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The Structure of Raney Nickel

VIII. Magnetic Properties Related to Particle Size and Hydrogen Evolution

J. IAN MACNAB* AND ROBERT B. ANDERSON

Department of Chemical Engineering and Institute for Materials Research,
McMaster University, Hamilton, Ontario, Canada

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The Langevin equation was applied to magnetization-field data for Raney nickel catalysts. For a given sample constant crystallite diameters were obtained for data measured at 293–473 K. Assuming that the nickel was present as a solid solution containing hydrogen and/or aluminum, the crystallite diameters from the Langevin equation were about 45% larger than values from X ray line broadening. Crystallite sizes increased with increasing temperature of treatment with aqueous alkali and with increasing temperature of evacuation.

The hydrogen evolved on heating was measured for two catalysts. The saturation magnetizations at 0 K increased about 0.63 μ_B per hydrogen atom removed. The hydrogen evolved on heating catalysts from 25 to 500°C could be estimated accurately from magnetic data for the samples heated at these temperatures, if hydrogen was assumed to be the only solute in the nickel solid solution.

INTRODUCTION

The application of ferromagnetism to the study of the structure of Raney nickel catalysts and the influence of the preparative method upon their ferromagnetic properties have been described recently (*1*). As ferromagnetism is a property of bulk solids there must be a particle size at which the effect of finite size significantly affects the magnetic properties. As the size decreases further, a stage is reached where all the particles are single Weiss domains (*2*). An assembly of monodomains is described as being superparamagnetic if plots of magnetization divided by saturation magnetization as a function of H/T superimpose over a range of temperatures. These phenomena are relevant to catalysis as the particles are of the same size range as found in typical metal catalysts. Superparamagnetism has been adequately defined and described by Jacobs and Bean (*3*) and Martin (*4*). Selwood (*5*) suggested "collective paramagnetism" as a more descriptive title for this phenomenon. Critical size measurements have varied considerably, but the greatest size below which particles consist only of monodomains is suggested by Martin (*4*) and Kittel (*6*) to be 300 Å. The orientation of these monodomains at a given temperature and field seems to be described adequately by the Langevin equation (*5*). This general principle has been utilized in a variety of ways by different workers to calculate mean particle sizes or size distribution functions for a number of supported nickel catalysts (*4, 5, 7, 8*).

Previous workers have observed copious evolution of hydrogen on heating Raney nickel. The magnetization of Raney nickel measured at room temperature was shown to increase linearly with the amount of hydrogen evolved (*9, 10*). Prettre and co-

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* Present Address: Research Department, Imperial Chemical Industries Ltd., Organics Division, Manchester 9, England.

workers (*11*) have recently published an important paper on the structure of Raney nickel including magnetic and hydrogen evolution studies. They conclude that most of the hydrogen evolved on heating was chemisorbed on the surface. Particle diameters estimated from the Langevin equation increased from 93 Å for an untreated sample to 150 Å for a catalyst heated at 600°C.

We present in the first part of this paper the results of particle-size calculations for three types of Raney nickel and show the influence of the preparative and subsequent treatments. The second part describes the evolution of hydrogen upon heating and relates the volume of hydrogen evolved to changes in the saturation magnetization at 0 K.

EXPERIMENTAL

Magnetic Measurements

Details of the apparatus and procedure for the magnetic measurements have been described (*1*). The sample preparation was described in the same paper; in brief, samples were prepared by evacuating cylindrical pellets of catalyst at several selected temperatures between 25 and 500°C and sealing in glass tubes under vacuum. Samples were then studied in the vibrating sample magnetometer over a temperature range from 4.2 or 77 K to the temperature of evacuation.

Hydrogen Evolution: Apparatus and Procedure

The volume of hydrogen evolved on heating the catalyst was determined in a glass vacuum system consisting of a volumetric adsorption apparatus equipped with a manostat. Samples of powdered Raney nickel of 0.3–0.4 g in water or ethanol were introduced into a glass sample tube and evacuated at about 10°C to remove adhering water or ethanol. The sample tube was heated in a resistance furnace with the temperature increased linearly to 550°C at a rate of about 1.5°C/min by manual adjustment of a variable transformer. Gas evolution was measured at a constant pressure varying from 20 to 250 Torr. In some experiments helium was introduced at the desired pressure at the start of the procedure, and in others the evacuated catalyst was heated and the manostat operated only after the pressure had attained a given value.

