the adsorbed layer, the rate constant observed by sampling the gas will be $k = n_s k_s/(n_g + n_s)$.

Relative values of $n_s$ and $n_g$ may be calculated, at least roughly, from the ratio of catalyst surface-to-gas volume. If this ratio is 30 m.²/ml., for example, there are about ten times as many hydrogen molecules in an adsorbed monolayer as in the gas phase. Then $k = 0.91k_s$. Taking $k = 1.0$ sec.$^{-1}$ at $\sigma = 30$ m.²/ml., $k_s = 1.1$ sec.$^{-1}$. The unbroken curve of Fig. 2 represents the variation of $k$ with $\sigma$, computed upon this basis. If the layer in which the reaction occurs contains two monolayers the values of $n_s$ would be everywhere doubled and the broken curve would result. In this case, $k_s = 1.05$. In either event, the observed rate constant should be nearly independent of surface area for $\sigma$ greater than about 20 m.²/ml. The data of Taylor and Liang[15] for the adsorption of hydrogen on ZnO support the supposition that the gas forms one, or perhaps somewhat more than one, monolayer, although we have no direct information about the extent of adsorption on zinc ferrite.

## Conclusion

The rate constants for the mixed catalysts heated at 600° or above fall much below either of these curves, from which it may be concluded that $k_s$ is markedly less on these catalysts than upon the others. These are, of course, the catalysts for which a significant structural change had occurred in the $\alpha$-$Fe_2O_3$, as evidenced by the magnetic data.

It then appears that the catalytic activity of the several solids investigated, as judged from the rate of conversion of ortho- to parahydrogen at −195°, decreases in the order: (a) $\gamma$-$Fe_2O_3$, (b) $\alpha$-$Fe_2O_3$, (c) $\alpha$-$Fe_2O_3$-ZnO mixtures, (d) intermediates leading to the formation of $ZnFe_2O_4$. The magnetic properties of these materials are, respectively, (a) ferromagnetic, (b) antiferromagnetic, (c) antiferromagnetic, diluted by diamagnetic ZnO, and (d) paramagnetic, accompanied by some ferrimagnetic structure. It may be inferred that ferromagnetic arrays of spins are more effective than antiferromagnetic arrays in inducing a change in nuclear spin in the orthohydrogen molecule, while the latter are more effective than paramagnetic arrays even when accompanied by some ferrimagnetic structure.

**Acknowledgment.**—The authors wish to thank Mr. R. V. Sarakauskas, National Carbon Company, for helpful discussions concerning the magnetic properties of zinc ferrite.

CORVALLIS, OREGON

[15] H. S. Taylor and S. C. Liang, THIS JOURNAL, **69**, 1306 (1947).

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

# The Preparation and Magnetic Properties of High Purity Raney Iron

BY W. D. JOHNSTON, R. R. HEIKES AND J. PETROLO

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The Raney method has been applied to the preparation of ultra-fine iron powder. The material obtained is of relatively high purity (95% iron) and has a high value of coercive force (∼560 oe.). An estimate of particle shape has been made from a consideration of the magnetic data.

## Introduction

During the course of a program devoted to fine particle permanent magnet materials it became necessary to prepare some relatively pure samples of ultra-fine iron particles which would display permanent magnet properties. A number of procedures for the preparation of ultra-fine iron powder appear in the literature[1–3] but in most cases the attainment of material of this particle size ∼ 200 Å., appears to be incompatible with high sample purity. This is not surprising since particles of this size are quite reactive and are in fact pyrophoric.

