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Influence of Aluminum and Hydrogen Contents on Magnetic Properties of Raney Nickel Catalysts

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Raney nickel catalysts free from Al_2O_3 have been prepared. Residual metallic Al is within the range 2.2–5.9%. The remanent to saturation magnetization ratio at low temperatures is 0.3, and the magnetic hardness is temperature-independent, indicating a sponge-like structure. When H_2 is completely evolved, saturation data suggest that Raney nickel catalysts are mainly α Al–Ni alloys. H_2 is thought to be mainly located on the surface. The variation of the saturation magnetization per molecule of desorbed H_2 is twice as great as the Ni magnetic moment: thus, adsorbed H_2 may be considered as bonded to two individual Ni atoms, magnetically decoupled from subjacent moments.

INTRODUCTION

Raney nickel catalysts are prepared by leaching out with soda the aluminum in Ni–Al alloys. A small part of the aluminum is not extracted and remains more or less combined with Ni. In the case of an α solution, the saturation magnetization is expected to decrease linearly with Al content within the 0 to 5% range (5% in weight is reported to be the upper limit of Al solubility in Ni). This change in magnetic and electronic properties is likely to affect the adsorptive and catalytic properties and raises the problem of the influence of metallic Al on Raney nickel properties.

A considerable amount of H_2 can be evolved upon heating the catalyst. Since this gas plays an important role in catalysis, various authors have attempted to shed some light on its origin. Besides chemisorption, a number of other possibilities have been considered, namely: (i) formation of a 3-dimensional hydride NiH_2 (*1,2*), (ii) dissolution of H into the bulk (*3,4*) or in interstices (*5*) (substitutional replacement of Ni atoms in the lattice) (iii) generation of H_2 by reaction of Ni with water, according to:

$$Ni + 2H_2O \rightarrow Ni(OH)_2 + 2H_{ads}.$$

This reaction is thermodynamically possible, since H_2 is adsorbed on a nickel surface (*6*), Mars *et al.* (*7*) have suggested that the total amount of evolved H_2 originates from 3 sources:

chemisorbed H_2

reaction of $Al(OH)_3$ with Al present as AlNi or Al_3Ni_2 according to:

$$Al(OH)_3 + Al \rightarrow Al_2O_3 + {}^3\!/_2H_2$$

reaction of adhering water with Al bound in NiAl or Ni_3Al_2.

Finally, in a recent paper, Macnab and Anderson (*8*) have interpreted their magnetic data on the basis of the catalyst containing a solid solution of H_2 (and/or aluminum).

This ambiguous situation prompted us to study Raney nickel catalysts by means of magnetic techniques, which have been shown to be very helpfull in this field (*5,8,9*). To simplify the problem, the catalysts were prepared in such conditions that Al_2O_3 (or $Al(OH)_3$) were completely dissolved in NaOH solution, and then removed from the solid system. In this paper, results on 15 samples containing from 2.2 to 5.9% by weight of Al are presented and discussed.

EXPERIMENTAL METHODS

The catalysts were prepared by leaching a finely ground 46% Ni–Al alloy with a concentrated solution of NaOH. The final Al content in the catalyst was monitored by varying the reaction time. The chemical composition was determined by titration (*10*) of both the metals (Ni, Al) and their oxides (Al_2O_3, NiO), after heating *in vacuo* at about 300°C (both H_2 and H_2O were completely removed). Chemical analysis showed these samples to be free from both Al_2O_3 and NiO. The Al content depended upon the leaching time and was within the range 2.2–5.9%. It is noteworthy that the upper limit of the Al content is of the same order of magnitude as the limit of solubility of Al in Ni, suggesting the formation of the α phase. A complete description of the morphological and catalytic properties of these Raney nickel materials is given in another paper (*11*).

The magnetization of Raney nickel was measured with an electromagnet providing moderate fields (20,000 Oe), at 300, 77, 4 and 2°K, by removing the sample rapidly from a coil. The relative accuracy on the magnetization was 10^{-3}. Some experiments were performed in a superconductive coil (50,000 Oe) at 4.2°K (*12*). The reproducibility and accuracy were better than 2×10^{-5}. Raney nickel catalysts were introduced in a glass sample holder containing water. After evaporating, molten paraffin was introduced *in vacuo* to embed the sample. In order to study the influence of evolved H_2 on saturation magnetization, powder was merely packed in the sample holder. It was checked that the moderate compression used here did not affect significantly the magnetic properties (remanence, coercive field, and saturation were found to be identical in the perpendicular and parallel direction of compression). Some experiments were performed at 0.16°K by adiabatic demagnetization. In these cases, samples were embedded in an "Apiezon" grease matrix, in order to ensure thermal conductivity.

