[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thermomagnetic Analysis of Supported Nickel Catalysts[1]

BY P. W. SELWOOD, STEPHEN ADLER AND T. R. PHILLIPS

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Thermomagnetic curves for certain supported nickel catalysts show no sharply defined Curie point. The form of these curves has been related to particle size effects, and has been made the basis of a method for obtaining particle size distribution in the region of diameters below 50 Å. The method agrees with X-ray line width broadening results in the range of overlapping applicability. The method may be used to study the rates of reduction and of sintering. It has been found that highly dispersed nickel particles show a change of magnetization on exposure to certain gases. Hydrogen produces a decrease of magnetization as does ethylene, while oxygen and nitrogen produce an increase. These effects produced by chemisorbed gases have been interpreted in terms of electron interactions between nickel and adsorbed gas.

Introduction

Michel[2-4] has shown that the slow reduction of certain catalysts and catalyst components containing nickel may lead to anomalous thermomagnetic curves which possess no unique Curie point. These curves have been interpreted by Michel as being related to imperfect crystallization of the nickel, and have been made the basis for curves showing the distribution of particle sizes as these are influenced by changing temperature of reduction. This work is of considerable importance in catalysis because it affords an estimate of particle sizes in the region of diameters below 50 Å. and hence of increasing surface area and, presumably, of catalytic activity. Such particle sizes are difficult to study by other methods.

The present work extends Michel's observations and places the interpretation on a more nearly quantitative basis. During the course of the work it was found that chemisorption of certain gases by particles of nickel in the lowest diameter region could appreciably modify the electronic state of the nickel. This observation provides a new and powerful tool for the study of chemisorption, and its effect on the catalyst, under conditions in which catalytic activity is actually being shown.

Experimental

All determinations of specific magnetization were made either on the recording thermomagnetic balance[5] or on a Faraday balance similar to that previously described[6] but with the addition of an appropriate sleeve furnace, and with the substitution of a beryllium bronze spiral spring instead of a silica spiral. The sample tube of the recording balance was modified so that the sample could be magnetically examined after reduction without exposure to air, and measurements could be made in vacuum or in any particular gas. The thermomagnetic curve for massive nickel was obtained as a reference standard. Throughout this paper the term "massive" will be used to designate pure polycrystalline metal showing a sharp X-ray diffraction pattern, negligible specific surface and normal magnetic properties. This will be contrasted with "disperse" metal showing a diffuse X-ray pattern, large specific surface and the abnormal magnetic properties described in the papers by Michel.

Surface areas were measured by gas adsorption and calculated by the usual B.E.T. method.

X-Ray measurements were made on a North American Philips recording X-ray spectrometer.

Catalytic activities were compared for the hydrogenation of benzene, at 121°. Weight of catalyst, reduction conditions and space velocity (55 cc. per cc. per min.) were the same for all runs. Hydrogen was bubbled through thiophene-free benzene (at 25°) and the product collected in 1 hour was analyzed refractometrically. Procedure was to reduce each sample *in situ* at 350°, and then to sinter progressively in purified helium up to 550°. One sample was treated with purified carbon monoxide for 4 hours at 50° after reduction. Some nickel carbonyl was formed, as the burning exit gases formed a nickel mirror at the jet. The nickel so removed was perhaps a per cent. or two of the total nickel present.

Most of the catalyst samples were prepared by reduction of nickel silicate gel, made in a similar method to that of Van Eyk Van Voorthuijsen and Franzen[7] and designated in their paper CLA-5421.

A 0.2 molar solution of sodium silicate was prepared, to which was added 4.2 g. of NaOH pellets for each 100 ml. of solution, and the mixture boiled. A boiling solution of 0.7 molar nickel nitrate solution was slowly added to this with continuous stirring, and a green gel was formed. The nickel nitrate solution was prepared by the dissolution of nickel, electrodeposited from reagent grade nickel sulfate. The gel was washed with distilled water, dried at 105° for 36 hours, and powdered; it was stored over magnesium perchlorate.

The nickel content (42.1%) was determined by dissolution of the gel in hydrofluoric acid followed by the addition of concentrated sulfuric acid, and boiling to expel silicon tetrafluoride. The solution was then diluted, and the nickel plated on to weighed platinum electrodes.

A few experiments were made with a catalyst of a lower nickel content (33.1%), but the results were essentially the same.

The catalyst was prepared by the reduction of pellets of the gel, either in the magnetic apparatus or in the surface area apparatus in a stream of hydrogen.

A few experiments also were made with impregnated alumina catalysts prepared as described by Selwood and Hill,[8] with a nickel-containing cracking catalyst obtained through the courtesy of Dean H. S. Taylor, and with an evaporated nickel film on glass provided by Dr. Hugh Rowlinson. The nickel film had been prepared *in vacuo*, near room temperature, with a concentration of roughly 0.3 mg. per cm.^{2}.