The apparent incompatibility of ultra-fine particle size and high purity is clearly illustrated in several instances where fine iron powder was prepared by reducing such compounds as iron formate or oxalate with hydrogen at relatively low temperatures.[1,2]

In these hydrogen reduction experiments the coercive force ${}_{I}H_c$ was measured as a function of reducing time and temperature. It is well established that the coercive force increases with decreasing particle size until a maximum value is reached. The coercive force then drops rapidly with decreasing particle size. This decrease comes about because thermal energies become sufficient to reverse the magnetization of such particles. Thus coercive force measurements can be used as an indication of particle size; however, it must be remembered that particle shape effects may cause calculable deviations from this behavior. In the formate reduction experiments the coercive force reached a maximum at approximately 65% reduction. At higher sample purities, which were obtained by longer reduction times or higher reduction temperatures, the value of ${}_{I}H_c$ dropped off sharply due to excessive particle growth. On the other hand, the value of the remanence $B_r$ increased with sample purity as would be expected. Because of these two opposed effects the maximum energy product $(BH)$ max. reached a maximum at roughly 85% sample purity. Work in this Laboratory has confirmed this inability to obtain simultaneously both high sample purity and high coercive force by the formate reduction method.

Another method, which has been used, is the electrodeposition of iron into a stirred mercury cathode.[3] In this procedure the electrodeposited iron was suspended as an ultra-fine powder in the

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[1] F. Lihl, *Acta Phys. Austriaca*, **4**, 360 (1951).

[2] E. W. Stewart, G. P. Conrad, II, and J. F. Libsch, *AIMME, J. Metals*, **203**, 152 (1955).

[3] W. H. Meiklejohn, *Rev. Mod. Phys.*, **25**, 302 (1953).

mercury cathode. In order to separate the iron from the mercury the surface of the iron was oxidized to "dewet" it from the mercury. No chemical analyses have appeared for the products of these reactions but the presence of a certain amount of oxide is assured.

A method that has received relatively little interest for the preparation of ultra-fine iron powder is the method commonly employed to prepare Raney nickel. In this method, an alloy of iron and aluminum is attacked by a concentrated alkali solution and yields very fine iron powder according to the reaction

$$FeAl_2 + 6NaOH \longrightarrow Fe^0 + 2Na_3AlO_3 + 3H_2$$

In one study this material was prepared and proved to be a selective catalyst for the reduction of acetylenic bonds to olefinic bonds.[4] However, in this catalytic work there was no interest in the purity or the magnetic properties of fine iron powder. Raney iron was mentioned by Néel as a permenent magnet material but in this case no details of the preparation or purity were mentioned.[5]

The most thorough work on the Raney iron method is that by Howell[6] who gives both a method for the preparation of Raney iron and data as to the range of chemical composition and magnetic properties of his products. Howell appears to attribute the permanent magnetic properties of his material to the presence of finely dispersed $Fe_3O_4$. Recent work on fine powder permanent magnet materials suggests that the finely divided $Fe_3O_4$ serves no useful purpose and the magnetic properties of this material arise solely as a result of the magnetically anisotropic properties of the single domain iron particles. In addition, several of the steps in the Howell method are subject to serious question as will be pointed out later. Although the coercive forces reported by Howell are not unusually high the purity of his products is somewhat superior to those of materials prepared by the formate reduction method. Accordingly the Raney method was reinvestigated with the objective being the preparation of high purity permanent magnet iron powder.

## Experimental

After a number of trials the following procedure was developed for the preparation of ultra-fine iron powder.

The apparatus used consisted of a 1 liter 3-necked round-bottom flask. The center neck was fitted with a ground glass sleeve type stirrer driven by a variable speed motor unit. A second neck was fitted with a reflux condenser at the top of which was a fine glass jet, serving as an exit for gas flow. The third neck was fitted with three items: a separatory funnel, an inlet for a stream of inert gas and a movable glass tube connected to an aspirator with which the liquids contained in the flask could be drawn off. During the entire operation a stream of inert gas such as argon flowed through the apparatus. Preliminary work showed that an inert gas flow was effective in minimizing oxygen contamination.

