Eq. (3)]:

$$\overline{v^2}/\bar{v} \approx 0.5v_1$$

and from the high field magnetization [Eq. (4)]:

$$\bar{v} \approx 2v_2$$

The equations given above apply only to systems which exhibit superparamagnetic behavior as evidenced by superposition of MI_0/I_{sp} versus (H/T) (I_{sp}/I_0) where I_0 is the spontaneous magnetization (often designated M_0) at 0°K. But if the sample contains quite small particles, such a plot might show deviations at higher values of HI_{sp}/TI_0, where very small particles make a larger contribution to M, because there is some dependence of I_{sp} on particle size (*6*), and this dependence should become more pronounced at higher temperatures.

On the other hand, if the particles become larger than a certain critical size, anisotropy effects start to have an influence on the magnetization curve. This influence becomes the more pronounced the larger the particle size, the lower the temperature, and the smaller the magnetic field. The effect is to lower the magnetization values below those to be expected by applying the Langevin equations (*7*). The source of this anisotropy may possibly be found in the crystal structure—thus leading to an anisotropy of cubic symmetry in the case of nickel, or it may arise from the shape of the particles, or from stresses inside the particles. In addition to these, the free surfaces and their structure may impose a kind of surface anisotropy on the particles, if they are small enough.

Nickel-silica coprecipitate. Prior to the magnetization measurements on the reduced sample it was decided to make a few measurements at 4.2°K on the unreduced sample. Some recent experimental work on small particles of antiferromagnetic oxides (*8*), and calculations on the same subject (*9*), have shown that these substances may exhibit an unexpectedly high magnetization, which increases strongly with decreasing temperature and with decreasing particle size. In the range of very small particle sizes such systems show magnetic properties quite analogous to superparamagnetism. Néel proposes the name "superantiferromagnetism" for this kind of magnetic behavior.

The sample of nickel-silica coprecipitate, prior to reduction, did indeed show a high magnetization, which was even higher than that expected for the totally reduced sample. The unreduced sample also showed appreciable remanence at 4.2°K. Figure 1 shows the magnetization curves for this sample before and after evacuation at elevated temperature. The anomalous magnetization observed at 4.2°K in the unreduced sample is much diminished at liquid nitrogen temperature, and is extremely low at room temperature. While this phenomenon does not concern us directly, it may introduce a possible source of error in the saturation magnetization of incompletely reduced samples, as measured at 4.2°K.

It is interesting to note that, because of the effect described in the preceding paragraph, reduction of the sample leads to an increase of magnetization as measured at 77°K, and a decrease as measured at 4.2°K. There is no perceptible growth of nickel metal particle size during the reduction, provided that the temperature does not rise above about 430°C. But unless reduction is continued for a long time, the magnetization at 4.2°K remains higher than that corresponding to complete reduction of the nickel to metal. Figure 2 shows the magnetization after 120 hr of reduction at a temperature rising from 390° to 430°C, with occasional 2 hr interruptions for evacuation at 390°. After this prolonged

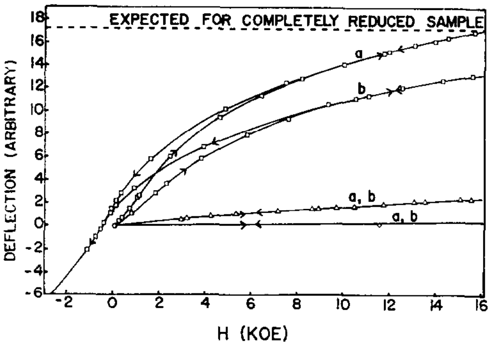

FIG. 1. Magnetization of nickel-silica coprecipitate as a function of field, prior to reduction but (a) after evacuation for 50 hr at 300°K, and (b) after further evacuation for 20 hr at 670°K. The temperatures are: ○, 297°K; △, 77°K; □, 4.2°K. The remanence observed at liq. He temperature, with decreasing field, is also shown. The remanence (M_r/M_s) was 1% at 297°; 22% at 77°; and 39% at 4.2°K.