RESULTS

A typical curve of the variations of the 4.2°K magnetization M with field strength H is shown in Fig. 1.

High Field Properties

Saturation magnetization M_s can be determined in the following manner. When M is plotted against $1/H$ (Fig. 2), a straight line is generally obtained when H varies within the 5– kOe range. For low fields, experimental points are located below the straight line, indicating the existence of a $1/H^2$ term in the saturation law.

At higher fields, the observed results are accounted for by a superimposed susceptibility $\chi = 10^{-6}$ emu/g. (It is noteworthy that this susceptibility is of the same order of magnitude (*11*) as the susceptibility of bulk and pure nickel). The saturation law

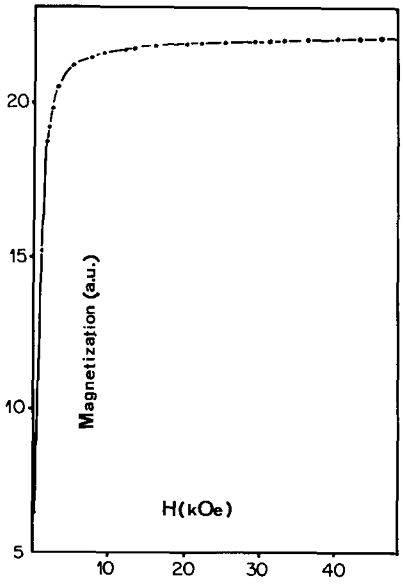

FIG. 1. The 4.2°K magnetization (arbitrary units) as a function of the field strength H (sample containing 5.5% Al, heated *in vacuo* at 100°C).

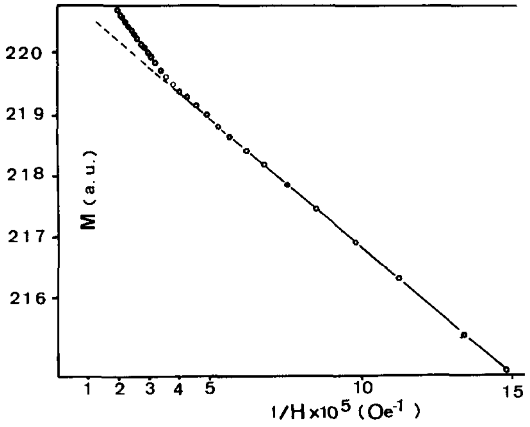

FIG. 2. Magnetization M (arbitrary units) versus reciprocal field for the same sample as in Fig. 1.

can be formally written as:

$$M = M_s(1 - a/H - b/H^2) + xH.$$

A very accurate determination of M_s can be achieved by extrapolating linearly the M–H curve to zero applied field. This method (*12*) cannot be used here, because fields higher than 50 kOe are required to observe a linear relationship between M and H (Fig. 1). Less accurate results are obtained using a $1/H$ extrapolation in the 5–20 kOe field region. The magnetization variations which are observed during H_2 evolution are so large that this method gives a sufficient accuracy, and $1/H$ extrapolation has been used in this work to calculate saturation magnetization.

The a coefficient (magnetic hardness) is of some interest from the morphological viewpoint. Some observed hardness values are listed in Table 1.

Two particular situations may give rise to a $1/H$ law: (i) the material is so finely divided that each particle is a single domain; (ii) the metal contains nonmagnetic inclusions such as holes. In the former case, a is proportional to T, the measurement temperature and to the inverse of the particle volume (*9*). In the latter case, Néel (*13*) showed that a is temperature independent, and varies with V, the volume fraction of nonmagnetic inclusions.

