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A Ferromagnetic Resonance Study of Chemisorbed Hydrogen on a Nickel Catalyst

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Complete demagnetization of metallic nickel by reaction of hydrogen with a Dow $NiCa_8(PO_4)_6$ catalyst is studied with electron spin resonance. Such catalytic domains are of the order of 400–1000 nickel atoms and are presumed to be films on the surface of unreactive catalyst. In the Curie point determination of "superparamagnetic" particles, ESR shows no significant lowering of the Curie point as opposed to results of bulk magnetic measurements. The magnetically active fraction of the catalyst is only 4% of the total nickel and approximately this amount of oxy or peroxy radical is generated during the oxidation cycle.

Hollis and Selwood (*1*) have reported on the ferromagnetic resonance of finely divided nickel and the effect of chemisorbed hydrogen on the resonance. Chemisorbed hydrogen accounted for an 18% decrease in ferromagnetism for nickel particles with an average radius of 15 Å. According to Selwood (*2*) chemisorbed hydrogen is expected to pair off enough *d* electrons to cause the ferromagnetism to fail completely if the radius is of the order 6.5 Å or less. As a supplement to this work, we wish to report the complete demagnetization of ferromagnetic domains by chemisorption of hydrogen on a commercial catalyst and to illustrate major differences between thermal magnetic curves determined by resonance methods as compared to static measurements, especially with respect to sub-domain or superparamagnetic particles.

In this article we shall study the reaction of hydrogen with the catalyst by two methods, (No. 1) by plotting the magnitude of the ferromagnetic resonance as a function of hydrogen treatment and (No. 2) by saturating the active nickel sites with hydrogen and observing the increase in the resonance signal after evacuation.

EXPERIMENTAL

The material used in these experiments was Dow "Type A" (*3*) butene-butadiene catalyst, which is a coprecipitated calcium-nickel phosphate salt of approximate composition $NiCa_8(PO_4)_6$ pelleted with an organic binder and fired at 650°. The pellets are cylinders 5 mm in diameter and 5 mm long.

The ESR spectrometer previously described (*4*) has been modified to use a 50-kc modulation system and the Varian V4531 cavity. The microwave circuit is similar to that described by Ludwig (*5*) with the exception that a circulator is used in the bridge rather than the hybrid Tee.

Most of the spectra were taken with a modulation field of 5 gauss and a microwave frequency of 9069 mc ($H_1 = 0.27$ gauss). In the temperature range, 100–400°, the spectrometer (*4*) using 700 cps field modulation was used to penetrate the thicker walls of the high temperature cavity. This TE_{102} cavity was constructed of ordinary brass X-band wave guide to operate as a reflection cavity and was connected to an electrically heated brass block. The temperature was controlled by means of a Variac and determined with a chromel-alumel thermocouple.

The first approach was to reduce the pellet with hydrogen for a 15-min interval at a constant temperature. After reduction, the pellet was examined by ESR at room temperature in air. The sample was returned to its initial oxidation state by allowing it to react with air for a period of 30 min at its reduction temperature. At the end of the reduction–oxidation cycle, the pellet was examined again by ESR at room temperature to confirm complete oxidation. This cycle was repeated with the same pellet for various temperatures between 400° and 800°C. It has been our experience that the reaction is reproducible when cycled at a constant temperature if a trace of moisture is present, but slightly erratic results are obtained if the gases are dried. Bubbling the gases through water at room temperature is sufficient. The reaction was accomplished in a U-shaped Vycor tube which could be easily set in and lifted out of a standard laboratory combustion furnace. The procedure was to flush the system with the reacting gas before setting it in the furnace and to allow the sample to cool to room temperature in the presence of the gas after removing it from the furnace.

The second method of studying the reaction is similar to that of Hollis and Selwood (*1*). We reduced the sample in a stream of hydrogen at 1100° for 1/2 hour and obtained the magnetic resonance spectrum before and after evacuation at 1100° for 1 1/2 hours.

A thermal magnetic analysis was made of a pellet which was reduced with hydrogen for 15 min at 650°. The temperature of the microwave cavity was varied from room temperature to +400° while recording ESR spectra.