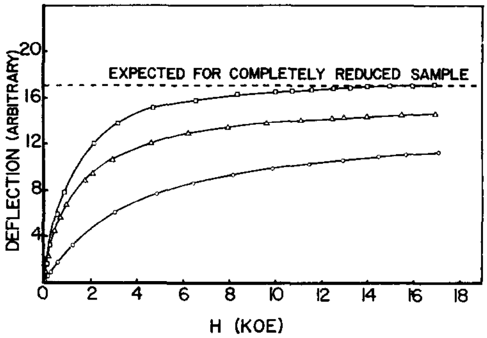

FIG. 2. Magnetization of reduced nickel-silica coprecipitate as a function of field. ○, 297°K; △, 77°K; □, 4.2° K.

treatment the magnetization at 77°K was near that expected for a sample scarcely contaminated by contributions from unreduced nickel.

Figure 3 shows the superposition test applied to the sample reduced as above. Data are given for the sample both with and without hydrogen adsorbed.

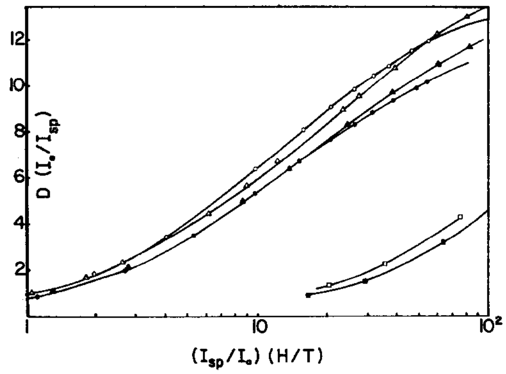

FIG. 3. Superposition test of magnetization (arb) for reduced nickel-silica coprecipitate, corrected for change of I_{sp} with T, against H/T. ○, 297°K; △, 77°K; □, 4.2°K. Open symbols refer to bare metal; filled symbols (●, ▲, ■) to the sample covered in part with adsorbed hydrogen, at the corresponding temperatures.

While the data at 297° and 77°K, with H_2 adsorbed, superimpose well at lower H/T values, the corresponding curves without H_2 show deviations as previously reported for similar samples by Dietz, and attributed by him to a decrease of anisotropy caused by the presence of the hydrogen. This effect is further shown by the fact that adsorbed H_2 causes an increase of low field magnetization at 4.2°K, but a decrease at higher fields. The deviation at high values of HI_{sp}/TI_0 is probably due to the effect of particle size on I_{sp}, as already mentioned.

The particle radius calculated from the initial slopes of the 297° and 77°K magnetization curves is 23 Å. The average particle radius derived from the final slope of the extrapolated magnetization curve at 77°K is about 15 Å, indicating the presence of particles even smaller than this average value.

Nickel-alumina impregnate. The reduction of these samples was even more difficult than that of the coprecipitated sample on silica. Very long reduction times and a temperature of about 450°C were necessary to obtain a high degree of reduction. It was found again that the unreduced samples showed a substantial magnetization at 4.2°K, but the magnetization at 4.2°K did not exceed that corresponding to complete reduction, as was the case for the nickel-silica coprecipitate. The remanence shown by the alumina-supported sample was also less.

The purposes of this work did not include a study of the unreduced phases present in the several supported systems. But, in view of the strong low-temperature ortho–para hydrogen conversion activity shown by a supported nickel-alumina catalyst (*10*), it was decided to make a brief study of a 5% nickel sample prepared on alumina by the technique of multiple, successive impregnations. This sample showed a linear increase of magnetization with increasing field at 4.2°K, and this was virtually unchanged by reduction at 420°C for 60 hr. Such a sample is, apparently, irreducible to metal at the temperatures employed. (The high catalytic activity of such a preparation is more probably attributable to more or less isolated Ni^{2+} ions built into the alumina surface, and lacking the usual coordination which normally leads to the Ni^{3+} state on the surface of nickel oxide.)