Four hundred ml. of distilled water which was freshly boiled to remove dissolved oxygen was introduced into the 3-neck flask. An excess of NaOH, 80 g., was introduced with rapid stirring. The NaOH solution was cooled to room temperature by using an ice-bath. Thirty g. of a 50% Al–Fe alloy was added through one of the side necks. (The 50% Al–Fe alloy was made by vacuum melting and subsequently ground to 170 mesh. Material coarser than this may react incompletely with NaOH, while substantially finer powder will become superficially oxidized during handling in the air.) The additions of the alloy were made to the rapidly stirred solution in 5-g. quantities over a period of 30 minutes. During the addition there was foaming in the flask due to evolution of hydrogen. The mixture attained a temperature of 70–80° due to the exothermic nature of the reaction. This heat evolution was sufficient for complete reaction to take place. When the evolution of hydrogen ceased, the flask was rapidly cooled to room temperature by using an ice-bath. The stirrer was stopped and the finely divided iron suspended in the liquid was drawn to the bottom of the flask by the use of a strong permanent magnet. The major portion of the liquid was drawn off by inserting the movable tube into the liquid and applying suction with the aspirator. In this and all subsequent decantations, it was essential that the liquid was not completely removed and that the fine iron powder was entirely covered by a layer of liquid at all times. After the initial decantation was completed, 100 ml. of freshly boiled distilled water (cooled to room temperature) was introduced through the separatory funnel and the fine powder was suspended by stirring for a minute. Again, the stirrer was stopped and this time the powder, being magnetically clustered, settled without the aid of a magnet. The major portion of the liquid was now drawn off by suction and a second portion of distilled water was added *via* the separatory funnel. This washing procedure was repeated $\sim$ 10 times. Finally, after the last partial decantation 100 ml. of C.P. pyridine was introduced through the separatory funnel and a series of rinses with pyridine was commenced. After $\sim$ 5 pyridine washings the iron was allowed to remain under $\sim$ 100 ml. of pyridine. The grey black iron powder was now easily removed from the flask for storage by pipetting both pyridine and solid and transferring to a ground glass bottle containing an initial quantity of pyridine. The iron in the ground glass stoppered bottle was stored in a desiccator. The entire operation was completed as rapidly as possible and took less than 3 hours. This method was rapid and simple and in addition was effective in preventing oxidation.

Samples for coercive force measurements were transferred by pipets to $^1/_{16}$ in. i.d. Pyrex tubes sealed at one end. The pyridine was removed from the sample by vacuum and the evacuated tube was sealed,

Coercive force measurements were made by first magnetizing the randomly oriented loosely packed sample in a field of 3000 oe. Reverse fields of increasing magnitude were then applied to the sample while the sample was moved in a small pick up coil, the output of which registered on a ballistic galvanometer. The field at which the galvanometer showed no deflection was taken as the coercive force $_IH_c$.

## Discussion

Table I shows the chemical analysis of various samples of Raney iron and the values of intrinsic coercive force obtained. In all cases high values of coercive force are associated with high sample purity. In the samples which were stored under pyridine, both the iron content and the coercive force are high and average 95.3% iron and 560 oe., respectively. In comparison the purity of the samples prepared identically but stored under freshly distilled *n*-propanol instead of pyridine (samples 4, 5 and 8) showed significantly lower purity and lower values of $_IH_c$. In addition, the samples stored in alcohol developed a brown oxide surface layer in about one weeks time. The lower purity in the case of alcohol storage was unexpected since alcohol is commonly used to store Raney nickel. In this connection, however, it should be remembered that iron is thermodynamically much more easily oxidized than nickel. Pyridine was chosen to improve the storage situation since it contains no oxygen in the molecule and thus cannot react with the iron and form oxides. It is also miscible in water and a basic solvent. In this connec-

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[4] A. F. Thompson and S. B. Wyatt, THIS JOURNAL, **62**, 2555 (1940).

[5] L. Néel, Fr. 979,043 (April 1951).

[6] H. A. Howell, U. S. Patent 2,553,768 (May 1951).

tion mention should be made of the iodine in acetone used as a storage medium by Howell who claims that iodine functions to reduce some of the oxides present. From a consideration of the fact that iodine is an oxidizing and not a reducing agent, it is difficult to see how this medium could function as described.