Results and Discussion

Figure 1A shows typical ESR spectra taken after reduction and oxidation cycles by method No. 1. Note that the spectrum of the oxidation cycle very nearly coincides with the base line, indicating little or no resonance, while the reduction cycle spectrum is a relatively large signal. Since the number of nickel ions in the "OX" spectrum is equal to or greater than the nickel atoms in the "RED" spectrum, these spectra serve to emphasize the difference between paramagnetic and ferromagnetic particles and to show the reversibility of the reaction. The line shape of the "RED" spectrum is very nearly gaussian, which indicates little or no exchange between the magnetic particles. The line width (720 gauss) is somewhat larger than found by Hollis and Selwood (470 gauss) (*1*). Their spectrum indicates a large amount of Lorentzian

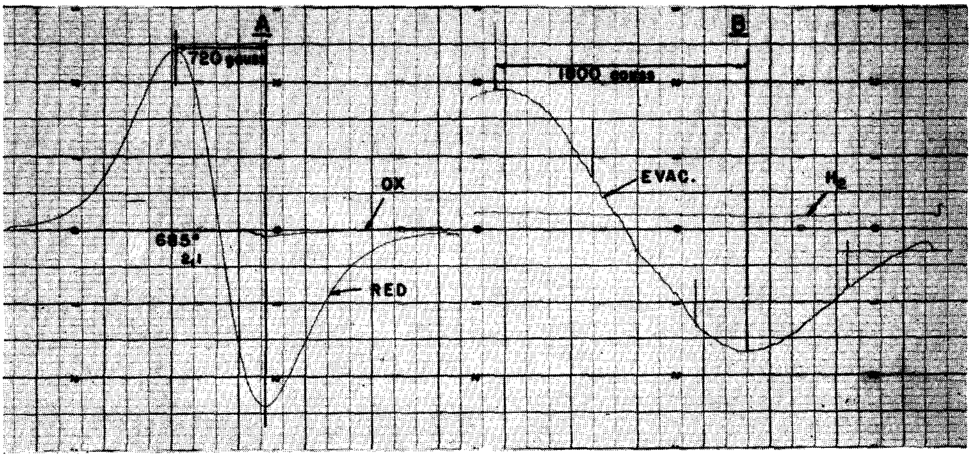

FIG. 1A. Spectra showing increase in magnetic resonance after reduction (RED) at 685° and decreases after oxidation (OX) at 685°. The spectroscopic splitting (g) factor is 2.22. B. Straight line (H_2) indicates no unpaired d electrons after reduction of 1100°. Evacuation (EVAC) at 1100° produces broad magnetic resonance from metallic nickel. The g value is approximately 2.55.

character which would indicate more exchange between domains.

We want to note the small asymmetrical line which appears in the oxidation-cycle spectrum of Fig. 1A. This line has a g value close to 2.0 and when amplified (Fig. 4) is very similar to asymmetric spectra reported for oxy and peroxy radicals (*6*, *7*). Such spectra are expected for randomly oriented, nonrotating free radicals having an anisotropic g factor.

The composite results of the first type of experiment are shown in Fig. 2, where the relative ESR absorption is plotted as a function of hydrogen treatment. The latter axis is a constant time and variable temperature coordinate and is labeled "H_2 Reaction." We interpret the results in Fig. 2 as two reactions. In samples treated below 670°, hydrogen reduces the divalent nickel ion to metallic nickel. For samples treated above 670°, the predominant reaction is hydrogen pairing off the d orbitals which can be thought of as hydride formation in or on the nickel crystallites. There is a color change associated with the reactions. Proceeding from left to right along the "H_2 Reaction" axis, the color changes from white to blue to blue-black to black. The blue color is apparently associated with the highest free nickel concentration. This may appear unusual, since a gray or black color is normally associated with a reduced metal catalyst but could be accounted for by a dilute solution of metallic nickel (ca. 0.2%). Possibly, the black color normally observed is a "hydride" coating and the gray is simply a mixture of the two colors. It may even be associated with some other component of the catalyst. It may also appear strange that the demagnetization reaction seems to occur at a higher temperature than the reduction temperature. We do not mean to infer that no demagnetization occurs below 670° but that the magnetic product of the reaction predominates over the diamagnetic product in this temperature region for this reaction time. In another experiment (*8*) the catalyst was reduced with hydrogen at 654° and samples were taken intermittently over a 2 hr period. In this case the ESR signal was a maximum at 15 min and gradually reduced to a negligible value at 120 min. Both reactions do occur at the same temperature but the rate of the first is significantly greater than the second. The ratio of the half-lives at 654° was estimated to be 1/16. We find that severe hydrogen treatment increases the pellet strength be a factor of two. X-ray analysis detects no free nickel in treated samples. However, as will be shown later, the Ni° concentration is too low for X-ray detection even if the domains were large enough. Samples, hydrogenated at 1000°, were compared with untreated samples by infrared analysis. No IR evidence was found for a nickel–hydrogen bond, although definite but uninterpreted differences were seen in the IR spectra.