The resulting volume evolved–temperature curves seemed to be independent of the measurement pressure and whether or not helium was present, and there was no consistent variation of the curves with these factors. For the commercial preparation (COM) in 3 experiments, the volume evolved per gram catalyst to a given temperature varied by about ±3%, but for 3 experiments with catalyst IIA the deviations were about ±10%. The volume–temperature curves for different samples of the same catalyst had the same shape, but the volumes differed by a small constant factor. On subsequently cooling the sample to 25°C, the gas volume decreased by 4–6 cc (STP)/g catalyst, presumably due to chemisorption. The weight of the sample was determined after the experiment.

The gas evolved was hydrogen. Trace amounts of hydrocarbons and other organic molecules were found in the gas evolved from catalyst samples that had been stored in ethanol such as IIA.

Catalysts

The preparative methods and the nomenclature used in this laboratory have been described previously (*12*). Particle-size calculations have been made for catalysts on which magnetic measurements were made: Type IIA, extracted at 50°C; Type IIA-B, prepared by heating IIA in 20% aqueous NaOH for 2 hr at 50°C and 2 hr at 107°C; Type IIIA, extracted at 107°C; and COM, a Davison commercial catalyst. Hydrogen evolution measurements were made only on IIA and COM.

PARTICLE SIZE ESTIMATION

The magnetization of nickel in Raney nickel is always substantially smaller than that of bulk nickel, even at high fields and

4 K, and Curie points for Raney nickel are lower than for bulk nickel.

In applying the Langevin equation to the Raney nickel data calculations were made on two premises: (A) the catalyst is an alloy containing nickel, aluminum and hydrogen, and (B) the catalyst contains pure nickel plus a nonferromagnetic nickel component.

Case A

For relative magnetizations greater than 0.75, the Langevin equation using the nomenclature of Selwood (*5*) may be taken as

$$M/M_s = 1 - kT/(HI_{sp}\bar{v}) \qquad (1)$$

where M, M_s, and I_{sp}, magnetization, saturation magnetization, and spontaneous magnetization, respectively, are given per unit volume, and $\bar{v}$ is the average volume of the magnetic particles. In the present studies at high fields $M_s \simeq I_{sp}$. Our data are given per gram Ni, and $M = \sigma\rho f$ and $M_s = I_{sp} = \sigma_s\rho f$, where σ and σ_s are the magnetizations per gram Ni at a field H and at saturation, ρ is the density of the alloy, and f is weight fraction of Ni in the sample. Equation (1) can be rearranged to

$$\sigma = \sigma_s - kT/(\rho f\bar{v}H) \qquad (2)$$

Case B

Here it is assumed that a fraction j of the nickel is metallic nickel and the remainder is nonferromagnetic. The Langevin equation may be written as

$$M/M_sj = 1 - kT/(HI_{sp}\bar{v}) \qquad (3)$$

and

$$\sigma = \sigma_s - kTj/(\rho f\bar{v}H) \qquad (4)$$

where ρ is the density of metallic nickel. For data at a given temperature j is the saturation magnetization of the catalyst per gram Ni divided by the corresponding quantity for bulk nickel.

According to Eq. 2 for a given catalyst (and evacuation temperature) plots of σ as a function of T/H should lead to a family of straight lines of constant slope, a line for each temperature of measurement, as shown in Fig. 1, for data measured in the temperature range 293–473 K. Although a straight line can be passed through the data within the estimated experimental uncertainties, the points indicate a slight upward curvature with increasing magnetization. At lower fractional magnetizations, usually <0.85, the data lie above the line chosen for the plot of the Langevin equation. Data measured at 4 and 77 K give linear plots with a slope that is very much larger than plots for data at higher temperatures. Due to anisotropy and remanence the Langevin equation is usually considered inappropriate at low temperatures (*5*).

For Case A density for the nickel alloy of 8.42 g/cc, estimated for a Ni–Al solid solution with an atom fraction of Al of 0.075, was used (*13*). From the average volume of the magnetic particles, $\bar{v}$, as-

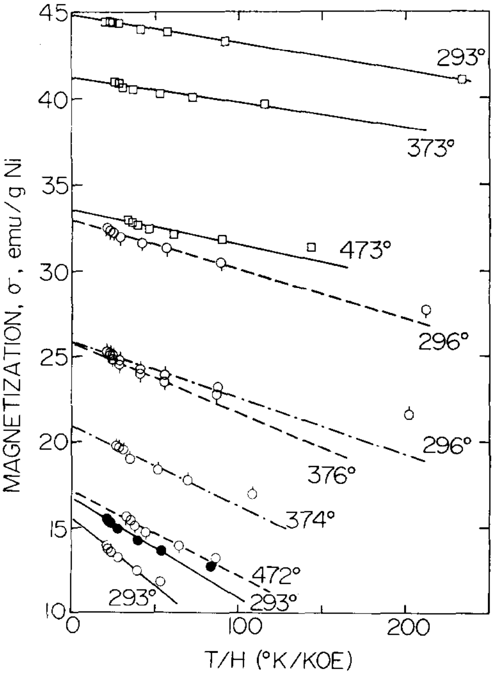

FIG. 1. Langevin plots of data for catalyst IIA. Numbers on the right side of graph are the temperatures of the magnetic measurements in K. Symbols denote the evacuation temperature: ○ 25°C, ● 104°C, ȯ 209°C, ♀ 310°C, and □ 500°C.

