JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 78 FEBRUARY 22, 1956 NUMBER 4

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Influence of Chemisorbed Gases on the Magnetization of Catalytically Active Nickel[1]

BY LOUISE E. MOORE AND P. W. SELWOOD

RECEIVED AUGUST 19, 1955

Thermomagnetic measurements have been used to study chemisorption on nickel–silica catalysts. Nitrous oxide, oxygen and carbon monoxide increase the magnetization of this highly dispersed nickel at room temperature. Water vapor and hydrogen decrease it. The results have been interpreted in terms of electron interaction between nickel and adsorbate. The interpretation for hydrogen is dependent on nickel particle size. Desorption of hydrogen in flowing helium was followed by determining the increase in magnetization with time. The effects of sintering the nickel, and of changing the temperature of chemisorption, also were studied.

Introduction

Michel, Bernier and LeClerc,[2] and Selwood, Adler and Phillips,[3] have reported anomalous thermomagnetic curves for highly dispersed nickel. These curves show no sharp Curie point and have been interpreted as being due to a distribution of nickel particle sizes. Selwood, Adler and Phillips have calculated particle size distribution curves for nickel supported on silica, assuming a linear relationship between coördination number and apparent Curie point. Heukelom, Broeder and van Reijen[4] have attributed the relatively low magnetization of such samples at room temperature to incomplete magnetic saturation of the small nickel particles. A discussion of the effect of incomplete magnetic saturation on the apparent particle size distributions obtained for samples of nickel on silica is given by Sabatka and Selwood.[1]

The nickel particles in catalysts of this type are small enough to show appreciable changes of electron density in the presence of chemisorbed molecules. This effect[3,5] is observed as a fractional change of magnetic moment of the nickel. The present paper describes further exploratory work on the effects of several gases chemisorbed on nickel–silica, and shows that, in favorable cases, the change of magnetic moment may be correlated with the quantity of chemisorbed gas.

Experimental

Magnetic measurements were made on a modified Faraday balance previously described.[1]

The nickel silicate gel was prepared by the method described by van Eijk Van Voorthuijsen and Franzen[6] for their catalyst CLA-5421. The gel is made by mixing boiling solutions of sodium silicate (basic) and nickel nitrate. The gel was washed, dried and powdered. It is referred to here as the "coprecipitate."

The nickel content of the coprecipitate was determined electrolytically. The two samples used contained 26.2 and 42.4% nickel before reduction. They were prepared by changing the concentration of the sodium hydroxide in the sodium silicate solution.

Each sample described in this paper was reduced for 24 hours at 350°. Some samples were, in addition, sintered as described below. Complete thermomagnetic curves were determined in purified helium. Values of the magnetization were also determined in flowing hydrogen from 625 to 77°K., and in helium containing a trace of hydrogen at 20°K. The helium and hydrogen were purified by removal of oxygen over hot copper, and of water vapor over silica gel at $-190°$. Water vapor, nitrous oxide, carbon monoxide and oxygen were carried in a helium stream for the chemisorption measurements involving these gases.

Results

The magnetic data given below are expressed as reduced specific magnetizations, σ/σ_0, where σ is

---

[1] This is our third paper on this general topic. The second by Jean A. Sabatka and P. W. Selwood appeared in THIS JOURNAL, **77**, 5799 (1955). The work was done under contract with the Office of Naval Research.

[2] A. Michel, R. Bernier and G. LeClerc, *J. chim. phys.*, **47**, 269 (1950).

[3] P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).

[4] W. Heukelom, J. J. Broeder and L. L. van Reijen, *J. chim. phys.*, **51**, 474 (1954).

[5] P. W. Selwood, T. R. Phillips and S. Adler, THIS JOURNAL, **76**, 2281 (1954).

[6] J. J. B. van Eijk Van Voorthuijsen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

the specific magnetization per gram of nickel in the sample, and σ_0 is the specific magnetization of massive nickel at 0°K. obtained by extrapolation. Massive nickel refers to the familiar polycrystalline element with a sharp X-ray diffraction pattern and a well-defined Curie point at 631°K. All magnetic measurements were made at 6500 oersteds.

