# Ferromagnetic Resonance Determination of Nickel-Hydrogen Magnetization–Volume Adsorption Isotherms

The effect of chemisorbed hydrogen on the magnetization of finely divided nickel has been investigated by several authors (*1–4*), most of whom used catalytically active preparations in various forms. Most previous studies of these phenomena have been made by static or low-frequency methods. In this note we present the theory, and some experimental data, related to the incremental chemisorption of hydrogen on nickel as studied by electron spin resonance techniques which yield, in this instance, the integral ferromagnetic resonance (FMR) absorption, $A$, defined by

$$A = Ng^2S(S+1)/T \qquad (1)$$

where $N$ is the number of uniform particles of total spin quantum number $S$ in a sample; $g$, the splitting factor; and $T$, the absolute temperature (*8, 9*).

The total spin quantum number (*10*) in a nickel particle containing $n$ atoms is approximately

$$S = 0.6n/2 \qquad (2)$$

Subsequent to the chemisorption of hydrogen, electron spin pairing changes $S$ to $S'$ (*11*) defined by

$$S' = (0.6n - \epsilon n_{\mathrm{H}})/2 \qquad (3)$$

where $\epsilon$ is the number of spins paired by one chemisorbed hydrogen atom and $n_{\mathrm{H}}$ is the number of hydrogen atoms adsorbed per particle. [This definition of $\epsilon$ is effectively the same as used previously for the low-frequency case given in ref. (*11*), p. 81].

Then, letting $A'$ be the integral FMR absorption subsequent to adsorption of hydrogen, we have the residual absorption

$$\frac{A'}{A} = \frac{S'(S'+1)}{S(S+1)}$$

and if $n$ is always large, then $S^2 >> S$ and $S'^2 >> S'$ so that

$$\begin{aligned} \frac{A'}{A} \doteqdot \left(\frac{S'}{S}\right)^2 &= \frac{[(0.6n - \epsilon n_{\mathrm{H}})/2]^2}{(0.6n/2)^2} \\ &= \left(1 - \frac{5\epsilon n_{\mathrm{H}}}{3n}\right)^2 \\ &= \left(1 - \frac{5\epsilon N n_{\mathrm{H}}}{3Nn}\right)^2 \end{aligned}$$

$Nn_{\mathrm{H}}$ being the total number of hydrogen atoms adsorbed on a sample containing $Nn$ nickel atoms. This expression is approximately analogous to that derived for the low-frequency case, ref. (*11*), p. 105, with the same reservations concerning the arbitrary simplifying assumption that all particles are the same size. It follows that a plot of magnetization vs. volume obtained in this way should be a straight line over the experimentally realizable region.

Equation (6) above may be expected to be valid provided that the following three conditions apply: First, there must be no change of $g$ during the adsorption; second, magnetization of the particle must be isotropic, and third, there must be no skin effect. That supported nickel samples meeting these conditions are readily prepared was shown in an earlier paper (*5*).

Figure 1 shows $(A' - A)/A$ plotted against volume of hydrogen adsorbed for a supported nickel-silica sample [No. 1 of ref. (*5*)]. These data were recorded with a Varian V-4502 X-band spectrometer with 100-kc/sec field modulation. The vacuum system and experimental procedure were

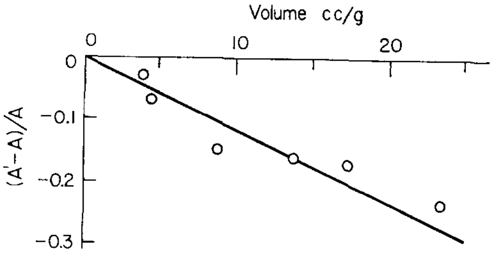

FIG. 1. Magnetization–volume isotherm derived from FMR absorption for nickel-hydrogen sample 1, ref. (*5*) showing the normal effect of a superparamagnetic assembly.

previously described (*5*). The nickel-silica sample, No. 1, contained 14.7% Ni, and X-ray linewidth broadening gave a mean nickel particle diameter of 30 Å. The magnetization–volume isotherm was constructed from the integral absorptions, $A$ before, and $A'$ after, adsorption of a measured volume of hydrogen at 25°C. Integral absorption was found for every point by fourfold graphical integration (*6*) of the FMR signal recorded at constant conditions. The maximum error of about 15% was due to graphical integration.

From Eq. (6) and Fig. 1 an estimate may be made of $\epsilon$. This yields $\epsilon = 0.46$ which, corrected for temperature (*4*) becomes 0.51. It is doubtful if this is significantly less than the value, $0.56 \pm 0.09$, previously reported (*3*) for a similar nickel-silica sample.

A sample exhibiting magnetic anisotropy or skin effects is not suitable for the determination of $\epsilon$ as above. Figure 2 shows $(A' - A)/A$ versus volume for sample No. 2 of ref. (*5*). This sample contained 36.2% Ni and particles of mean diameter 60 Å. As could have been predicted from the low-frequency studies on similar samples, the magnetization showed an increase after hydrogen adsorption owing to the effect of hydrogen in diminishing the magnetic anisotropy. Experimental criteria for the absence of such effects, corresponding to criteria for superparamagnetism in classical studies, include the following: (a), no change of $g$ from near 2.22 during adsorption; (b), homogeneous broadening of the FMR signal; (c) relatively narrow linewidth; and (d), *decrease* of magnetization after hydrogen adsorption.