TABLE I

| Sample | Stored under | Total Fe, % | Metallic Fe % | Total Al, % | Total Na, % | $_{\rm I}H_c$ (oe) |
|---|---|---|---|---|---|---|
| 4 | *n*-Propanol | .. | ....... | .. | .. | 460 |
| 5 | *n*-Propanol | 87.0 | 86.6–86.9 | .. | .. | .. |
| 6 | Water | 86.3 | 81.3 | 1.3 | 0.2 | [a] |
| 7 | Pyridine | 97.0 | 93.7 | 0.4 | .. | 520 |
| 8 | *n*-Propanol | 86.6 | .. | 2.8 | 0 | 360 |
| 10 | Pyridine | 92.5 | .. | 1.0 | .. | 560 |
| 11 | Pyridine | 96.3 | .. | 1.2 | 0 | 600 |
| Raney Co | Pyridine | (91.3 Co) | | 5.3 | .. | 140 |

[a] $_{\rm I}H_c$ decreases with increased time in water.

The table also shows that Raney iron prepared identically but stored in water is of comparatively low purity. Gas bubbles could be seen slowly escaping from this sample indicating that the iron was reacting slowly with the water at room temperature and forming hydrogen. In addition the coercive force decreased rapidly with increased time in water. This information emphasizes that the preparation reaction should be run as quickly as possible and at as low a temperature as possible in order to minimize the iron–water reaction. Although Howell recognizes the need for running the reaction quickly, he requires that the reaction be performed at 110–120°. It is clear that such an elevated temperature will be detrimental for the formation of a relatively oxide free product.

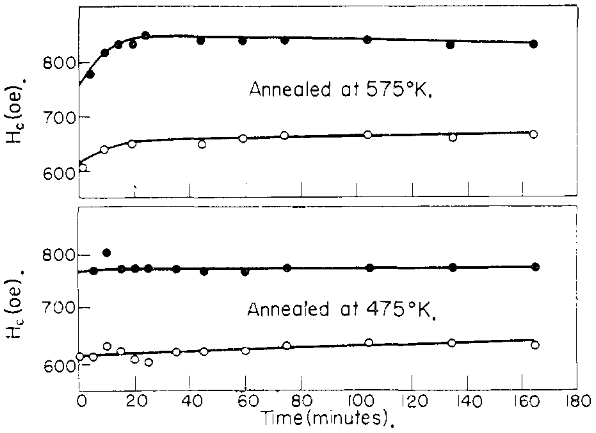

Fig. 1.—$H_c$ as a function of annealing temperature and annealing time for Raney Iron no. 11: ●, measured at 90°K.; ○, measured at 300°K.

These materials were all examined by X-ray diffraction. In all cases the iron lines were quite broad as would be expected for ultra-fine particles. Samples 7 and 11 show only lines of iron, substantiating the high purity achieved by storing samples under pyridine. Sample 6 which has been stored under water shows large quantities of a spinel impurity, probably either $Fe_3O_4$ or an iron–aluminum spinel. Samples 4 and 5 show smaller quantities of this impurity. Sample 8 shows a different impurity phase which is probably in some way connected with the high aluminum content of this sample. Sample 10 shows trace amount of the latter impurity.

Raney cobalt also was prepared by this procedure. Analytical data are given in the table. The crystal structure of this material is hexagonal according to its X-ray pattern although the presence of small amounts of cubic cobalt cannot be ruled out. The coercive force of this material is low as has been reported previously.[3]

The saturation magnetization of a sample of Raney iron 11 was found to be 208 c.g.s./g. If the impurities present are assumed to be non-magnetic, purity of 95.5% is indicated. If one assumes that the impurity is mainly $Fe_3O_4$, a good possibility, the indicated purity is lowered to 94%.

It was decided to examine the effects of annealing on the coercive force, as such annealing might cause particle growth and thereby effect $_{\rm I}H_c$. One sample was annealed at 475°K. while a second was annealed at 575°K. $_{\rm I}H_c$ as measured at 90 and 300°K. is shown as a function of time for these two samples in Fig. 1. The insensitivity of this Raney Fe to annealing is rather remarkable.