Experimental Results

Thermomagnetic Analysis.—Initial experiments indicated that the supported catalysts were difficult to reduce in comparison with pure nickel oxide or hydroxide; the latter could be quantitatively reduced in hydrogen at 250° in 16 hours, whereas the supported material did not show any ferromagnetism after such treatment. Measurable reduction took place at temperatures above 300°, and typical thermomagnetic curves are shown in Fig. 1. For samples obtained at the lower reduction tem-

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[1] A preliminary communication concerning this work appeared in THIS JOURNAL, **76**, 2281 (1954).

[2] A. Michel, *Ann. chim.*, **8**, 317 (1937).

[3] A. Michel and M. Gallissof, *Compt. rend.*, **206**, 1252 (1938).

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

[5] R. F. S. Robertson and P. W. Selwood, *Rev. Sci. Instr.*, **22**, 146 (1951).

[6] P. E. Jacobson and P. W. Selwood, THIS JOURNAL, **76**, 2641 (1954).

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

[8] F. N. Hill and P. W. Selwood, THIS JOURNAL, **71**, 2522 (1949).

peratures, there was a gradual decrease in the specific magnetization with rising temperature of measurement, with no evidence of a sharply defined Curie temperature. But as the reduction temperature was raised, the thermomagnetic curves increased their resemblance to that of massive nickel.

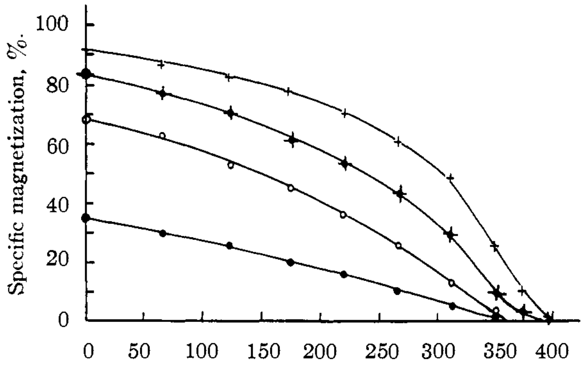

Fig. 1.—Thermomagnetic curves for increasing reduction temperatures, nickel-silica: ●, 360°; ○, 490°; ✦, 606°; +, 710°.

It is sometimes considered that the extent of reduction in a supported iron, cobalt or nickel catalyst may be obtained by comparing the observed and expected ferromagnetism developed per gram of total metal in the catalyst. That this procedure must be used with caution is clear from the following in which the above thermomagnetic results are separated into the effect of reduction on the one hand, and the effect of sintering on the other. Figure 2 shows thermomagnetic curves for a nickel–silica sample reduced for 16 hours at 350°, and then sintered in purified helium, at progressively higher temperatures. Figure 3 shows that a sample reduced at 270° for 66 hours exhibited only a trace of ferromagnetism at room temperature, but if this sample was now sintered *in vacuo* a substantial ferromagnetism developed. These results show that extensive reduction may take place at moderate temperatures without appreciable ferromagnetism appearing, but if the sample is then strongly sintered the thermomagnetic curve becomes essentially that of massive nickel. This phenomenon suggests an accurate magnetic method for determining degree of reduction. The partially reduced sample is sintered. The specific magnetization per gram of total nickel at room temperature is then compared with that of massive nickel. By this method a sample heated in hydrogen at 350° for 16 hours was found to be 90% reduced. A direct measure of the catalyst sample gain of weight when it was heated in oxygen suspended on a silica spiral balance showed that reduction must have been 92.5% complete.

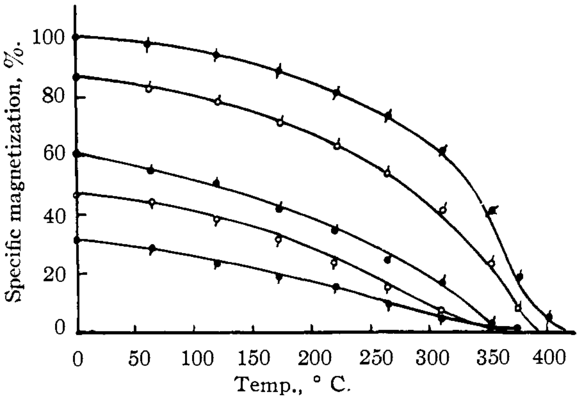

Fig. 2.—Thermomagnetic curves for identical reduction temperature and increasing sintering temperature in helium, nickel–silica: ●, reduction at 350°; ♀, sintered at 450° in helium; ●, sintered at 550° in helium; ♁, sintered at 725° in helium; ●, massive nickel reduced 300°.

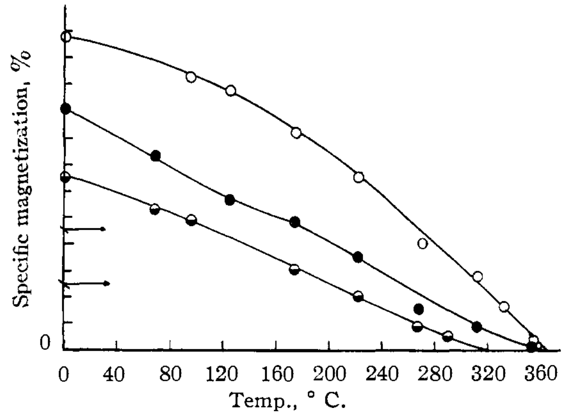

Fig. 3.—Curves for sintering *in vacuo* nickel–silica: 1st arrow, reduced 270°, 66 hr.; 2nd arrow, evacuated 240°, 1 hr.; ⊖, evacuated 450°, 10 min.; ●, evacuated 500°, 15 min.; ○, evacuated 660°.