Figure 1 summarizes the sintering data. The massive nickel curve was obtained by reducing pure NiO at 250° for two hours. Both coprecipitates were sintered for two hours at each of several temperatures. The final sintering temperature for the 26.2% sample was 570°; for the 42.4% sample it was 680°. The sintering was done in hydrogen because strong heating of these samples *in vacuo* or in helium sometimes causes slight reoxidation, presumably from a trace of liberated water vapor. The thermomagnetic curves for the intermediate steps in the sintering series lay in each case between the curves shown in Fig. 1. The curve for the 42.4% sintered sample resembles that for massive nickel, but the 26.2% sintered sample showed little magnetization above 77°K.

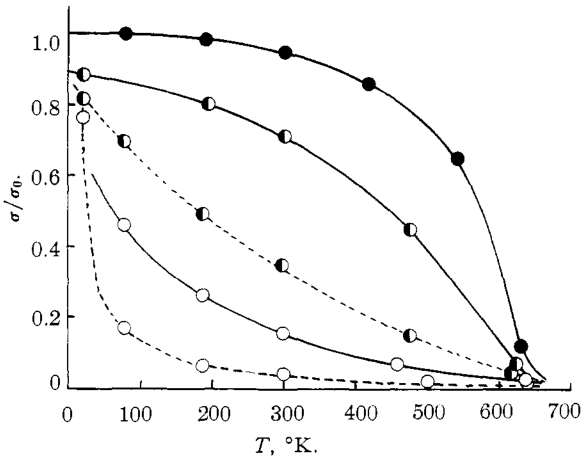

Fig. 1.—Thermomagnetic curves for: (---○---) 26.2% Ni-SiO_2; (—○—), the same sintered; (---◐---), 42.4% Ni-SiO_2; (—◐—), the same sintered; (—●—), massive nickel.

The same samples were used to study the effect of sintering on the change of magnetization caused by chemisorption of hydrogen at room temperature. Figure 2 shows the thermomagnetic curves obtained in helium and in hydrogen for 26.2% coprecipitate before and after sintering. Figure 3 shows similar data for the 42.4% coprecipitate.

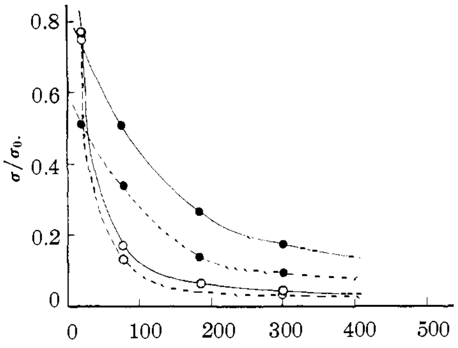

Fig. 2.—The influence of chemisorbed hydrogen on the magnetization of supported nickel: (—○—) 26.2% Ni-SiO_2 reduced; (---○---), the same in H_2; (—●—), the same in He after sintering; (---●---), the same sintered sample in H_2.

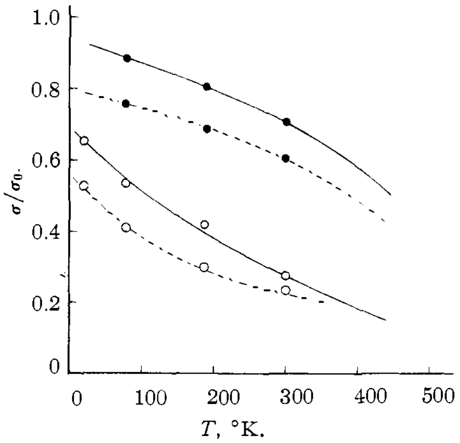

Fig. 3.—The influence of chemisorbed hydrogen on the magnetization of supported nickel: (—○—), 42.4% Ni-SiO_2 reduced; (---○---), the same in H_2; (—●—) the same in He after sintering; (---●---), the same sintered sample in H_2. The sample was similar to but not identical with that referred to in Table I.