TABLE 1

MAGNETIC HARDNESS OF Ni RANEY CATALYSTS

Sample no.	Al (%)	Treatment temp (°C)	Measurement temp (°K)	a (Oe⁻¹)	V
1	2.56	26	4.2	230	0.36
		160	4.2	240	0.38
		320	4.2	250	0.39
		460	4.2	190	0.32
2	3.5	20	4.2	170	0.30
		20	77	160	0.29
		20	300	140	0.26
3	4.7	20	4.2	190	0.32
4	5.2	20	300	235	0.37

From Table 1 it can be seen that a does not vary significantly with measurement temperatures; thus, the hypothesis of nonmagnetic inclusion is very plausible. The volume fractions of inclusions, calculated from a (*13*), are listed in Table 1. They are in good agreement with density measurements obtained by helium techniques (*5*). Another feature is the independence of V on treatment temperature: this morphological stability is not surprising since these temperatures do not exceed the Tammann temperature. All these results are hardly compatible with a model of Ni spheres, but fit better with a sponge-like structure, as suggested in earlier works on Raney nickel catalysts.

Low Field Properties

The remanent to saturation magnetization ratios (M_r/M_s) for some samples are listed in Table 2: at very low temperatures a limit of 0.3 was observed for M_r/M_s. It can be deduced that the system cannot be described as an assembly of noninteracting single domains, since this limit is expected to be 0.5 (case of uniaxial anisotropy, stressed nickel Ni–SiO_2 catalyst) or about 0.8 (magnetocrystalline anisotropy). Thus, the remanence method cannot be applied

TABLE 2
M_r/M_s FOR SOME SAMPLES

Sample no.	Al (%)	Treatment temp (°C)	Measurement temp (°K)	M_r/M_s
1	2.56	100	4.2	0.28
2	3.5	100	298	0.165
		100	77	0.243
		100	4.2	0.32
		100	2.2	0.32
		100	1.4	0.32
		100	0.16	0.32
3	4.76	Not treated	4.2	0.32
		23	4.2	0.30
		198	4.2	0.197
		430	4.2	0.16

to obtain Raney catalyst granulometry, as has been previously supposed (*14*).

Various hypotheses may be invoked to account for the 0.3 value for M_r/M_s. Flux-closure configurations may keep clusters from contributing to the remanence of the system (*15*). However, it is difficult to understand why M_r/M_s at low temperature is the same for the 3 samples studied; it would suggest that the percentage of clumping particles would be identical, an unlikely feature because of morphological differences (BET surfaces, pore radii) as can be seen elsewhere (*11*).

The second possible way involves polydomain particles, and the superposition of a cubic magnetocrystalline anisotropy and uniaxial anisotropy (due to stresses). In this case, the calculated value for M_r/M_s is 0.278 (*17*), a value which is very close to the observed one. It may be concluded that low field properties are not compatible with a model of single domain particles, but are consistent with a sponge-like structure, which was previously proposed.

Variation of Saturation Magnetization with Al and H_2 Contents

Figure 3 shows the specific saturation magnetization (measured at 300°K) of various samples as a function of the amount of evolved H_2. The gas has been desorbed by heating the samples stepwise up to about 500°C, and collected in the rough vacuum volume of the pumping system where the pressure increase has been measured (*10*).

Results of magnetic measurements performed at 4.2°K are plotted in Fig. 4. These data indicate that saturation magnetization increases linearly with the amount of evolved H_2 until about 80–90% is removed. As first observed by Kokes and Emmett (*5*), removal of the last traces of H_2 causes a rather sharp drop in magnetization. The final saturation magnetization thus obtained depends upon Al content, as appears clearly from Fig. 5, where σ_s has been plotted versus Al content. The

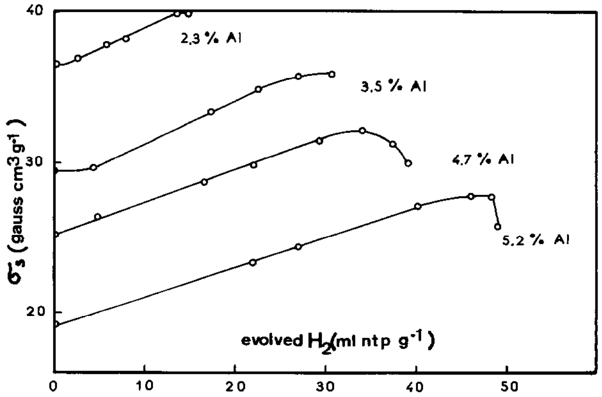

FIG. 3. Specific saturation magnetization measured at 300°K as a function of the volume of evolved H_2.