Michel and his co-workers have postulated that the anomalous thermomagnetic curves are produced by the presence of small particles of nickel which do not have a unique Curie temperature, but rather that the Curie temperature is dependent on the size of the particle. In the sintering experiments, there is presumably no change in the amount of metallic nickel present, so it might be expected that the specific magnetization of sintered and unsintered samples would have the same value. The fact that they do not have the same value at room temperature implies that some nickel in the unsintered sample has a Curie temperature range below room temperature, and it is only when the temperature is lowered so that all the nickel becomes ferromagnetic that the specific magnetization of sintered and unsintered samples will become equal. This was confirmed, as shown in Fig. 4, where the extrapolated thermomagnetic curve for an unsintered sample was found to coincide with that for a sintered sample at 0°K. This further shows that though the Curie temperature of a small particle may vary with its dimensions, the very low temperature specific magnetization remains constant for particles of all sizes; otherwise, the two curves could not have coincided.

Once a sample had been sintered, it was impossible to obtain the original thermomagnetic curve by oxidation followed by another reduction; the curve obtained on making this experiment was that given by the sintered sample. Furthermore, if a partially reduced and sintered sample was further

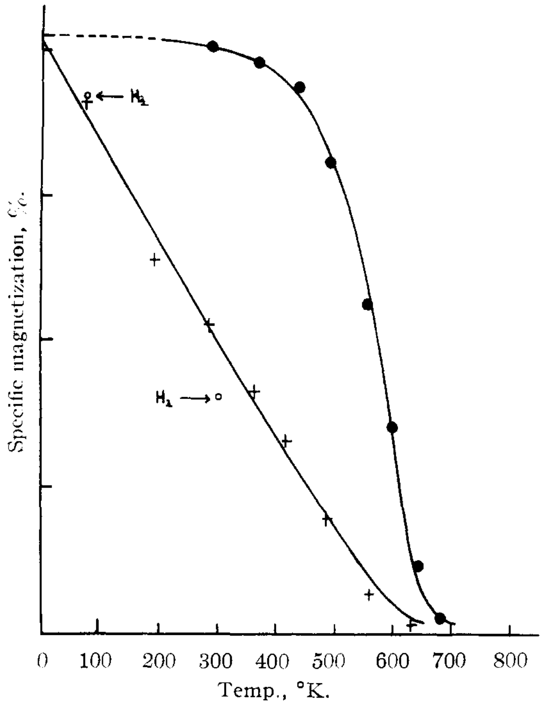

Fig. 4.—Thermomagnetic curves at low temperatures, nickel–silica: +, reduced in H_2, 18 hr. at 350°; ●, reduced in H_2, 18 hr. at 350°, then sintered 40 min. at 650° in purified He (measurements in helium with two exceptions shown).

reduced it was of interest to know whether the further reduction took place through the growth of nickel nuclei already present, or whether new metallic nuclei were formed. That the former actually took place is shown by Fig. 5. The magnetization due to the freshly produced nickel, which was found by subtracting the initial values from the final result, was of the massive nickel type.

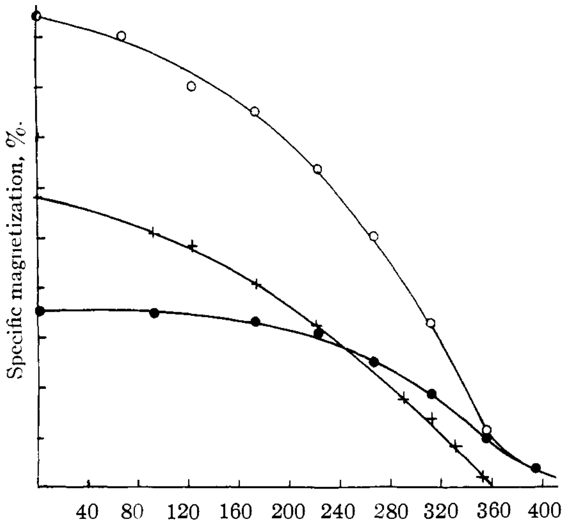

Fig. 5.—Further reduction of a partially reduced sample nickel-silica: +, reduced 270° for 66 hr., sintered 660° *in vacuo*; O, further reduction 410° for 16 hr.; ●(O − +) = new nickel.