suming the crystallites to be cubes, the length of cube edge, l, was computed by $l = \bar{v}^{1/3}$. Values of l tabulated in Table 1 show good agreement for measurements at 2 or 3 different temperatures.

Values of l from Eq. 4, Case B, are also given in Table 1; the particle sizes computed were substantially smaller than those for Case A. The agreement of particle sizes from measurements at different temperatures was not as good as for Case A.

The complete Langevin equation rather than the limiting simplified equation was also fitted to the data by superimposing logarithmic plots. This procedure leads to essentially the same values as simplified Eqs. 2 and 4. This result seems to eliminate the possibility that the sample contains material showing collective paramagnetism plus a ferromagnetic component that saturates at very low fields.

The crystallite sizes for both Cases A and B in Table 1 usually changed in the same order as particle sizes from X-ray diffraction line broadening (*14*) or surface areas (*12*), as the method of preparation or evacuation temperature was varied. The postulates of Case A, that the nickel is present as an alloy, are more consistent with other magnetic data that also suggest that the composition of nickel alloy in the catalyst was not uniform (*1*).

HYDROGEN EVOLUTION RELATED TO MAGNETIZATION

Hydrogen evolution from catalysts IIA and COM was measured at constant pressure as the temperature was increased from 25 to 550°C at a rate of about 1.5°C/min. Data reported for hydrogen evolution in Table 2 are averages of 3 experiments. For IIA gas evolution began at 50–80°C and for COM at about 120°C; these temperatures are somewhat higher than the highest temperature used in the extraction procedure.

TABLE 1

ESTIMATES OF CRYSTALLITE SIZES OF RANEY NICKEL

Sample	Evacuation temp., °C	Average particle diameter, Å, from							
		Magnetic data							
		Temperature of measurement, K							
		Case A			Case B			Surface area	X-ray line broadening
		293	373	473	293	373	473		
IIA	25	64.5			41.7				36
	104	71.2			47.3			57.0	
	209	86.3	77.0		61.1	56.0			
	310	81.6	80.5	75.4	67.8	62.7	53.3		40
	500	108.8	113.1	101.3	100.0	103.0	89.6		57
IIA-B	25	95.7			78.1				
	299	103.2	99.7	97.0	88.0	88.5	83.1		
IIIA	25	89.9			74.5				52
	104	82.4	83.4		72.8	71.6		64.8	57
	204	90.7	87.1	77.9	78.5	73.7	61.8		
	304	89.9	93.1	88.1	83.5	84.4	76.2		
	475	95.5	99.5	97.9	88.7	90.8	84.0		
COM	25	74.3			58.5				50
	103	78.3	79.8		63.2	62.1		75.4	61
	202	86.4			71.3				
	300	94.2		76.7	81.0		61.5		75
	500	92.1	94.4	91.4	79.5	78.3	69.6		104

TABLE 2

Hydrogen Evolution and Magnetization

		All data per g Ni		
Sample	Treatment temp., °C	Hydrogen evolved, cc(STP)[a]	Saturation magnetization, emu, at 0 K	293 K
IIA	25	0	23.0	13.8
	209	38.0	35.4	25.3
	310	66.8	41.9	32.5
	500	78.4	49.6	44.6
COM	25	0	34.7	27.5
	103	0.1	37.4	29.5
	202	5.1	38.8	31.8
	300	14.4	42.3	36.3
	500	23.3	44.5	36.5

[a] Total hydrogen evolved during experiments with linearly increasing temperatures up to the treatment temperature.