The theoretical value for $_{\rm I}H_c$ (due to crystalline anisotropy) for fine iron is 490 oe. in the case of a perfectly oriented sample, 150 oe. in the case of random orientation. In the present measurements no attempt was made to orient the particles; however, it is likely that short range orientation may exist in the sample. This might tend to increase $_{\rm I}H_c$ over the value for random orientation. An examination of $_{\rm I}H_c$ as measured indicates that there is an additional contribution from another source, probably shape. If we make the assumption that the particles are ellipsoids of revolution with the long axis parallel to the easy axis of magnetization, we may write for $_{\rm I}H_c$ of a single particle

$$_{\rm I}H_c = (N_t - N_l)I_s + \frac{2K}{I_s} = {}_{\rm I}H_{cn} + {}_{\rm I}H_{ck}$$

$N_t$ = transverse demagnetizing factor
$N_l$ = longitudinal demagnetizing factor
$K$ = magnetocrystalline anisotropy constant
$I_s$ = saturation magnetization
$_{\rm I}H_{cn}$ = shape anisotropy coercive force
$_{\rm I}H_{ck}$ = magnetocrystalline anisotropy coercive force

As $K \propto I_s^{10}$, we can write

$$_{\rm I}H_c = AI_s + BI_s^9$$

where $A$ and $B$ are the appropriate constants for $_{\rm I}H_{cn}$ and $_{\rm I}H_{ck}$, respectively. In order to determine the dependence of coercive force on $I_s$, $_{\rm I}H_c$ was measured as a function of temperature. From the experimental data, plus the knowledge of $I_s$ as a function of temperature, it was determined that $_{\rm I}H_c \propto I_s^{8.6}$. Therefore, the temperature dependence appears to be due principally to the crystalline anisotropy term. As has already been mentioned, $H_c$ (exp.) > $H_{ck}$. Something of the order of 200–300 oe. must be accounted for by shape. This requires $(N_t - N_l) \simeq 0.15$. For this to be the case the axial ratio of the particles would have to be ~ 1.3. Unfortunately, magnetic clustering makes it difficult to verify the axial ratio by the use of electron micrographs.

## Conclusion

A method has been developed for the preparation of fine iron powder of particle size suitable for permanent magnet applications. The method is simple and rapid and yields iron powder of purity higher than hitherto reported. In addition to the obvious use in the field of permanent magnets, this material may be useful in catalysis or in specialized powder metallurgy application.

**Acknowledgment.**—The authors take pleasure in acknowledging the work of Mr. E. W. Beiter who performed the chemical analyses of these samples.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Mechanism of Chemisorption: Hydrogen on Nickel. II

BY EDWARD L. LEE, JEAN A. SABATKA AND P. W. SELWOOD

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Further work has been done on the magnetic changes which occur when hydrogen is chemisorbed on a nickel–silica catalyst. It has been shown that no simple relation exists between surface bond type and magnetic change, as observed in a variety of samples. The thermal transients which are observed on admission of hydrogen have been used to obtain the differential heat of adsorption. This has shown that, for the samples studied, the heat approaches zero for hydrogen pressures near one atmosphere. The slow, so-called activated, sorption of hydrogen on these samples has been shown to be a true chemisorption, but one which occurs on the smaller nickel particles. It has been confirmed that hydrogen adsorbed on these samples at room temperature gives a small positive, rather than a negative, change of magnetization if the magnetization is measured at liquid hydrogen temperature.

## Introduction

The purpose of this work was to extend our studies on the mechanism of chemisorption through the use of magnetization–volume adsorption isotherms, as previously described.[1] In the present paper we take up four groups of observations, all of which relate to the chemisorption of hydrogen on supported nickel, and to the changes of magnetization, and hence presumably of d-band electron concentration, which occur during this process. The four groups of observations are, first, a series of exploratory measurements on the effect of changing experimental conditions; second, determination of the differential heats of chemisorption; third, a study of the "slow" process, that is, the slow take up of hydrogen which may be observed following the rapid chemisorption; and fourth, a further study of the "hydride" effect, namely, the apparent reversal of electron transfer which may be observed at very low temperatures.