The influence of the method of preparation on dispersion of the nickel is shown by the thermomagnetic curve for a 3.9% nickel on a silica–alumina cracking catalyst. The nickel was deposited on this catalyst by an impregnation procedure and it gave the thermomagnetic curve of massive nickel. Some of the coprecipitated catalysts containing ten times as much nickel gave, as described above, the curve characteristic of disperse nickel. This is not to say that impregnation always yields massive nickel, because certain nickel–kieselguhr samples prepared by impregnation indicated a fairly high degree of dispersion. The influence of procedural detail in catalyst preparation is shown in Fig. 6 where two samples containing 10% nickel on γ-alumina are compared. One sample was prepared by a single impregnation step from a fairly concentrated nickel nitrate solution, followed by the usual ignition and reduction. The other sample was prepared by repeated impregnation, and ignition, but with the use of dilute nickel nitrate solution until the 10% nickel concentration was reached. Thermomagnetic curves on these two samples obtained under several reduction conditions clearly show the more effective dispersion obtained by repeated impregnation.

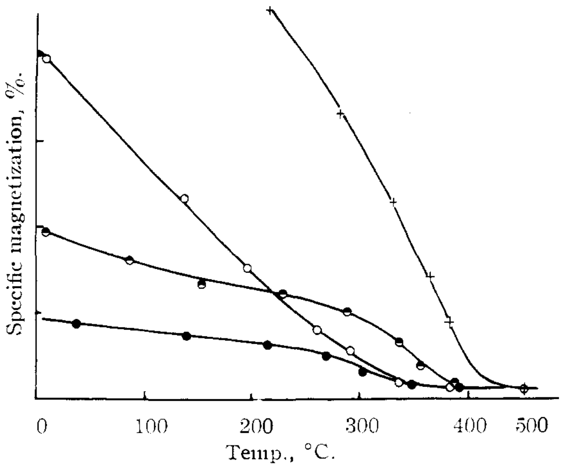

Fig. 6.—Comparison of catalysts prepared by single and multiple impregnations, nickel–alumina: ●, multiple impregnation, 400° reduction; ◓, single impregnation, 400° reduction 1 hr.; O, multiple impregnation, 500° reduction; +, single impregnation, 500° reduction.

A nickel film prepared by evaporation on to Pyrex glass gave the magnetic curve of massive nickel only.

Attempts were made to obtain disperse nickel by the very slow reduction of pure nickel oxide or hydroxide. Massive nickel was obtained in every case except for a slight diminution in sharpness of the Curie point.

Influence of Absorbed Gases.—It was found that the thermomagnetic curves for disperse nickel were appreciably changed by changing the atmosphere surrounding the sample. If, for instance, a measurement of magnetization were made at room temperature in hydrogen, and the sample was then flushed with purified helium, a small but definite increase of magnetization took place. The effect was reversible. Similar effects were observed when vacuum was substituted for the helium flush. The maximum diminution of magnetization observed at room temperature on exposure to hydrogen occurred instantaneously and amounted to about 20%.[9] But the increase in magnetization on removal of the hydrogen by vacuum or by flushing with helium occurred more slowly and was not complete until the sample had been heated to about 200°. No effect of hydrogen was observed in one observation made at liquid nitrogen temperature.

The drop in magnetization on exposure to hydrogen was found to be dependent on degree of sintering as shown in Table I.

TABLE I

EFFECT OF HYDROGEN ON MAGNETIZATION OF NICKEL CATALYST AS A FUNCTION OF CATALYST PRETREATMENT

Catalyst treatment	Decrease in magnetization, %
H_2 reduction 48 hr. at 300°	20
Same plus 1 hr. in He at 600°	10
Same plus 1 hr. in He at 700°	4

The effects produced by other gases were also briefly investigated. Nitrogen produced an increase of magnetization over that found *in vacuo* or helium. To observe the maximum effect the sample had to be heated moderately in the presence of the nitrogen. Figure 7 shows a sequence of results starting with the sample freshly reduced in hydrogen, then exposed to nitrogen. Comparable results were obtained if the sample were evacuated to remove hydrogen before the exposure to nitrogen. Exposure to hydrogen of a sample previously exposed to nitrogen resulted in a sharp drop of magnetization; this drop became even larger when the sample was heated moderately.

The effect produced by nitrogen is unexpected, because nitrogen is not generally considered to be chemisorbed on nickel. The nitrogen had been purified by passage over copper on asbestos at 600°, but the possibility remains that the increase of magnetization described might have been due to the cumulative effect of a minute trace of oxygen remaining in the nitrogen. The absence of a similar effect in helium, purified by the same procedure, argues against this view.

Oxygen was found to increase the magnetization. Exposure to pure oxygen or to air at room temperature resulted in almost instantaneous oxidation with loss of all ferromagnetism. But tank helium containing 0.2% oxygen[10] proved very satisfactory for demonstrating the anticipated increase of magnetization produced by chemisorbed oxygen.

Ethylene was found to reduce the magnetism, but only on heating. A drop of 14% (at room temperature) was observed on heating in ethylene at 175° for two hours. Further heating in helium at 450° for 45 minutes restored most of the loss. There was no effect produced by exposure to ethylene at room temperature and only very little at 60°. The possibility must be considered that at the elevated temperature, the ethylene had dissociated into hydrogen atoms and an acetylenic type of residue, and that the effect observed was due to the hydrogen.