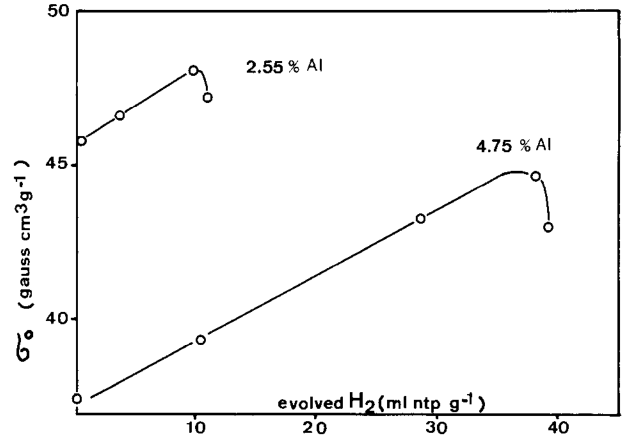

FIG. 4. Specific saturation magnetization measured at 4.2°K as a function of the volume of evolved H_2.

curves can be compared with data given in the literature for bulk Ni–Al alloys (*17*). The agreement is satisfactory, especially for low Al concentrations, indicating that Raney nickel catalysts are mainly α Al–Ni alloys, as we suggested previously (*10*). At higher Al concentrations, part of this metal is either inactive or less efficient in decreasing the saturation magnetization: some Al clusters, or nonmagnetic Ni–Al alloys may be formed besides the α phase. The diffusion of Al from these Al patches into the α phase due to thermal agitation may explain (*5*) the drop of magnetization observed in the high temperature region of Figs. 3 and 4.

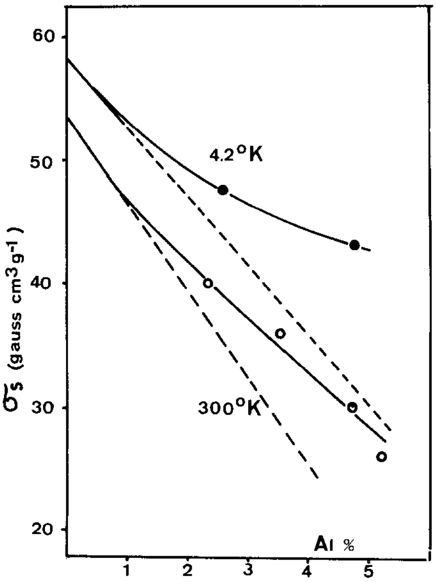

FIG. 5. Specific saturation magnetization of desorbed samples as a function of Al content; (--) corresponding curves for bulk Ni–Al alloys [see for instance Bozorth, R. M., *in* "Ferromagnetism," p. 300. Van Nostrand, New York, 1953 (*16*)].

The linear increase of σ_s with the amount of evolved H_2 is only due to H_2 evolution. The slopes vary with Al content, thus, with the final saturation magnetization (after treatment at 500°C). If the slope α is expressed in Bohr magnetons (μ_B) per H_2 molecule, and the final saturation magnetization in Bohr magnetons per Ni atom (magnetic moment of Ni atoms, μ), the curves of Fig. 6 are obtained. The formulas which are used to calculate α and μ from macroscopic data are:

$$\mu = 1.114\ 10^{-2}\ kM_s,$$
$$\alpha = 4\ k\Delta M_s/\Delta q,$$

where μ and α are expressed in Bohr magnetons, M_s and ΔM_s in gauss cubic centimeters per gram, Δq in milliliters NTP per gram k is a temperature coefficient, nearly equal to 1, taking into account the small variations of M_s with temperature (for pure Ni, $k = 1$ at 4.2°K and 1.056 at 300°K; it is assumed that k is nearly the same for Raney Ni). Data for pure nickel (*18*) are also reported in Fig. 6 and it can be seen