Figure 4 shows the superposition of M versus H/T at 4.2°, 77°, and 297°K for the standard sample. At the two higher temperatures the superposition is satisfactory, although there is a very small remanence at 77°K. The particle radius derived from the initial slope is 26 Å, while that from the final slope is about 13 Å. The highest degree of reduction, as estimated from the magnetization at liquid nitrogen temperature, was 75 to 80%. At this temperature the magnetization was not greatly influenced by the contribution from unreduced nickel.

Nickel-alumina sintered impregnate. This sample reached a final magnetization, cor-

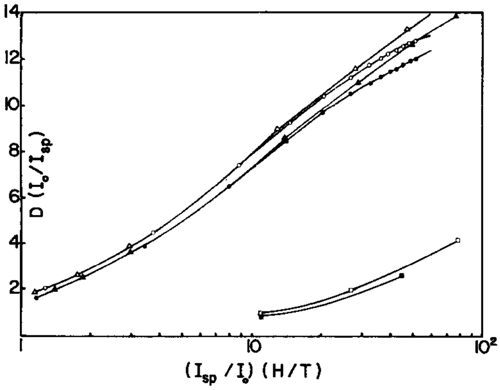

FIG. 4. Superposition test for reduced nickel-alumina impregnate. ○, 297°K; △, 77°K; □, 4.2°K. ●, ▲, ■, same with adsorbed H_2.

responding to 85 to 90% reduction, after 20 hr in flowing hydrogen at 400°C. This treatment was, of course, subsequent to the previous heating in hydrogen at considerably higher temperature, for the deliberate purpose of increasing the particle volume. The particles of nickel so formed were no longer superparamagnetic below room temperature. The apparent radius derived from the low field magnetization curve was 58 Å. The magnetization curves are shown in Fig. 5. A large remanence was present at 4.2° and 77°K. This sample, and all other samples of nickel on alumina, must contain an appreciable fraction of extremely small unreduced nickel particles, down to isolated Ni^{2+} ions. These are apparently not reducible under the applied conditions, and this view is supported by the experience with the sample containing 5% nickel, prepared by multiple impregnation, mentioned above.

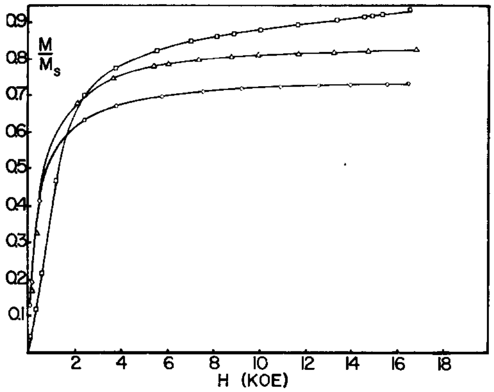

FIG. 5. Virgin magnetization of reduced nickel-alumina sintered impregnate. ○, 297°K; △, 77°K; □, 4.2°K.

Nickel-silica impregnate. The reduction of this sample was comparable with that of the sintered nickel-alumina impregnate. There was an appreciable remanence at 4.2° and 77°K. Superposition of M vs. H/T data was not good over the range 77° and 297°K but, once more, it was improved by the adsorption of hydrogen. Figure 6 shows magnetization curves at several temperatures for the reduced sample. Owing to the larger particle size, the magnetization of the unreduced sample was much smaller than that of the unreduced nickel-silica coprecipitate. The low field radius was 44 Å. The estimated degree of reduction was better than 95%.

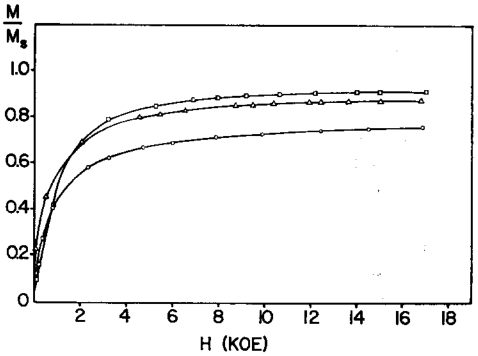

FIG. 6. Magnetization of reduced nickel-silica impregnate. ○, 297°K; △, 77°K; □, 4.2°K.