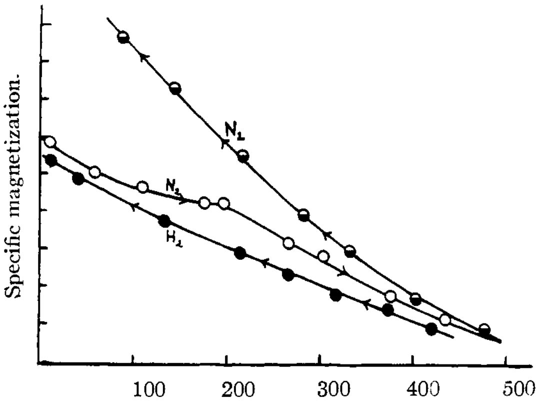

Fig. 7.—The adsorption of hydrogen and nitrogen, reduced 360°, 48 hr.

No reversible effects were found with boron trifluoride, iodine vapor, or sulfur dioxide; heating caused a permanent loss of magnetization in each of these cases. Benzene vapor, carried in helium, gave no measurable effect up to 100°. A mixture of benzene and hydrogen at 100° gave only the decrease of magnetization observed for hydrogen alone. At this temperature the nickel is actively catalyzing hydrogenation of the benzene.

X-Ray Results.—Powder patterns of the catalyst samples were obtained where the angles of incidence for diffraction, the observed lattice spacings and the relative intensities of incident and diffracted rays corresponded well with values given in the literature.[11]

The diffracted peak when $2\theta = 44.7°$ (where θ = angle of incidence) was examined for several sintered samples, to determine the size of the nickel particles by line broadening calculations. The region of two or three degrees on either side of the above value was scanned and the time required to receive 6400 pulses measured with a stop watch. The half width B (*i.e.*, the width of the peak at half its maximum intensity) is related to the mean linear dimension, Λ, of the diffracting particle by the relation[12]: $\Lambda = K\lambda/B \cos\theta$, where K is a constant equal approximately to unity, λ is the wave length of the radiation (1.541 Å.), and θ is the angle of incidence at the maximum intensity of diffraction ($\theta = 22.4°$). Calculation gave the data shown in Table II.

TABLE II

EFFECT OF SINTERING ON X-RAY LINE WIDTH AND PARTICLE DIAMETER (REDUCTION TEMPERATURE 350°)

Sintering temp., °C.	B (radians)	Particle diameter (Å.)
450	0.0445	38
500	.0305	55
550	.0237	70
650	.0113	150
Standard nickel	.0068	250

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[9] Later experiments by Mr. Virgil Kurfman in this Laboratory have shown effects of hydrogen amounting to nearly 50%.

[10] As found by Miss Jean A. Sabatka in this Laboratory.

[11] A.S.T.M. X-ray diffraction data card, No. 3379.

[12] J. Bouman, "X-Ray Crystallography," Interscience Publishers, Inc., New York, N. Y., 1951, p. 59 ff.

Adsorption Measurements.—Adsorption measurements were made on the catalyst samples with nitrogen and with carbon monoxide, and surface areas per gram of nickel were calculated according to the B.E.T. procedure. The samples were reduced in a stream of hydrogen in the adsorption apparatus, which was then evacuated and the sample tube sealed off. Evacuation was continued overnight at 200–300°, and then the sample was immersed in liquid nitrogen and the nitrogen adsorption isotherm obtained. Overnight heating and evacuation were then repeated, and the volume for monolayer adsorption of carbon monoxide determined at liquid nitrogen temperatures. The liquid nitrogen coolant was then replaced by one of CCl_4–$CHCl_3$–solid CO_2 and the system evacuated for at least another 8 hours. This removed physically adsorbed carbon monoxide, and the volume removed was determined by a final carbon monoxide adsorption at liquid nitrogen temperatures. If V_1 was the first volume of CO adsorbed, and V_2 the second, the surface area, A, of the nickel is given by $A = T(V_1 - V_2)/V_1$ where T is the total area determined from the adsorption of nitrogen. The results were not very reproducible, but the order of magnitude was given, as shown in Table III.

TABLE III

SURFACE AREAS PER GRAM OF NICKEL OBTAINED BY CARBON MONOXIDE CHEMISORPTION

Sample treatment	Total area, T, m.^{2}/g.	Area of nickel, A, m.^{2}/g.
Unreduced	244	..
Reduced 15 hr. at 350°	185	75.3
Reduced 42 hr. at 350°	228	59.8
Reduced 15 hr. at 350° then heated 1 hr. *in vacuo* at 550°	177	..
Reduced 15 hr. at 365° then heated 1 hr. *in vacuo* at 450°	189	31.5

Some attempts were made to obtain two surface area measurements on samples, one after reduction, and another after sintering the sample *in situ* in the apparatus. These met with no success as it was found that carbon monoxide treatment had a profound effect on the surface area of the catalyst. On pumping off the adsorbed carbon monoxide, and evacuation and heating, there was a very large reduction in the surface area, even if the original reduction temperature were not exceeded. The effect is probably a result of carbonyl formation, but its precise mechanism is not understood.