The effect of changing the temperature of chemisorption was studied on an unsintered 42.4% sample. It was found that the decrease in magnetization of an evacuated sample when hydrogen was admitted at 77°K. was almost the same as that when the same sample was cooled from above room temperature to 77°K. in an atmosphere of hydrogen. But no appreciable change took place when the hydrogen was admitted at 77°K. in the presence of helium. The data are shown in Table I.[6a]

TABLE I

INFLUENCE OF HYDROGEN CHEMISORBED AT 77°K. ON 42.4% NICKEL–SILICA COPRECIPITATE

Treatment	σ/σ_0
Cooled from 620°K. in helium	0.811
Cooled from 620°K. in hydrogen	.640
Cooled from 620°K. *in vacuo*, then hydrogen admitted at 77°K.	.621

It was found that a 42.4% sample, supposedly saturated with hydrogen and then kept in flowing helium at room temperature, suffered a slow increase of magnetization. This effect was reversible. It was also found that in pure hydrogen at room temperature the magnetization remained constant for many hours. A time study of the change of magnetization in flowing helium is shown in Fig. 4. A trace of hydrogen in the flowing helium was found sufficient to maintain the magnetization constant. It was also found that flowing helium was unable to alter the magnetization of a hydrogenized sample at 77°K.

The effects of nitrous oxide, carbon monoxide and water vapor on the 42.4% sample at room temperature were observed. Nitrous oxide and carbon

---

(6a) NOTE ADDED IN PROOF.—Later work, to be presented in a subsequent paper, has shown the above result to be a special case.

monoxide raised the magnetization above that in helium, while water vapor lowered it. Oxygen, as previously reported, raised the magnetization of a 26.2% sample. All gases were carried at low concentration in flowing helium. The data are summarized in Table II.

TABLE II

INFLUENCE OF CHEMISORBED GASES ON THE MAGNETIZATION OF A REDUCED 42.4% COPRECIPITATE

Gases adsorbed and system measured at room temperature

Gas	% change in magnetization
H_2	−13
N_2O	+13
CO	+ 5.1
H_2O	−24
O_2 (on 26.2% sample)	+13

The influence of water vapor also was studied at 187°K. and at 77°K. The magnetization was less at each temperature when water vapor had been admitted (at room temperature) than at the same temperature in helium as shown in Table III.

TABLE III

INFLUENCE OF WATER VAPOR ADSORBED AT ROOM TEMPERATURE ON THE MAGNETIZATION OF 42.4% $NiSiO_2$

Temp., °K.	σ/σ_0 in He	σ/σ_0 in H_2O vapor
297	0.316	0.272
185	.443	.417
77	.600	.543

Discussion

The ferromagnetism of metallic nickel arises from parallel coupling of unpaired electrons in the d-band. There is thought to be an average of 0.6 electron hole, and unpaired electron, per nickel atom. Changes in the specific magnetization of nickel occurring simultaneously with chemisorption of a gas may be interpreted as a change in the density of unpaired electrons in the nickel. An increase of magnetization indicates an increase in the number of unpaired electrons. It follows that a gas which causes such an increase is chemisorbed by accepting electrons from the catalyst, and the gas molecule becomes the negative end of the gas–metal bond. If the magnetization decreases, the number of unpaired electrons must have decreased; the gas must be chemisorbed by donating electrons to the nickel, and the gas molecule must be the positive end of the gas–metal bond.

If hydrogen is chemisorbed on these catalysts the specific magnetization observed at room temperature drops substantially, thus showing that the process is one of electron transfer from hydrogen to nickel. This is consistent with the current view that hydrogen is chemisorbed on nickel by the formation, primarily, of covalent bonds.[7] (The magnetic method is not able to distinguish between electron transfer with formation of a covalent bond as opposed to adsorption as protons—a view held by some.)