RESULTS

The several complications mentioned in the previous section make it difficult to obtain accurate data for μ_{Ni}. The results for ϵ appear, however, to be accurate within about ±10%. One source of the inaccuracy of μ_{Ni} is given by the unknown degree of reduction of the systems. Some information about this may be obtained by the difference between the extrapolations of the relative magnetization vs. $1/H$ to $1/H = 0$ at 77° and 4.2°K, because the observed magnetization at 4.2°K may contain contributions from unreduced nickel, while the magnetization at 77°K is only slightly influenced by those factors, as shown in Fig. 1.

A second source diminishing the precision of μ_{Ni} is the uncertainty of extrapolation in those cases where anisotropy effects have an influence on the magnetization, and this is true for all systems described, at 4.2°K. Under these circumstances, the $1/H$ extrapolation, which is valid only for true superparamagnetic systems, will lead to saturation values which are too high. A contribution due to a $1/H^2$ term, taking anisotropy influences into account, may also have to be considered (7). The maximum error imposed on μ_{Ni} by the $1/H$ extrapolation is estimated to be about 2 to 3%, by which the extrapolated saturation magnetization may be too high.

The first factor mentioned above is of greater importance than the latter one for the nickel-silica coprecipitate, and the nickel-alumina impregnate catalysts.

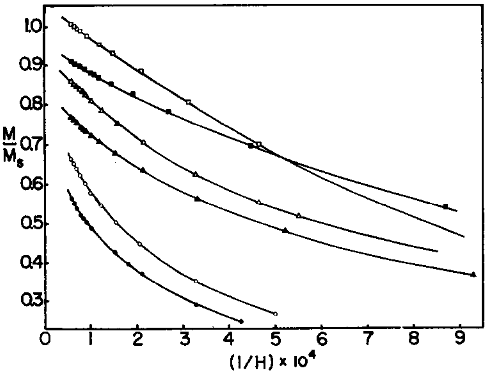

FIG. 7. Approach to saturation magnetization for reduced nickel-silica coprecipitate without (○, △, □), and with (●, ▲, ■), 15.7 cm^3 adsorbed H_2/g Ni, at 297°, 77°, and 4.2°K, respectively.

Nickel-silica coprecipitate. Figure 7 shows magnetization curves in a plot of M/M_s vs. $1/H$, both with and without adsorbed hydrogen. At 4.2°K the presence of chemisorbed hydrogen causes an increase of magnetization in fields up to 2 koe. The reversal in the sign of the effect caused by adsorbed hydrogen is doubtless related to anisotropy effects and, as previously observed, the anisotropy is diminished by the presence of the adsorbed gas. This is indicated by a decrease of remanence from $M_r/M_s = 0.20$ to 0.14. In the low-field region this anisotropy effect is larger than the normal loss of magnetization caused by adsorbed hydrogen, and the effect is not negligible at higher fields. The appreciable change in anisotropy caused by adsorption of hydrogen cannot be explained by the concept of a smaller effective particle size caused by the loss of magnetization due to chemisorption of hydrogen alone. The sensitiveness of the anisotropy change to changes on the particle surface (caused by the chemisorption of hydrogen) suggests that surface anisotropy may be involved. The steeper slope of the extrapolation for the case without adsorbed hydrogen, compared to that with adsorbed hydrogen, at 4.2°K in Fig. 7 shows the strong anisotropy influence even at high field strength.

In view of the above it is probably better to use the magnetic data at 77°K for the calculation of ϵ where the extrapolations to infinite fields are parallel, indicating true superparamagnetic behavior at high field strength. One finds, however, that calculating ϵ from the differences of magnetization at the highest available field, gives about the same numerical value at 4.2°, 77°, and 297°K. This somewhat surprising result is true for all samples described. It will be noted nevertheless in Fig. 7 that the difference in magnetization at 77° and 297°K is quite large, thus indicating a substantial fraction of the nickel to be in quite small particles.

The collected ϵ values for all samples at several degrees of surface coverage with hydrogen are shown in Table 1, the average value for the nickel-silica coprecipitate being 0.67 Bohr magnetons.