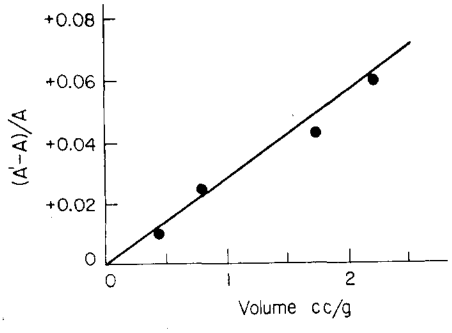

FIG. 2. Magnetization–volume isotherm for sample 2, ref. (*5*) showing the effect of (anisotropy induced) deviations from superparamagnetism.

ACKNOWLEDGMENTS

This work was in part performed under a grant from the Army Research Office (Durham). Grateful acknowledgment is made to the Bulgarian Academy of Sciences for assistance given to A. A. A.

## REFERENCES

1. SELWOOD, P. W., ADLER, S., AND PHILLIPS, T. R., *J. Am. Chem. Soc.* **76,** 2281 (1954); **77,** 1462 (1955); MOORE, L. E., AND SELWOOD, P. W., *ibid.,* **78,** 697 (1956); SELWOOD, P. W., *ibid.,* **78,** 3893 (1956); **79,** 3346, 4637 (1957); **83,** 1033, 2853 (1961).
2. BROEDER, J. J., VAN REIJEN, L. L., AND KORSWAGEN, A. R., *J. Chim. Phys.* **54,** 37 (1957).
3. DIETZ, R. E., AND SELWOOD, P. W., *J. Appl. Phys.* **30,** Suppl. 102S (1959); *J. Chem. Phys.* **35,** 270 (1961).
4. HAHN, A., AND LÖCKENHOFF, D., *Phys. Kondens. Materie* **2,** 284 (1964).
5. ANDREEV, A. A., AND SELWOOD, P. W., *J. Catalysis* **8,** 375 (1967).
6. WILLERS, F. A., "Practical Analysis, Graphical and Numerical Methods." Dover, New York, 1948
7. MOLIN, U., *et al., Zavodskaja Lab.* **32,** 933 (1966).
8. INGRAM, D. J. E., "Free Radicals," pp. 33–34, 97–98. Academic Press, New York and London, 1958.
9. LOY, B. R., AND NODDINGS, C. R., *J. Catalysis* **3,** 1 (1964).

*10.* Ingram, D. J. E., "Spectroscopy at Radio and Microwave Frequencies," p. 196. Butterworth, London, 1955.

*11.* Selwood, P. W., "Adsorption and Collective Paramagnetism." Academic Press, New York and London, 1962.

*12.* Geus, J. W., Nobel, A. P. P., and Zwietering, P., *J. Catalysis* **1**, 8 (1962).

A. A. Andreev
P. W. Selwood

*Department of Chemistry*
*University of California*
*Santa Barbara, California*

*Received February 6, 1968;*
*revised June 6, 1968*

# Inhibition of Silica-Alumina-Chromia Polymerization Catalysts

Controlled amounts of water, oxygen, acetaldehyde, trimethylmonochlorosilane and argon have been added from the gas phase to the catalyst and its activity determined. With water and oxygen inhibition proved reversible. The results could be explained by assuming that inhibition occurred by adsorption and above a critical partial pressure of inhibitor also by reaction at the active site. Activation of the catalyst increased the number of active sites rather than their specific activity. The rate of polymerization was not diffusion controlled under the prevailing conditions.

Silica-alumina-chromia catalysts for ethylene polymerization are known to be sensitive to traces of foreign substances, notably water, oxygen, and oxygenated hydrocarbons. Most previous work on the action of poisons has been performed in the presence of solvents (*1*, *2*, *3*) which might modify poison activity. Recently Kazanski and Turkevich discussed the influence of oxygen and water (*4*) on the activity of the catalyst when polymerization was carried out in the gas phase.

In this work the action of inhibitors was studied quantitatively by adding minute controlled amounts which caused only slight reduction in the activity of the catalyst. The dose of the inhibitor was then increased in successive runs until the catalyst became completely inactivated. The inhibition curves thus obtained show significant differences between the various poisons. The results are consistent with the hypothesis that $Cr^{IV}$ is the active species (*5*).

## EXPERIMENTAL

The method for preparing the catalyst and for measuring activity were the same as reported before (*5*). The amount of inhibitor to be added was determined by reading the pressure when the gaseous inhibitor was contained in a vessel the (small) volume of which was exactly known. The gas was then transferred to the reaction vessel, containing the catalyst which adsorbed the inhibitor.

## RESULTS

The first poisons to be investigated were oxygen and water. As can be seen from Fig. 1, small amounts of both had a strong inhibiting effect. But while additional amounts of oxygen depressed the activity of the catalyst further, the activity curve for water inhibition showed a shoulder.

The effect of oxygen and of water was reversible; evacuation at 300° restored the original activity of the catalyst. However, when after poisoning with oxygen evacuation was carried out at 200°, only about 60% of the original activity could be restored and at 100° evacuation did not restore activity at all.

Experiments were carried out with two catalysts prepared in identical ways except that Catalyst A was treated with 10 mg of ethylene per gram of catalyst at 100° and evacuated at 300° while Catalyst B re-