Catalytic Activities.—Activities obtained for reduced nickel silicate catalysts and for the same at several stages of sintering are shown in Table IV.

TABLE IV

ACTIVITY (% HYDROGENATION OF BENZENE) FOR Ni–SiO_2 CATALYSTS REDUCED AT 350° AND SINTERED AS SHOWN

Sintering temp., °C.	Activity	Sintering temp., °C.	Activity
350	91.4	475	1.4
350	100.0	475	0.0
400	89.0	500	2.2
425	39.2	500	1.3
450	39.8	550	1.4
450	44.4	350 (after CO treatment)[a]	99.4

[a] 4 hours at 50° followed by sweeping with H_2 at 125°.

Discussion of Results

In a ferromagnetic substance the Curie temperature is believed to depend directly on the coördination number, z, with respect to atoms of the same kind. In nickel, as for any close-packed structure, $z = 12$. But if the nickel particles are very small it is perhaps legitimate to consider the average coördination number, $\bar{z}$, as being appreciably less than 12, because those atoms on the surface have less than a complete atomic neighborhood.

Neglecting other possible influences on the magnetic properties of the nickel we may write $T/T_c = T/631° = \bar{z}/12$, where T is the Curie point of a particle for which the average coördination number is $\bar{z}$, and $T_c = 631°$ is the Curie point for massive nickel.

Thus, in the unsintered catalyst, there is a preponderance of particles which have an average coördination number less than 12. Furthermore, as there is no sharp break in the thermomagnetic curve, it is concluded that there is present an extended range of particle sizes. On sintering the samples, the number of particles of larger size increases; this is confirmed by the data from the line broadening of X-rays. The change in shape of the thermomagnetic curves on sintering may therefore be ascribed to the change in profile of the particle size distribution, and it should be possible to obtain this distribution from the magnetic data.

By construction of a cork ball model, the average coördination number of the atoms in a particle containing n atoms and of diameter d may be estimated. It was impractical to build models with larger average coördination number than 9.5, so for larger values of $\bar{z}$, it was assumed that the particles were spherical, and the $\bar{z}$ value was calculated. The number, n, of nickel atoms in a sphere of radius r is found by dividing the volume of the sphere by the effective volume of one nickel atom, $5.66a^3$ for close packed structures, where a is the radius of the atom. Thus for nickel $n = 4/3\ \pi r^3/5.66(1.25)^3 = 0.379r^3$. If the sphere is large, the surface may be approximated to a flat close packed layer of nickel atoms of area $A = 4\ \pi r^2$. As the particles become larger the average coördination number may be estimated without reference to particle shape by consideration of the fact that for each surface atom $z = 9$, while all other atoms have a normal coördination number[13] of 12.

Figure 8 gives the relations, determined as above for Curie point, average coördination number, number of atoms in particle, and diameter of a spherical particle.

Interpretation of the thermomagnetic curves then follows the following procedure: The data are first replotted as σ/σ_0 where σ is the observed specific magnetization of nickel in the catalyst sample, and σ_0 is the specific magnetization of massive nickel at the same temperature. Then the quantity $\Delta\sigma/\sigma_0$ as shown in Fig. 9 represents that fraction of the nickel mass having a Curie point in the range ΔT and hence being present in particles larger than the diameter represented for T in Fig. 8. Similarly, the slope of σ/σ_0 *vs.* temperature gives

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(13) S. F. Adler, Doctorate Thesis in Chemistry, Northwestern University, 1954.

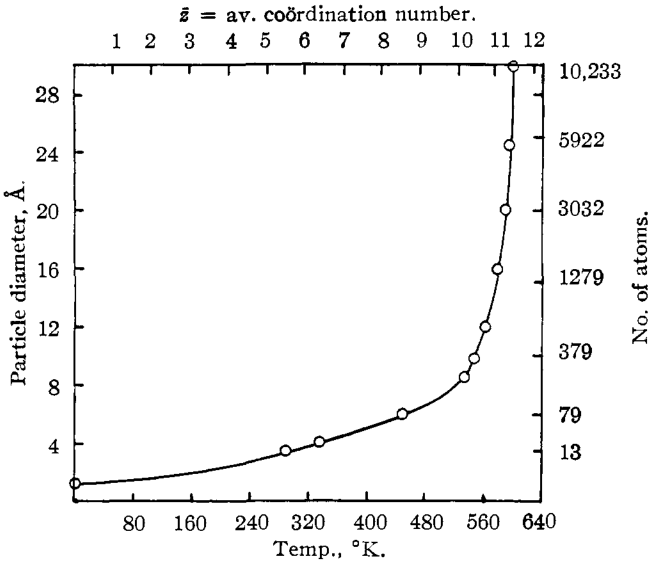

Fig. 8.—Relationship between particle diameter, number of atoms, temperature and z.

directly the weight fraction of nickel with Curie points in a one degree range, as was done by Michel.