Nickel-alumina impregnate. A comparison of Fig. 7 with Fig. 8 shows the similarity between the magnetization curves at 77° and 297°K; but at 4.2°K the magnetization is quite different. Both curves contain contributions from unreduced nickel, but with the difference that these

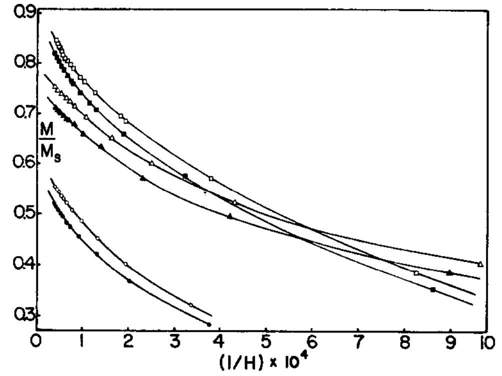

FIG. 8. Approach to saturation magnetization for reduced, nickel-alumina impregnate without (○, △, □), and with (●, ▲, ■), 15.0 cm² adsorbed H_2/g Ni, at 297°, 77°, and 4.2°K, respectively.

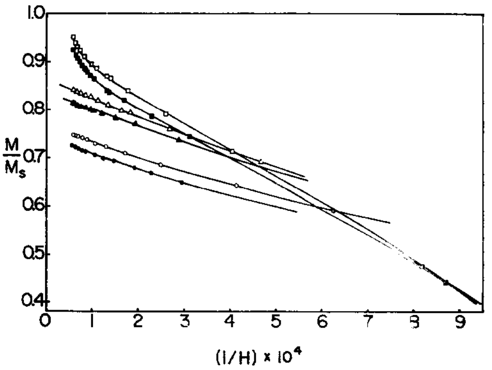

FIG. 9. Approach to saturation magnetization for reduced nickel-alumina sintered impregnate without (○, △, □) and with (●, ▲, ■), 6.3 cm² adsorbed H_2/g Ni, at 297°, 77°, and 4.2°K, respectively.

contributions are small at low fields and large at high fields for the alumina-supported sample, corresponding to the shape of the magnetization curve at 4.2°K for the nickel-alumina sample prior to reduction. Another difference is that in the alumina-supported sample the anisotropy is not changed to a large extent by the adsorption of hydrogen. The magnetization curves at 4.2°K do not cross at any field strength down to 100 oe, the remanence is 0.25 M_s at this temperature, and it is decreased just slightly by the presence of adsorbed hydrogen. The average ϵ for this sample is only $0.35 \pm 0.0_7\,\beta$ and, again, the same value may be derived from the magnetization curves at 4.2° and 297°K.

Nickel-alumina impregnate sintered. Figure 9 shows that the sintering process has made a marked change in the magnetic properties of the nickel. The magnetization of the nickel is larger, and especially so at the higher temperatures. The ϵ value has increased to $0.65 \pm 0.1\,\beta$, and the shape of the magnetization curves show that they are strongly influenced by anisotropy factors up to 77°K. At 4.2°K the remanence is 0.4 M_s, and even at 77°K $M_r = 0.2$ M_s, both values being only slightly influenced by the presence of adsorbed hydrogen.

Nickel-silica impregnate. Although the nickel particle size in this system is smaller than that in the sample discussed immediately above, the influence of anisotropy effects on the magnetization is still large. For instance M_r/M_s at 4.2°, 77°, and 297°K is 0.3, 0.1, and 0.01, respectively. The average ϵ value was found to be $0.55 \pm 0.1\,\beta$.