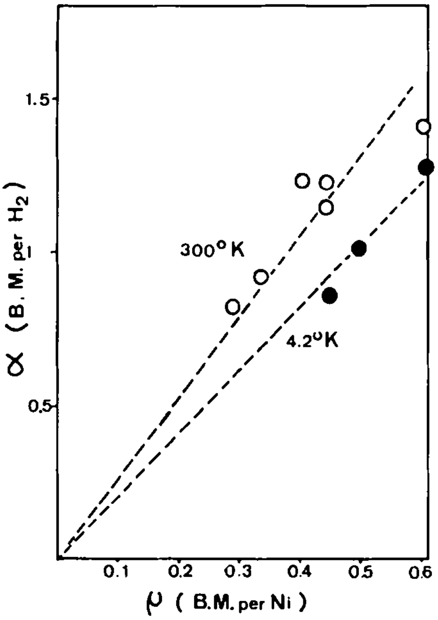

FIG. 6. α (magnetic moment increase per molecule of desorbed H_2), as a function of μ (saturation magnetization).

that all experimental points are located on straight lines obeying the following law:

$$\alpha = k'\mu,$$

with $k' = 2$ at 4.2°K and 2.3 at 300°K. Unfortunately, experimental values cannot be obtained for low μ due to the Al solubility upper limit.

DISCUSSION

The observed α values enable us to rule out some of the hypotheses about the nature of H_2 in Raney nickel catalysts. The reaction of adhering water with Al ($3H_2O + 2Al \rightarrow Al_2O_3 + 3H_2$) would lead to an increase of M_s, which can be calculated in the following way: as $3H_2$ are evolved, 2 Al atoms are extracted from the alloy; Al lowers saturation magnetization by 3 μ_B, then, evolution of one H_2 molecule corresponds to an increase of $M_s : \alpha = (2 \times 3)/3 = 2\ \mu_B$. This value is not consistent with the observed one. In the same way, the reaction $H_2O + Ni \rightarrow NiO + H_2$, for which the corresponding α value is negative, can be excluded. The hypothesis of dissolved or adsorbed H_2 is now considered. Figure 6 (α vs μ) indicates a continuity between points corresponding to Raney catalysts and to pure nickel. As H_2 is thought to be adsorbed on pure Ni rather than dissolved (*18*), it could be deduced that the situation is the same for Raney nickel catalysts.

However, as α values for adsorbed or dissolved H_2 in (on) pure nickel are very close (*19*), magnetic data do not allow an unambiguous discrimination between the two possibilities. Only the fact that BET surfaces and catalytic activities for acetone hydrogenation are proportional to the amount of evolved H_2 (*11*), shows clearly that H_2 is mainly on the surface of these catalysts.

Figure 6 suggests that the variation of magnetization per adsorbed molecule is twice as large as the magnetic moment of Ni atoms in the investigated range. This result fits fairly well with the concept of a localized adsorption on individual nickel atoms which are magnetically decoupled from subjacent moments upon chemisorption (*20*).

It is noteworthy that k (the slope of the curves of α vs μ), is slightly temperature dependent ($k = 2$ at 4.2°K and $k = 2.3$ at 300°K).

This result may be explained assuming that at room temperature, magnetic moments are higher on the surface than in the bulk. This view has recently gained some theoretical support: Levy *et al.* (*21*) have introduced surface anisotropy coupling to describe the surface conditions in ferromagnetic compounds. They have shown that the distribution of the magnetization from the surface to the bulk at finite temperatures is not uniform and that in some cases ("hard surfaces"), surface magnetization is higher. This distribution is flat at very low temperatures. Their conclusions account for the observed variations of k with temperature.

CONCLUSION

Magnetic measurements performed on Raney nickel catalysts containing from 2.2 to 5.9% Al show that these solids may be considered as α alloys, with a sponge-like morphology: they cannot be considered as an assembly of noninteracting small particles. This makes the use of magnetic methods of granulometry rather hazardous.

Evolved H_2 cannot be the result of the reaction of H_2O with metallic Ni or Al. Experimental observations can be best interpreted assuming that H_2 is mainly present as chemisorbed gas. The variation of saturation magnetization per molecule of desorbed H_2 is twice as great as the magnetic moment of Ni. Adsorbed H_2 may be considered as bonded to two individual Ni atoms, magnetically decoupled from subjacent moments. It should be emphasized that the above conclusions hold only for the present samples, for which special care was taken to ensure complete removal of Al_2O_3, making comparison with samples containing aluminum oxide difficult.

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