## Experimental

**Magnetic Measurements.**—All magnetic studies involving adsorbed hydrogen were made on the low frequency a.c. permeameter previously described.[1] Some modification of procedure was required for those runs in which hydrogen was adsorbed on the sample at room temperature but in which the magnetic measurements were made at liquid hydrogen temperature. For this purpose the Dewar flask situated inside the primary solenoid and around the sample and secondaries was fitted with a brass cap so that the whole internal Dewar assembly could be made air-tight. After the sample had been reduced, the secondaries, Dewar, and primary were all clamped in position and not moved until the completion of a series of measurements. This arrangement necessitated some means of evaporating liquid hydrogen and of bringing the sample up to room temperature without interminable delay. This was achieved by placing a small, non-magnetic, electric heating element just below the sample. In all runs a fraction of a mm. of purified helium was admitted to the sample to promote heat transfer. In the apparatus used the RMS field was about 90 oersteds.

A few measurements of specific magnetization in a helium atmosphere at relatively high field (6000 oersteds) were made on the Faraday balance.[2,3]

**Catalyst Samples.**—Measurements were made on several different samples of supported nickel catalysts. One group of samples was a coprecipitated nickel–silica prepared as described by Van Eyk Van Voorthuisjen and Franzen, and designated by them CLA 5421.[4] This catalyst was prepared in several different concentrations of nickel as indicated below. All are referred to as "coppt."

Another group of samples consisted of Universal Oil Products Company nickel–kieselguhr hydrogenation catalyst containing 52.8% Ni. Some of this catalyst was used as received (after reduction); this is referred to below as "U.O.P." Some of the U.O.P. catalyst was sintered at 600° for 3 hr. before use. It appeared to make little difference in the results if sintering were carried out in pure helium or in hydrogen. This sample is called "sintered U.O.P."

Another portion of U.O.P. catalyst was treated with carbon monoxide for the removal of part of the nickel. This was done in apparatus similar to that described by Schuit and DeBoer.[5] The sample was first reduced in hydrogen at 350° until no water could be collected at the exit end of the sample chamber. Commercial carbon monoxide was passed through a glass furnace at 300° to decompose iron carbonyl impurity. The purified carbon monoxide was then passed over the sample at 80°. The carbon monoxide plus nickel carbonyl emerging from the sample chamber was heated to 300° to decompose the carbonyl. The nickel thus deposited was determined gravimetrically as a check analysis and for evidence of completeness of reaction. The treated sample also was analyzed. After 80 hr. of such treatment the amount of nickel carbonyl coming off the sample was found to be negligible. In two typical runs the residual nickel content was found to be 29.0 and 34.5%, respectively, corresponding to the removal of nearly $^{2}/_{3}$ of the nickel in the original sample. Reduced samples of catalyst thus treated with carbon monoxide were not pyrophoric on exposure to air, whereas all other original samples (even including some sintered samples) became quite hot in contact with air. If, however, the sample treated with carbon monoxide was itself sintered it became, once more, mildly pyrophoric. Furthermore, after this sintering operation a moderate additional proportion of nickel was found to be removable with carbon monoxide. Samples treated with carbon monoxide (but not further treated by sintering) are referred to below as "CO-treated U.O.P."

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[1] P. W. Selwood, THIS JOURNAL, **78**, 3893 (1956).

[2] P. E. Jacobson and P. W. Selwood, *ibid.*, **76**, 264 (1954).

[3] J. A. Sabatka and P. W. Selwood, *ibid.*, **77**, 5799 (1955).

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

[5] G. C. A. Schuit and N. H. DeBoer, *J. chim. phys.*, **51**, 9 (1954).