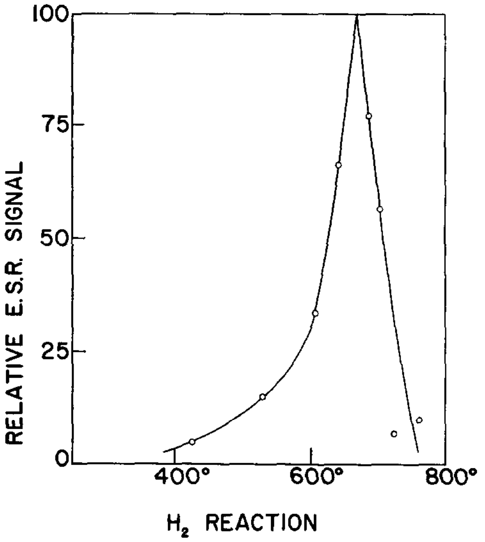

FIG. 2. ESR as a function of hydrogen treatment. Graph shows increase in ferromagnetism below reaction temperature of 670°. Above 670°, hydrogen reduces ferromagnetism by pairing off d electrons.

Figure 1B shows the ESR spectra of a sample which was hydrogenated for 1/2 hr at 1100° before and after evacuation for 1 1/2 hr at 1100°. Before evacuation according to method No. 2, the color is jet-black and there is no ESR signal, which is evidence for complete demagnetization of the particle. After evacuation the color change from black to blue is accompanied by the appearance of a very broad magnetic resonance line, illustrating the return of the magnetic species. There appears to be an anomalous change in the *g* value from 2.22 to 2.55 in the Figs. 1A and B indicating some unexplained difference in the magnetic species produced by the two methods.

These pellets show remarkable thermal stability at 1100° whereas a pure $Ni_3(PO_4)_2$ pellet will sinter and break up under the same conditions. A partially reduced pellet can be stored in air for several months without loss of ESR signal, indicating that the magnetic particles are protected by an impermeable substrate. There is considerable loss of signal if the sample is powdered and exposed to air. These observations and the fact that the reducibility of a $NiO-SiO_2$ system decreases with increasing quantities of SiO_2 (*9*), indicates that the "redox" kinetics of this system may be for the most part related to the high percentage of calcium phosphate support.

Figure 3 is a plot of ESR signal as a function of temperature. The Curie point at 360° serves to identify the magnetic resonance as ferromagnetic nickel. Since the magnetic species is oxidized in the presence of air at increased temperatures, this experiment was performed under a blanket of nitrogen. The ESR signal, of course, returned reversibly, upon cooling.

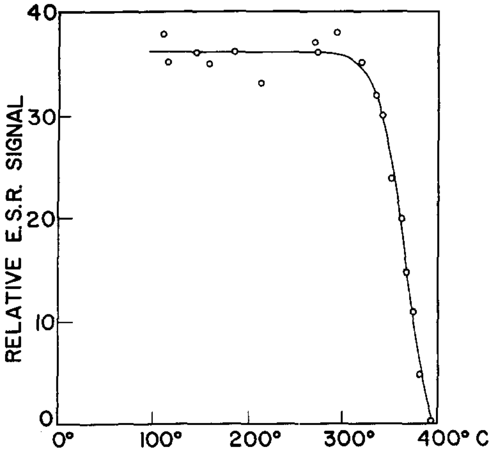

FIG. 3. Thermomagnetic analysis by electron spin resonance. Curie point at 360° identifies resonance as ferromagnetic nickel.