It is clear that the observation of this phenomenon depends on having the metal present in particles so small that a measurable change of electron density occurs in the particle when the surface is covered with a layer of adsorbed molecules. If we assume that each nickel atom on the surface accepts an electron from one hydrogen atom, then a simple calculation will show that a measurable (>1%) change of magnetic moment should occur for nickel particles having more than 3 m.^{2}g.$^{-1}$ of surface and, hence, of spheres under 1000 Å. in diameter. In this work we are, therefore, dealing with particles which are small enough to show significant deviations from the properties of ordinary colloids and to approach those of single atoms. This area of sub-colloid chemistry has not been much investigated.

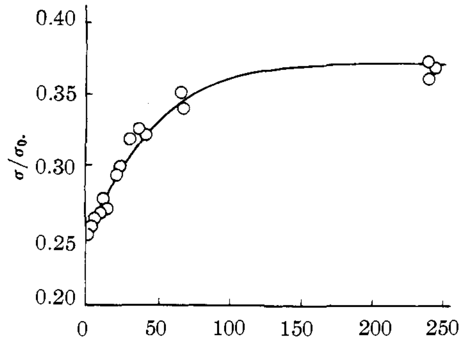

Fig. 4.—Desorption of H_2 from 42.4% Ni–SiO_2 at room temperature, measured by progressive increase of magnetization.

Following the original suggestion of Michel[2] we[3] proposed a method for determining particle size distributions from thermomagnetic curves. An apparent particle size distribution is obtained by assuming that the mass of nickel in particles of a given size is proportional to the slope of the thermomagnetic curve at the Curie temperature corresponding to that size. As mentioned above the appropriate Curie temperature is found from the average coördination number possessed by the nickel atoms in the particle. Distributions of particle sizes obtained in this way make it possible to study the effect of particle size on the mechanism of chemisorption.

In the following discussion a distinction must be made between the temperature at which chemisorption is caused to occur, and the temperature at which the magnetic measurements may be made. Another point which must be mentioned is the failure to saturate magnetically these nickel particles at realizable fields above 0°K. The resolution of this difficulty will have to wait for a detailed description of specific magnetization as a function of field, temperature and particle size. Our neglect of this complication does not invalidate the qualitative conclusions given below.

Turning now to Fig. 1 we see that, as previously reported,[1] the specific magnetization at 0°K. is independent of particle size. It will be noted that the 26.2% sample, before sintering, shows an astonishing degree of dispersion. This sample is scarcely ferromagnetic at all at room temperature, but becomes very strongly so at 20°K. In a previous paper[3] we indicated that the specific magne-

---

[7] D. D. Eley, *Quart. Revs.* (*London*), **3**, 209 (1949).

tization per g. of nickel of a strongly sintered sample approached that (at room temperature) of the same weight of massive nickel, and that this could form the basis of a simple method for measuring extent of reduction. We see now, however, that the method will apply only to samples, such as the 42.4%, which contain nickel in sufficient amount to permit aggregation to large particles. The 26.2% sample, even after strong sintering, still contains no particles that could be regarded as massive nickel. The silica support presumably prevents further aggregation in this sample.

If the magnetic measurements are carried down to lower temperatures we may, in effect, scan the particle-size spectrum. At lower temperatures smaller particles come more prominently into view, so to speak; they become more ferromagnetic and hence contribute more to the observed magnetization. It must, however, be remembered that the larger particles also contribute to the low temperature magnetism. In Figs. 2 and 3 we show the results of this scanning operation over a range of particle sizes for hydrogen chemisorbed at room temperature or higher.

If the view described above is correct, namely, that lowering of the magnetization by chemisorbed hydrogen is due to filling of the d-band of the nickel, and that this occurs through electron donation from one hydrogen atom to one surface nickel atom, then it is clear that the specific magnetization of the nickel particle in hydrogen should be zero when 0.6 or more of all nickel atoms reside on the surface of the particle. The loss of magnetization should thus be 99% complete for nickel with a specific surface of ~600 m.^{2}, corresponding to a sphere ~13 Å. in diameter.