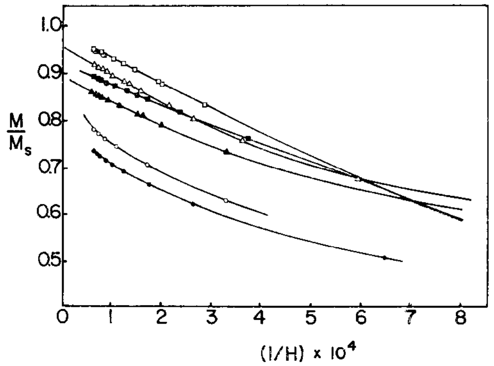

FIG. 10. Approach to saturation magnetization for reduced nickel-silica impregnate without (○, △, □), and with (●, ▲, ■) 13.3 cm³ adsorbed H_2/g Ni, at 297°, 77°, and 4.2°K, respectively.

DISCUSSION

The problems to be considered are (1) the origin of ϵ, (2) the influence of particle size, and (3) the influence of the catalyst support.

TABLE 1

Summary of ϵ Values for All Samples

Sample	Ni (%)	Low field radius (Å)	High field radius (Å)	H_2 ads. (cc/g Ni)	ϵ (β)
Ni-SiO_2 coppt.	25.5	23	~15	8.2	0.66
				10.0	.67
				14.8	.68
Ni-Al_2O_3 impreg.	13.5	26	~13	7.7	.30
				14.2	.32
				14.4	.37
Ni-Al_2O_3 impreg. sint.	13.5	58	—	3.0	.67
				4.1	.77
				5.4	.58
Ni-SiO_2 impreg.	13.5	44	—	10.7	.58
				13.3	.51
				16.2	.62

The present status of electron distribution in transition metals is so confused (*11*) that a discussion concerning the origin of ϵ can be little more than speculative. Following the suggestion of Grimley (*12*), it may be thought that the adsorption of a single hydrogen atom on a metal surface will create additional energy levels for the system, and that these levels may be situated either outside the metallic bands, as localized states, or within them. Which kind of states are created will depend largely on the kind of interaction between the hydrogen and the metal. Below a critical distance the bond will be essentially metallic (*13*)—leading to nonlocalized states within the metallic band. Above the critical distance the bond may be described as mostly covalent (*13*)—leading to localized states outside the metallic bands. If a large number (N_H) of hydrogen atoms is covalently attached to the metal surface, a band of N_H localized states is to be expected (the N_H degenerate level is split into N_H sublevels by interaction between the hydrogen atoms taking place through the metal crystal). This band may or may not overlap the normal metal band. Reducing the distance between the hydrogen atom and the metal surface atom reduces the number of levels in the above surface band to N; the remaining $N_H - N$ levels being nonlocalized states in the metallic band corresponding to a larger metallic character of the hydrogen–metal bond.

Unfortunately, there are no available experimental data about the hydrides of iron, cobalt, or nickel, which could give information concerning the kind of bonding in these systems. The best value for ϵ obtained, namely $0.67\,\beta$, suggests that about ⅓ of the levels created by the hydrogen sorption process are located in the energy region of the metallic band—the remaining electrons being used to fill localized states in the narrow *d*-band, which is responsible for the magnetism of the metal. Thus the magnetic moment of the nickel is lowered by $\frac{2}{3}\beta$ for every hydrogen atom chemisorbed. There is no obvious reason why the type of bonding should change very much in going from nickel to cobalt or iron as adsorbent, hence ϵ may be expected to be about the same for all three systems, namely Ni–H, Co–H, and Fe–H. Results previously obtained (*3*) on the cobalt-hydrogen system suggest that this view is correct. Furthermore, the view that the chemisorption of hydrogen has an influence not only on the localized *d*-band of the metal adsorbent (which is the only band accessible to the magnetic measurements), but also on other bands has been shown by Lewis (*14*). X-ray K absorption edge studies showed that the chemisorption of hydrogen on nickel caused a lowering of the *sp* hybridization of the nickel; the *p*-character of the *s*-band is diminished; that of the *p*-band is increased.

The second problem to be discussed is the possible influence of particle size on ϵ. That such an influence may exist is shown by the results of Yates and Garland (*15*) on the infrared absorption spectrum of carbon monoxide adsorbed on supported nickel. But Table 1 shows that, at least on silica as support, there is no obvious effect of nickel particle size over the range 23 to 44 Å radius, and previously reported (*1*) results on even larger nickel particles supported by silica gave about the same value for ϵ. We are probably justified in saying that, for nickel supported on silica, over the range of diameters normally encountered in catalytic practice, there is no important change of ϵ which could account for catalyst specificity.