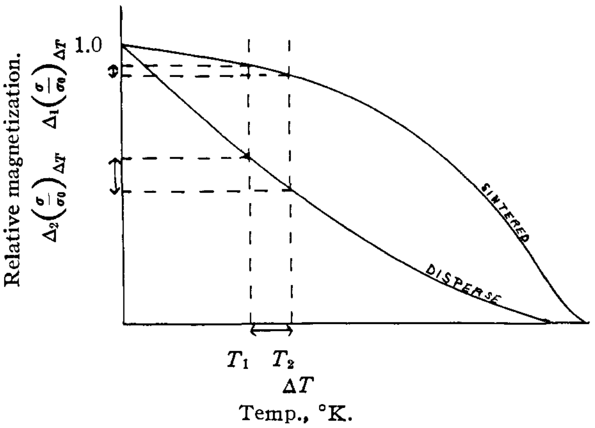

Fig. 9.—Weight fraction of particles with Curie temperature T_1 to T_2 in sintered and disperse samples.

These data may then readily be replotted as weight fraction of particles with diameters within the range of ±0.5 Å. Figure 10 is a curve showing distribution of particle sizes in a sample at several stages of sintering. It will be noted that for all the nickel to be represented by this method it is essential that $\sigma/\sigma_0 = 1$ at absolute zero. With the limited experimental data so far available this seems to be true.

Within the overlapping range of applicability it will be seen that the magnetic method yields particle diameters in good agreement with the X-ray method of line width broadening. It is also possible to calculate surface areas from the distribution of particle sizes, again assuming spherical particles. The results of this calculation are shown in Table V.

TABLE V

SURFACE AREA PER GRAM OF NICKEL COMPUTED FROM MAGNETIC DATA

Sintering temp., °C.	350	450	550	600
Area, m.²/g.	1456	1185	970	477

These areas are considerably larger than those estimated from the gas adsorption studies. But this is to be expected because the adsorption method does not allow for any of the nickel being inaccessible to the gas molecules.

The effects of chemisorbed gases in changing the magnetic properties of the dispersed nickel are attributed to electronic effects within the nickel particle.

It is believed that nickel has an average of 0.6 electron holes per atom in the d-band. The parallel coupling of unpaired electrons resulting from this deficit causes ferromagnetic phenomena. For the case of nickel, if extra electrons are introduced into the metal, the specific magnetization may be expected to fall, and if some are withdrawn, an increase will occur. Thus it is postulated that hydrogen on adsorption, acts as an electron donor, while oxygen and possibly nitrogen withdraw electrons from the metal. The effect is not normally noticeable, as the ratio of surface to volume is too small, and insufficient electrons are added or withdrawn from the material to produce any effect. The larger the size of the particle, the smaller the expected effect, and this is actually observed, as shown in Table I. It is possible that a very small particle could become completely non-magnetic on adsorp-

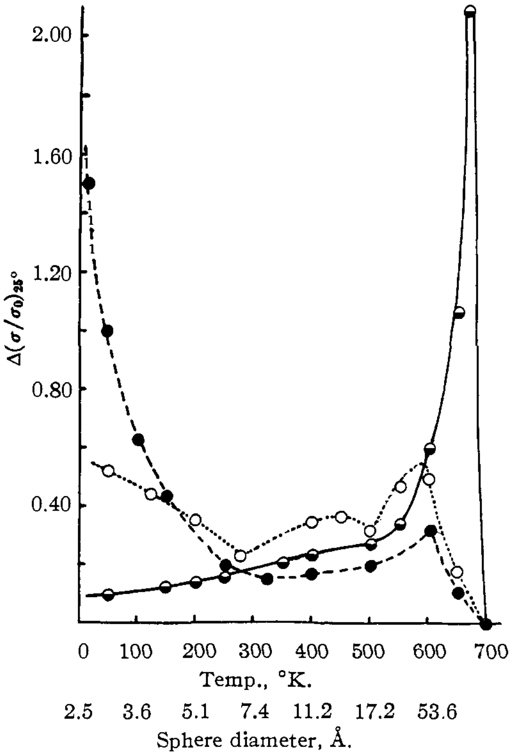

Fig. 10.—Particle size distribution for disperse and sintered samples. The abscissa is given in degrees K., but a sphere diameter scale reaching infinity at 631°K. is superimposed. ●, reduced 15 hr., 350°; ○, reduced 15 hr., 350°; sintered 1 hr., 450°; ◒, reduced 15 hr., 350°; sintered 1 hr., 600°.

tion of a monolayer of hydrogen atoms, each of which would donate an electron to the nickel. It is to be noted that these observations give a powerful new method for studying the electronic consequences of chemisorption on metals. The interpretation offered for the effect described is parallel to that suggested by Suhrmann and Sachtler[14] for the change of work function produced by chemisorbed gases on metals.