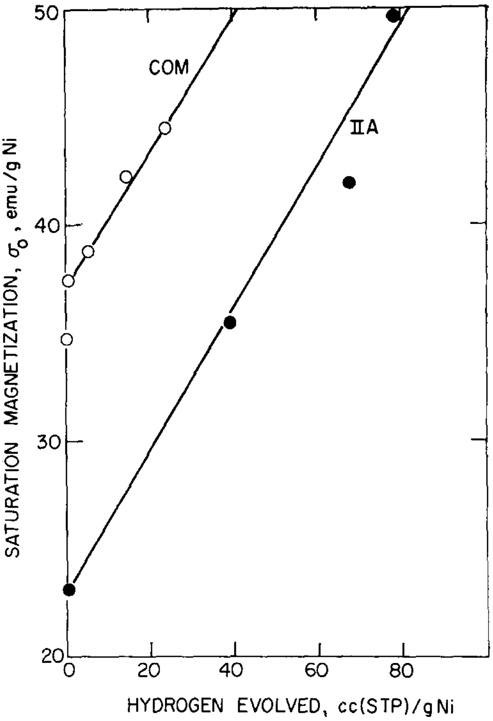

Fig. 2. Saturation magnetization at 0 K as a function of volume of hydrogen evolved.

Before relating gas evolution to magnetization, we note that the treatment of the catalyst in the gas evolution and magnetic experiments differed in the following respects:

(a) In gas evolution tests the catalyst was used in the powder form as obtained in the preparation, but for magnetic studies the sample was pelleted.

(b) Gas-evolution data were obtained at a moderate pressure and with temperature increasing at a slow linear rate, whereas samples for magnetic tests were evacuated at a constant final temperature.

We believe that these differences in procedures do not have large enough effects to invalidate comparison of the data. This situation seems to hold particularly for samples treated at 500°C, because the gas evolution has nearly stopped at this temperature and only increases by 1 or 2 cc as the temperature is increased to 550°C. The same conclusions are reached if only the data at 25 and 500°C are considered.

Table 2 presents hydrogen-evolution data and saturation magnetizations at 0 and 293 K, and Fig. 2 shows a linear relationship between magnetization at 0 K and hydrogen evolved. The slopes of the lines in Fig. 2 correspond to increases in magnetization of 0.62 and 0.65 μ_B per hydrogen atom evolved. Similar plots using magnetizations at 293 K have a less clearly defined relationship, but the slopes of the best straight lines were not greatly different from those in Fig. 2.

Discussion

The magnetic data in our previous paper (*1*) were interpreted as indicating that the activated catalyst was a nickel alloy containing aluminum and/or hydrogen and that the composition of this alloy was not uniform. Particle sizes from the Langevin equation assuming the nickel is present as an alloy, Case A, were about 45% larger than estimates from X-ray diffraction line broadening. If the catalyst does contain nickel alloys of different compositions and presumably different lattice spacing, some additional line broadening would be superimposed on that produced by the fine particles, leading to smaller than actual crystallite diameters. Furthermore, the crystallite diameters from line broadening are generally considered to be useful relative measures rather than absolute values.

The crystallite sizes in Raney nickel from the Langevin equation, 65–100 Å, are relatively large compared with those found in some catalysts containing nickel dispersed on high area supports. Thus, on Raney nickel at the high fields employed in the present work the effects of anistropy and remanence would be expected to invalidate the use of the Langevin equation at low temperatures (*5*). A method based on remanence at low temperatures as used by Weil (*15*, *16*) has given particle size distributions for Raney nickel with maxima at about 130 Å. In the present work the Langevin equations gives constant particle sizes for measurements at 293, 373, and often 473 K. Data at 4 and 77 K lead to very much smaller particles. Langevin plots at the higher temperatures were reasonably linear at relative magnetizations exceeding 0.85 or 0.90, but the data points have a slight upward curvature with increasing magnetization. The cause and significance of the deviations is not known.

The size of the "nickel" particles as given in Table 1, as well as the magnetization, increased with increasing temperatures of preparation and evacuation. The temperature of treatment with aqueous NaOH was very much more effective in increasing the particle size than the temperature of evacuation. Increasing the temperature of aqueous NaOH treatment from 50 to 107°C had about the same effect as increasing the evacuation temperature from 25 to 450°C.

As hydrogen was removed from Raney nickel by heating, the magnetization increased about 0.63 μ_B per hydrogen atom, which may be compared to 0.55–0.60 from other work on Raney nickel (*9*, *11*) and with average values of 0.71 obtained for the chemisorption of hydrogen on supported nickel (*5*, *17*).

According to Eq. (2)[a] of the previous paper (*1*), on increasing X_H from 0 to 0.55 to eliminate ferromagnetism, the average decrease in magnetization is 0.496 μ_B per hydrogen atom. The corresponding value for aluminum is 2.71 μ_B per aluminum atom. The relationship between magnetization per gram Ni and atom ratios of H or Al to Ni is not linear. For very dilute solid solutions the changes are 1.09 and 3.02 μ_B per atom of H or Al, respectively, according to this equation.