The third and last problem which might have some connection with the second one, is the possible influence of the chemical or the electronic structure of the carrier on the magnetic behavior, or the structure, of the supported nickel, and on its behavior towards adsorbed gases. This is a problem which has been much debated as being related to catalyst specificity. For instance, Eischens and co-workers (*16*) have observed differences in the infrared absorption spectrum of carbon monoxide adsorbed on silica-supported platinum versus alumina-supported platinum. It is not certain whether the infrared results may be complicated by large differences in particle size between the two samples but, be that as it may, the magnetic data in Table 1 appear to show a clear example of support influence in changing the value of ϵ. The larger particles of alumina-supported nickel (as in the sintered sample) have the same value of ϵ as do all silica-supported samples, regardless of particle size. The alumina-supported catalyst containing small nickel particles yields, however, an ϵ only about half of that observed on all other samples studied. A possible reason for this low value may be seen in the electronic properties of the support, changing the electron distribution in the nickel band by the extensive contact between the small metal particles and the carrier. It is doubtful if such an electronic effect could explain the large change of ϵ. Furthermore, it would be difficult to explain the "normal" ϵ value for the sintered alumina-supported catalyst. Even when taking the larger particle size, and for this reason less extensive metal-support contact into account, one would still expect some influence on ϵ.

An alternative, more probable, explanation may be based on the structural properties of the carrier as it influences the particle size, the particle shape, and the particle size distribution of the attached nickel, and a possible chemical interaction in the interfaces between the carrier and the metal.

For instance, Adler and Keavney (*17*) have derived from hydrogen adsorption studies on platinum-alumina catalysts that samples prepared by impregnation probably contain the platinum as very thin layers covering large parts of the alumina surface, with an appreciable fraction of the metal having extremely small dimensions. Co-gelled platinum-alumina preparations (comparable to coprecipitation samples) contain the metal as nearly spherical particles of more uniform size.

This would mean for the problem presented above that the low value for ϵ is caused by a fraction of extremely small nickel particles (down to isolated Ni^{2+} ions, which cannot be reduced under the experimental conditions) in a size range where the metal might start losing its bulk metallic and magnetic properties.

This view is supported by the following observations on the specific surfaces of the silica and the alumina used as carriers for the samples designated nickel-alumina impregnate, and nickel-silica impregnate. The alumina originally had a specific surface of 281 m^2 and this fell to 216 m^2 in the finished catalyst, or a loss of 482 m^2/g of nickel added. By contrast, the silica originally had a specific surface of 501 m^2 and this fell to 483 m^2, or a loss of only 126 m^2/g of nickel added.

The large relative decrease of the alumina surface can only be explained by assuming that the alumina surface itself is diminished by the impregnation process, with thin nickel layers or very small nickel particles filling out pores or surface holes and defects of the carrier. The smaller decrease of the silica surface area by the impregnation can be explained by the picture of spherical silica particles mixed with nickel particles of the same shape.

If the second explanation presented is true, the low ϵ value for the nickel-alumina sample is caused by a large fraction of extremely small metal particles present in the catalyst. These are obviously removed by the sintering process at 600°C, by particle growth, thus leading to the "normal" ϵ value. This would mean that the support influence on ϵ is indirect, consisting merely in imposing certain structural properties upon the supported metal, and thus suggesting that the particle sizes, together with their distribution, are the important factors changing the magnitude of ϵ.

Some further remarks with respect to these factors and to questions of particle size distribution are briefly discussed in the Appendix.

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Appendix

Some information about the distribution of particle sizes was obtained from $\overline{v^2}/\bar{v}$ and $\bar{v}$ as calculated from the initial (*1*) and final (*3*) slopes of the magnetization curves.