The ESR signal is not proportional to concentration since the line width and cavity *Q* vary somewhat with temperature. According to the literature (*2*), particles small enough to show complete demagnetization by chemisorption of hydrogen should show a significant lowering of the Curie point. We hope to reconcile this difference by making the obvious point that resonance methods detect and measure transitions in individual domains. Bulk measurements include coupling between domains; hence with small isolated particles, this coupling will be disturbed by thermal energy. Since no coupling is indicated in the line shape, it is predicted that static measurements would have difficulty in detecting the Curie point. It is a matter of regret that there are no facilities available in this laboratory to attempt this type of measurement. The expression for ferromagnetic resonance of small spheres, or particles that are small in all dimensions, is the same as for normal paramagnetic resonance (*10*). Therefore we expect particle size and thermal vibrations to be reflected in line width rather than in masking the Curie point. It is noted that the popular expression relating the Curie temperature and the exchange integral (*11*), $T_c = 2JzS(S + 1)/3k$, does not include dimensions other than in z (the number of nearest neighbors). It has been shown that ferromagnetism in the iron group will occur only if the ratio of the atomic radius (half the internuclear distance in the crystal) to the radius of the unfilled $3d$ shell is 1.5 and slightly higher (*12*), and that the exchange energy decreases as the atomic radius increases. We may view kT_c as that energy necessary to produce a sufficiently large atomic radius that the exchange is inoperative.

An order of magnitude calculation of domain size was made on the basis of the following experiment. One hundred fifty pellets consumed an average of 0.254 ml of hydrogen per pellet at 640° and atmospheric pressure. Assuming one nickel atom per hydrogen molecule, we have 2.23×10^{18} Ni°/pellet, which is about 4% of the nickel present. The area under the magnetic resonance curve for one of said pellets is equivalent to 2.83×10^{19} Mn^{2+} in a reference sample of $MnSO_4 \cdot H_2O$. Since the integrated absorption curve (area) is proportional to the (magnetic moment)^2, the number of paramagnetic species present and inversely proportional to absolute temperature (*13*, *14*), we then have:

$$N_s = \frac{T_s A_s g_0^2 (S_0)(S_0 + 1) N_0}{T_0 A_0 g_s^2 (S_s)(S_s + 1)}$$

where

N = number of paramagnetic species,
A = area under the absorption curve,
T = absolute temperature,
S = total spin quantum number.

Subscripts 0 and s refer to standard and sample, respectively. The effective spin quantum number of a domain (S_s) will be equal to the product of D (atoms/domain), 0.6 (unpaired electrons/atom) (*10*) and 1/2 (spins/electron), $S_s = 0.3D$. Since $g_0 = 2.0$ and $S_0 = 5/2$ for Mn^{2+} and $T_s = T_0$; $A_s = A_0$,

$$N_s = 2.23 \times 10^{18} \times \frac{1}{D}$$
$$= \frac{(2.0)^2 5/2(5/2 + 1)}{(2.22)^2 0.3D(0.3D + 1)} \times 2.83 \times 10^{19}$$

Solving for D, $D = 1000$. As a sphere with random dense packing of atoms the radius would be of the order of 14 Å. This is not a rigorous calculation and we do not intend to emphasize the result. There is no assurance that all of the reduced nickel atoms have clustered to form domains. Possibly some phosphate was reduced. However, if these possibilities are neglected, the calculated particle size is too large to exhibit complete demagnetization by chemisorption of hydrogen on the surface.

As an alternative calculation one A may consider that the RED spectrum in Fig. 1A and the OX spectrum in Figs. 1A and 4 result from the same number of nickel atoms. The ratio of the areas under the absorption curves for the RED cycle (Ni°) to the OX cycle [Ni(II)] is 22/1. As before, one considers the domain as a superparamagnetic ion with an effective spin quantum number of 0.3 D.