For samples containing a distribution of particle sizes, lowering the temperature at which the magnetic measurements are made should bring in to view, so to speak, particles which have suffered progressively greater loss of magnetization. This does not mean that the magnetization of the sample should actually decrease with decreasing temperature. The larger particles are still contributing to the magnetization at low temperatures. We should rather expect that under these circumstances the magnetization would tend to become parallel to the temperature axis and that the extrapolated magnetization at 0°K. would be substantially lower than that for the same sample in the absence of adsorbed gas. It might be anticipated that the most highly dispersed nickel samples would then show the greatest lowering of the magnetization at 0°K. in the presence of hydrogen.

This expected effect does not occur. It will be seen in Fig. 2 that for a 26.2% sample the magnetization is substantially the same at 20°K. with and without adsorbed hydrogen, and that the effect of the hydrogen as observed at the lowest temperatures is actually greater for the sintered sample which, presumably, contains larger particles of nickel.

Before attempting to explain this anomaly we shall refer to the results on the sintered 42.4% sample shown in Fig. 3. Here there is probably no appreciable fraction of the nickel in the very small particle range. The magnetization observed in the presence of hydrogen is that expected for medium sized particles adsorbing hydrogen by the mechanism described. We may, therefore, note that the extrapolated lowering of 14% in the specific magnetization at 0°K. could be caused by an average increase of electron density in the d-band amounting to $0.14 \times 0.6 = 0.084$ electron per nickel atom. (The specific magnetization or moment per gram is directly proportional to the atomic moment and this in turn, expressed in Bohr Magnetons, is numerically equal to the number of unpaired electrons.)

We have no adsorption data on the identical sample of catalyst, but Schuit and De Boer[8] have published data on samples prepared identically and reduced and sintered in comparable fashion. They find that the chemisorption of hydrogen is about 20 cc. per g. of nickel.[9] This corresponds to a ratio of hydrogen atoms to nickel atoms of 0.11. It is clear that, within the limits of experimental error, each hydrogen atom adsorbed actually donates one electron to the d-band of the nickel. Furthermore, a nickel atom with 0.08 of its atoms located on the surface would have a surface (111 plane) of 47 m.^{2}g.$^{-1}$, and this particle, if spherical, would have a diameter of 133 Å. In an earlier paper[3] we gave X-ray line width data showing that similar catalyst samples treated in comparable fashion contained nickel particles about 100 Å. in diameter, and this is also in agreement with our particle diameter estimates from the thermomagnetic curves. There seems little doubt that the views expressed above concerning the mechanism of chemisorption of hydrogen on nickel are correct so far as this particular sintered sample is concerned.

We turn now to consider the anomaly that in those samples possessing the smallest nickel particles and in which, as a consequence, the effect of chemisorbed hydrogen is expected to be the greatest at low temperatures, it is actually quite small and even negligible. It might be thought that the smallest particles failed to adsorb hydrogen. But this would not account for the fact that for both unsintered samples the fractional change of magnetization after admission of hydrogen (at room temperature) is actually less as measured at 20°K. than at 300°K.

We wish to suggest that the equilibria for adsorbed hydrogen represented as

$$\begin{tikzcd} & H_2 \arrow[d, shift left] & \\ 2H^- \arrow[r, shift left] & 2H^\circ \arrow[l, shift left] \arrow[u, shift left] \arrow[r, shift left] & 2H^+ \arrow[l, shift left, dashed] \end{tikzcd}$$

depend on the nickel particle size.

The decrease in magnetization normally observed on hydrogen chemisorption may be caused by the formation of some protons as the hydrogen atoms donate their electrons to the nickel surface or as the electrons of the covalent bond are more strongly attracted to the nickel. But since the individual

---

[8] G. C. A. Schuit and N. H. De Boer, *Rec. trav. chim.*, **70**, 1068 (1951).