A more rigorous method would, however, be a curve-fitting experiment with the help of a computer. Feeding observed M/M_s versus $X = I_{sp}\ H/kT$ data into the computer, and comparing the requested power series:

$$M/M_s = \sum_{n=1}^{(\infty)} D_n X^{2n-1}(-1)^{n+1}$$

with that theoretically derived, one should be able to obtain details about the width and shape of the particle size distribution.

Under the basic assumption of superparamagnetic behavior, and I_{sp} being independent of particle size, the magnetization of an assembly of fine ferromagnetic particles may be described by:

$$M/M_s = 1/V_0 \int_0^\infty (\coth X \cdot v - 1/X \cdot v)v \cdot n(v)dv$$

Expanding the hyperbolic cot into a series, one finally obtains:

$$M/M_s = \sum_{n=1}^{(\infty)} A_n X^{2n-1} \cdot \overline{v^{2n}}/\bar{v}(-1)^{n+1}$$

where

$$An = 2^{2n}/2n!\ B_n$$

B_n being the Bernoulli coefficient; and

$$\overline{v^m} = \frac{\int_0^\infty v^m n(v)}{\int_0^\infty n(v)} \frac{dv}{dv}$$

Relating the corresponding coefficients of the two series to each other one obtains:

$$\overline{v^{2n}}/\bar{v} = D_n/A_n$$

Comparison of $\overline{v^{2n}}/\bar{v}$ for various particle distributions with D_n/A_n will give the desired information about the particle distribution.

Other sources of information are magnetization measurements on systems with and without hydrogen adsorbed, as performed with the ac induction apparatus at low fields and with the dc assembly under saturation conditions on the same type of catalyst. Dietz and Selwood (*1*) calculated the low field magnetization as influenced by the chemisorption of hydrogen:

$$\frac{\Delta M}{M} = -\alpha \frac{\Delta M_0}{M_0} = -\alpha \frac{\epsilon N_{\mathrm{H}}}{\mu_{\mathrm{Ni}} N_{\mathrm{Ni}}}$$

where

$$\alpha = 2 \frac{\overline{v^{5/3}}\bar{v}}{\overline{v^{2/3}}\,\overline{v^{2}}}$$

is merely a function of the particle size distribution. With the help of ϵ as determined by the high field experiments described in this paper, α is now easily obtained from the ac data.

Table 2 contains α-values for various particle distributions. It will be noted that α is always $\leqslant 2$, being smaller the wider the distribution and greater the percentage of small particles present in the sample. The limiting value of 2 is reached if the particles are uniform in size.

Recent measurements on nickel-silica coprecipitate catalysts by Zwietering and co-workers (*18*), with the low field apparatus yielded a value of

$$\frac{\Delta M}{M} \Big/ \frac{N_{\mathrm{H}}}{N_{\mathrm{Ni}}} = -2.0_2$$

which is very close to that which may be calculated from the initial magnetization of the dc measurements applied in this work for the same catalyst. With $\epsilon = 0.67\beta$ (Table 1) one finds α equal to 1.81, which value suggests a distribution of Maxwellian shape (Table 2).

TABLE 2

VALUES OF α FOR SEVERAL ASSUMED PARTICLE SIZE DISTRIBUTION FUNCTIONS

Particle distribution[a]	α
Uniform particle size	2.00
$n(v) = av^2 \cdot e^{-bv^2}$	1.91
$n(v) = C$ (infinitely wide rectangle)	1.88
$n(v) = aV \cdot e^{-bv}$	1.78
$n(r) = ar^2 \cdot e^{-br^2}$	1.66
$n(v) = C/v$ (distribution assumed by Becker, ref. *2*)	1.60
$n(r) = are^{-br}$	1.14

[a] Dietz and Selwood (*1*) collected α values for a differently defined function $f(v)[f(v) \sim vn(v)]$. The α value for the Maxwellian distribution of volumes in the cited paper is wrong and should be replaced by 1.867.

If the low ϵ value for the nickel-alumina preparation (Table 1) is caused by a peculiar particle distribution, such as the presence of a higher percentage of very small particles, hints should be found in the magnitude of α. Unfortunately no ac induction measurements on this kind of catalyst have been performed as yet.

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