Let N = no. of Ni° = no. of Ni(II). Subscripts 1 and 2 refer to Ni° and Ni(II), respectively. Considering the same relationship between the integrated curve, the magnetic moment, and the number of paramagnetic species as above:

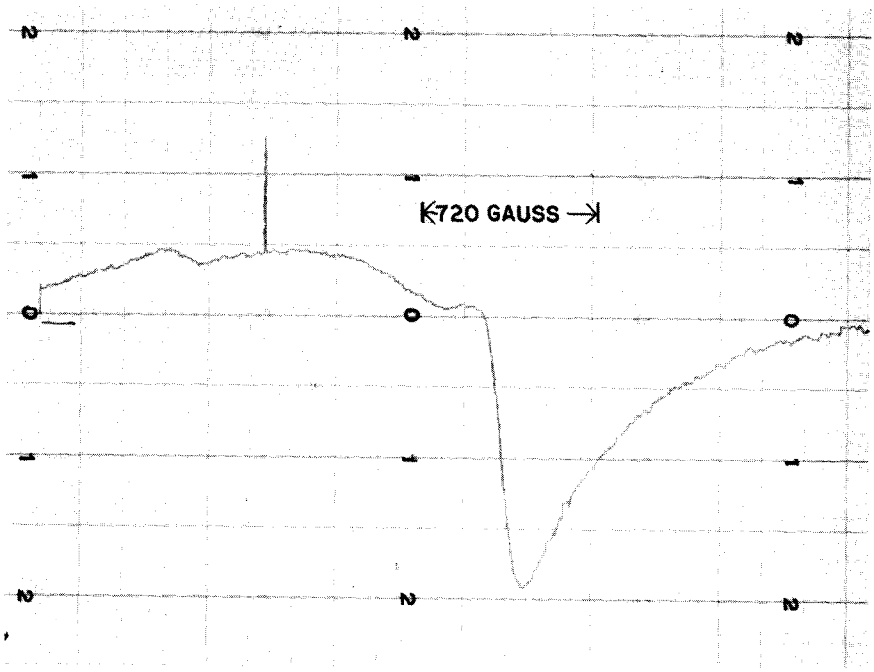

FIG. 4. [OX] spectrum at 685°C, $g = 2.0$. Amplifier gain is a factor of ten greater than in Fig. 1B.

$$\frac{A_1}{A_2} = \frac{22}{1} = \frac{N/Dg_1^2S_1(S_1+1)}{N \quad g_2^2S_2(S_2+1)}$$
$$= \frac{1/D(2.22)^2 0.3D(0.3D+1)}{(2.0)^2 \quad 1 \quad (1+1)}$$
$$D = 400$$

Since a double integration is involved in both calculations, an error factor of two is not uncommon for this type of analysis. The latter method may be preferred since the hydrogen measurement is eliminated. As a sphere, the radius (8.5 Å) is still too large. A reviewer has suggested that "the 4% of the nickel present which is accounted for by the ESR signal is probably present as a film on the surface of unreduced particles rather than as very small particles." One can only speculate as to the shape of the magnetic particle and the mechanism whereby the reduced nickel atoms migrate to form domains. The catalyst is a solid solution (*15*) of nickel phosphate in calcium phosphate with an approximate crystallite size of 1100 Å. Possibly only the ions on the surface of the catalyst particle are reduced. The free nickel atoms could migrate over the surface of the crystal to form a film or particle with a large surface to volume ratio. A hard catalyst particle with dimensions of 1100 Å is too large to be consistent with the above scheme but a porous particle with surface defects could be consistent with the 4% surface requirement and permit several domains per catalyst particle. It would be unwarranted to say that the experimental data presented here is evidence for such a mechanism. It is merely suggested as a possible explanation of the experimental observations.

SUMMARY AND CONCLUSIONS

The fact that the magnetism increases to a maximum value, then decreases to zero as a function of hydrogen treatment is evidence of the complete demagnetization of nickel by reaction with hydrogen. Further evidence of this conclusion is demonstrated when a demagnetized sample exhibits ferromagnetism after hydrogen is pumped off. An approximate calculation of nickel atoms/domain indicates that the domain has a large surface-to-volume ratio in order to be completely demagnetized by the reaction of hydrogen with nickel atoms on the surface. Since the gaussian line shape indicates little or no exchange between domains, they are not truly ferromagnetic in the sense that they do not exhibit permanent magnetism. Nor are they really paramagnetic since they exhibit a well-defined Curie point, but rather represent a transition between paramagnetic and ferromagnetic behavior. It is evident that the magnetically active fraction of the catalyst comprises only a small percentage of the total nickel (about 4%) and approximately this amount of oxy or peroxy radical is generated during the oxidation cycle.

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