The fall of catalytic activity near sintering temperatures of 450° is accompanied by other changes in properties of the catalyst; below this temperature the catalyst reoxidizes very vigorously when exposed to air, but is relatively stable above. Also, at this temperature there is a sharpening of the X-ray diffraction pattern and the thermomagnetic curves begin to become convex in shape. It is approximately the same temperature at which mobility of nickel atoms may be expected, as the Tammann temperature lies within this range. The drop in activity greatly exceeds the fall of specific surface during sintering. This suggests the existence of some intensive activity factor present in very small particles, over and above the effect of surface.

Acknowledgment.—It is a pleasure to acknowledge support of the Office of Naval Research in connection with this work. It is also the pleasant duty of Stephen Adler to acknowledge receipt of the Sinclair Research Fellowship.

EVANSTON, ILLINOIS

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(14) R. Suhrmann and W. Sachtler, *Z. Naturforsch.*, **9**, [a] 14 (1954).

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. VIII. Density and Surface Tension of Molten Sodium Phosphates

BY CLAYTON F. CALLIS, JOHN R. VAN WAZER AND JOE S. METCALF

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Density and surface tension data have been determined for the Na_2O–P_2O_5 melts with Na_2O/P_2O_5 mole ratios between 1.0 and 2.15, at temperatures from slightly above the liquidus to above 1000°, using special platinum equipment. The densities are given by the general relationship $d = 2.372 + 0.089\,(Na_2O/P_2O_5) - 0.000338t$, where d is the density in g./ml., t is the temperature, and Na_2O/P_2O_5 is the mole ratio in the molten phosphate. The surface tension values for ratios from 1.0 to 1.5 are given by the equation $\gamma = 150.6 + 67.7\,(Na_2O/P_2O_5) - 0.0379t$, where γ is the surface tension in dynes/cm. The surface tension and density data can be represented by the MacLeod equation, with the constant equal to 1.74 ± 0.07.

The density and surface tension of melts made by heating sodium trimetaphosphate at temperatures from above the liquidus to around 1200° have been measured by Jaeger.[1] The surface tension data were obtained using the method of maximum bubble pressure. In this study the measurements have been extended from the metaphosphate to beyond the pyrophosphate composition in the Na_2O–P_2O_5 system.

Experimental

Materials.—The Na_2O–P_2O_5 melts were prepared by melting varying proportions of dry sodium trimetaphosphate and dry tetrasodium pyrophosphate. The trimetaphosphate was prepared by heating a special grade of Monsanto insoluble sodium metaphosphate for several hours at 500°. The Na_2O/P_2O_5 mole ratio was 1.001 and the loss of weight on ignition with zinc oxide[2] was 0.08% in this sample of sodium trimetaphosphate which contained only spectrographically detectable amounts of impurities. The pyrophosphate was prepared by heating analytical reagent disodium phosphate, anhydrous, at 500°. Melts with Na_2O/P_2O_5 mole ratios greater than two were prepared by melting pyrophosphate with the desired proportion of crystalline trisodium orthophosphate and heating for an extended period to remove the water. The density measurements were found to be sensitive to traces of water; but the melts were all carefully dehydrated before the measurements were made.

The above preparations were carried out in platinum equipment and the compositions near the Na_2O/P_2O_5 ratio of unity were contaminated with enough dissolved platinum to cause a slight yellowing of the glasses quenched from the melts. Although previous work indicated that the platinum content of the discolored melts would be well below 1%, it is believed that platinum was present in all melts in considerably greater weights than any elements other than sodium, phosphorus and oxygen.

Methods and Procedure.—The samples were heated (in a platinum container) in a pot-type furnace equipped with a special lid to permit the desired manipulations from above. A small hole in the center of the lid permitted free movement of the supporting wire. The temperature of the liquid was measured to ±5° with a Pt:Pt-Rh thermocouple immersed a few centimeters in the liquid.

Density.—The densities were determined by application of Archimedes' principle using a procedure similar to that described by Jaeger.[3] A platinum bob of known volume, suspended by means of a fine wire from the beam of an analytical balance, was weighed in air and then submerged in the liquid. Corrections were made for the surface tension of the liquid by adding to the buoyancy the product of the surface tension and the circumference of the wire (diameter = 0.0508 cm.) supporting the bob. The densities were then calculated by dividing the volume of the bob into the sum of the difference in weights in air and in the liquid and the surface tension correction.

The bob used in this work was fabricated by attaching a thin platinum wire to a short section of 0.20-inch diameter platinum rod. The bob weighed about 15.5 grams in air. The volume of the bob was obtained from the weights in air and in water of known temperature and density. The volumes of the bob at the higher temperatures were calculated from the measured volume at room temperature and the known coefficient of volume expansion for platinum.

Surface Tension.—The surface tension measurements were made with a du Nouy interfacial tensiometer. The regular platinum-iridium ring supplied with the instrument was modified for high temperature usage by welding on the top of its supporting bars an eight inch extension of platinum wire. The platinum extension was jointed to the connecting shaft of the instrument with a loose fitting hook and eye.

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(1) F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

(2) Procedure used in analytical laboratories of Monsanto Chemical Company. Details will be included in Scott's "Standard Methods," 6th Edition.

(3) F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 278–282.