If the relative amounts of H and Al in the nickel solid solution are known, the atom fractions of H and Al can be calculated from magnetic data using Eq. 2 of Ref. 1. Taking the limiting cases of the solute being only H or Al, the amount of hydrogen evolved on heating the catalyst to 500°C can be calculated from the magnetic data for samples pretreated at 25 and 500°C. For aluminum it is assumed that 3/2 moles H_2 are produced in the oxidation of 1 atom Al. No correction is made for the differences in the amount of chemisorbed hydrogen at 25 and 500°C, because the change in magnetization would at least approximately account for the chemisorbed hydrogen; i.e., chemisorbed and interstitial hydrogen have the same effect on magnetism. As shown in Table 3 the calculated and experimental values of hydrogen evolved agree within experimental uncertainties for hydrogen as the only solute. For Al as the only solute, as well as for other assumed mixtures of Al and H, the calculated hydrogen evolution is smaller than the value for hydrogen as the only solute. For example, assuming that all of the hydrogen is removed by heating to 500°C and that aluminum is present but not oxidized, results in calculated hydrogen evolutions of 58 and 18 cc (STP)/g Ni for IIA and COM, respectively.

These data support the postulate that hydrogen is the principal solute in the nickel component; however, the importance of this conclusion is decreased by the fact that Eq. 2 has not been established for Ni–H solid solutions. In addition, for hydrogen as the only solute in Ni, the hydrogen remaining at 500°C seems unrealistically large, 25–35 cc (STP)/g Ni.

Prettre and co-workers (*11*) also attributed the increase in magnetization of

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[a] $\sigma_0^* = 57.5\ (1 - 1.82\ nX)$, where σ_0^* is the saturation magnetization at 0K per gram of alloy, $n = 1$ for hydrogen and $n = 3$ for Al, and X is the atom fraction of H or Al in the solid solution. Here, 57.5 corresponds to 0.606 μ_B.

TABLE 3

CALCULATING HYDROGEN EVOLUTION FROM MAGNETIC DATA

		Assuming the nickel component contains			
		Hydrogen only		Aluminum only	
Sample	Pretreatment temp., °C	Atom fraction H[a]	Hydrogen content, cc(STP)/g Ni	Atom fraction Al[a]	Hydrogen content,[b] cc(STP)/g Ni
IIA	25	0.3480	101.9	0.1160	75.1
	500	.1143	24.6	.0381	22.7
	Calculated H_2 evolved		77.3		52.4
	Observed H_2 evolved		78.4[c]		78.4[c]
COM	25	0.2389	59.9	.0796	49.5
	500	.1507	33.9	.0502	30.4
	Calculated H_2 evolved		26.0		19.1
	Observed H_2 evolved		23.3[c]		23.3[c]

[a] From magnetic data, Table 4 of Ref. 1.

[b] Hydrogen that would be liberated if this amount of Al were oxidized by water.

[c] From Table 2.

Raney nickel on heating to the removal of hydrogen bonded to nickel, but stated that this hydrogen was chemisorbed. Although the surface may possibly be large enough to accomodate this amount of hydrogen, 30 cc (STP)/g, it seems unlikely that surface will be completely covered at room temperature (*18*). In the authors' laboratory the hydrogen chemisorbed at 25°C on Raney nickels heated and evacuated in the range 25–200°C was less than 11 cc (STP)/g. The larger amounts of hydrogen evolved from sample IIA (Table 2) certainly cannot be attributed only to chemisorption.

Except for the evidence presented in Table 3, the present paper makes no definitive contribution regarding the source of hydrogen evolved on heating Raney nickel (*9*, *11*), as most of the magnetic results may be explained equally well in terms of release of interstitial hydrogen, decomposition of a nickel "hydride," or oxidation of metallic aluminum by water. Nickel "hydrides" of the type produced in electrolysis (*19*) or by preparing evaporated nickel films in the presence of hydrogen at −196°C (*20*) seem hardly stable enough to be important in Raney nickel. The oxidation of aluminum in high nickel (e.g., 90–95%) Ni–Al solid solutions seem equally unlikely, as these alloys are generally remarkably resistant to oxidation. Submicroscopic islands of Ni–Al alloy containing at least a substantial fraction of the original aluminum and buried within the catalyst particles might be sufficiently reactive; however, this postulate seems inconsistent with the Curie point data because these alloys would probably not be ferromagnetic. Another possibility is the presence of a nickel–aluminum–hydrogen alloy in the activated catalyst. Apparently this system has not been investigated.

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