[9] The adsorption of hydrogen on the silica support at room temperature is negligible according to M. van der Waarden and F. F. C. Scheffer, *ibid.*, **71**, 689 (1952).

nickel atom is an electron donor, and very small particles begin to resemble the individual atom, a new mechanism may be considered for these particles. They may tend to hold electrons more loosely than does hydrogen and, in the extreme, a hydride ion may be formed. This would increase the magnetization of the small particles of nickel. The magnetization at low temperatures is the sum of contributions from particles of all sizes, and the effect of hydrogen chemisorption would be the resultant of an increase for small particles and a decrease due to electron donation by hydrogen to the larger particles. If a large fraction of the nickel were present as very small particles, hydride ion formation might cause an actual increase in magnetization at very low temperatures, but for most samples the decrease from the larger particles tends to obscure the increase due to small ones even for measurements at 20°K. The increase in fractional effect of hydrogen at 20°K. after sintering can be interpreted as the result of growth of medium and large particles at the expense of small ones.

In connection with the explanation offered here it may be pointed out that Schwab[10] has recently reached the conclusion, on the basis of selective catalyst poisoning studies, that nickel–silica may contain two types of nickel, one consisting of large well-crystallized particles, the other of small poorly crystallized metal. It has also been shown by Wright and Weller[11] that the salt-like alkaline earth metal hydrides resemble typical metals in their catalytic activity. It appears that this may be true because hydride ions are actually formed on the surfaces of very small metal particles.

In conclusion we consider the remaining results on hydrogen and other gases. From Table I it is clear that the adsorption of hydrogen may occur by the same mechanism at liquid air temperature as it does at room temperature. But the initial presence of helium is sufficient to prevent, or at least greatly retard, the chemisorption of hydrogen at 77°K. It is clear also from Fig. 4 that the desorption of hydrogen at room temperature occurs slowly but steadily in flowing helium, but this desorption does not occur at 77°K.

The results with gases other than hydrogen are particularly interesting because of the correlation with other work. Carbon monoxide, nitrous oxide and oxygen increase the magnetization. Water vapor and hydrogen (normally) decrease it. The first three gases must take electrons from the nickel, and the last two must donate electrons. This corresponds exactly to the interpretation of resistance measurements on thin nickel films given by Suhrmann and Schulz.[12]

Gas	O_2	CO	N_2O	H_2O	H_2
Direction of electrons	↑	↑	↑	↓	↓
Conductivity[12]	−	−	−	+	+
Magnetization	+	+	+	−	−

In an earlier paper[13] we reported that carbon monoxide lowered the magnetization of supported nickel. But the support in those experiments was metallic copper which, of course, means that the whole catalyst mass was electrically conducting. The results presented here on small nickel particles insulated by silica are in no way comparable with those previously reported.

The results shown in Table III merely indicate that no significant change occurs in the mechanism of chemisorption of water vapor over the nickel particle size represented between the temperatures 77 and 300°K. A sidelight in this connection is that while the effect of chemisorption of gases which donate electrons is limited by the 0.6 electron hole in nickel, that of gases accepting electrons may be very much larger as the magnetization will increase, at least in principle, until the maximum of 5 unpaired electrons is attained. It will also be noted that the nickel particle in accepting or donating electrons takes on, by a kind of pseudo-transmutation, some of the properties of elements respectively above or below nickel in atomic number.[14]

The results presented in this paper suggest that selective poisoning as, for instance, by sulfides may have a rational basis in the reduced ability of small metal particles to accept electrons, while still showing marked ability to chemisorb molecules in the electron donor sense. Similarly, some light is thrown on the selective action of partial sintering.

EVANSTON, ILLINOIS

---

[10] G. M. Schwab and M. Waldschmidt, *J. chim. phys.*, **51**, 461 (1954).

[11] L. Wright and S. Weller, THIS JOURNAL, **76**, 5948 (1954).

[12] R. Suhrmann and K. Schulz, *J. Colloid Sci.*, Supplement 1, 50 (1954).

[13] H. Morris and P. W. Selwood, THIS JOURNAL, **65**, 2245 (1943).

[14] A. R. Ubbelohde, *Discs. Faraday Soc.*, **8**, 203 (1950), uses the term "pseudo-silver" in referring to the palladium–hydrogen system.