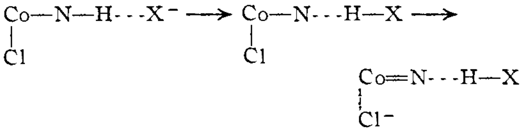
be based on the possibility that there is a strong interaction of a basic anion with the acidic protons of the complex in an ion-pair. Such interaction, which is indeed expected on electrostatic grounds, would permit the electrons of the N–H bond to behave at least somewhat like the electrons of an amido group. That is, they would perhaps be labilized enough to form a partial π-bond to the cobalt atom, and help to release chloride ion.[12]



$$\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Co}}}\text{—N—H- - -X}^- \longrightarrow \underset{\mathrm{Cl}}{\underset{|}{\mathrm{Co}}}\text{—N- - -H—X} \longrightarrow \underset{\mathrm{Cl^-}}{\underset{\vdots}{\mathrm{Co}}}\text{=N- - -H—X} \quad (5)$$

There are some reasons for preferring this mechanism. One is that the complex *cis*-Co(trien)Cl_2^+ shows a very large rate of reaction with azide ion in buffered media, Table VI, in comparison with *cis*-Co(en)$_2$$Cl_2^+$ although the rates of reaction with neutral ligands is nearly the same. The trien complex also has a rate of reaction with hydroxide ion in water which is about 200 times greater than for the bis-(ethylenediamine) complex.[6] However, it is not the methoxide rate which is involved in the azide ion solutions as shown by changing the buffer ratio. Another reason for preferring an SN1 IP mechanism is that, if optically active *cis*-Co(en)$_2$$Cl_2^+$ is used, an inactive product is formed with azide ion and acetate ion and the rate of racemization is the same as the rate of reaction with the two anions (see Tables II, III and V). It would be expected that a bimolecular displacement process should be more stereospecific.

TABLE VI

RATES OF REACTION OF *cis*-Co(en)$_2$$Cl_2^+$ AND *cis*-Co(trien)$_2$-Cl_2^+ WITH AZIDE ION AND RADIOACTIVE CHLORIDE ION IN METHANOL AT 25°

Complex	$[N_3^-]$	[HN]	k, min.$^{-1}$
cis-Co(en)$_2$$Cl_2^+$	0.0048	0.0024	4.8×10^{-3}
	Rate with *Cl^-		2.0×10^{-3}
cis-Co(trien)Cl_2^+	0.0048	0.0024	5.3×10^{-1}
	.0048	.0048	4.8×10^{-1}
	Rate with *Cl^-		1.3×10^{-3}

One final observation of interest is that a complex containing no acidic protons, *e.g.*, *trans*-Co(py)$_4$-Cl_2^+ reacts quite rapidly with azide ion and acetate ion in methanol, but by decomposition of the entire complex. Pyridine (py) is released as in the reaction with hydroxide ion in water. In these cases it appears that an SN2 reaction occurs but leads to a fundamental change in the structure of the compound.

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[12] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Conversion of Ortho- to Parahydrogen on Iron Oxide–Zinc Oxide Catalysts[1]

BY R. ELDO SVADLENAK AND ALLEN B. SCOTT

RECEIVED MARCH 29, 1957

The conversion of normal hydrogen to the equilibrium form at −195° over γ-Fe_2O_3, α-Fe_2O_3, and a series of iron oxide–zinc oxide mixtures heated at several temperatures to produce varying degrees of reaction to form zinc ferrite, has been studied. γ-Fe_2O_3 is the most efficient of these catalysts, followed by α-Fe_2O_3. The mixed catalysts heated at temperatures not greater than 500° were moderately efficient, the first-order rate constant k being about 1.0 sec.$^{-1}$. k was nearly independent of σ, the catalyst surface per unit volume of reacting gas. The shape of the k *vs.* σ curve was calculated on the basis of simple assumptions. Mixtures heated at temperatures over 500° yielded values of k far below the calculated curve, and also underwent a marked change in magnetic susceptibility. It is concluded that an antiferromagnetic structure is a better catalyst for this conversion than a paramagnetic structure even when the latter is accompanied by some ferrimagnetism, but that the ferromagnetic form is superior to either.

Introduction

The study of ferrite catalysts has for some time been a matter of interest because of the possibility that a distinct relationship may be found between the catalytic activity and the magnetic state of the solid. Hüttig[2] and co-workers studied the oxidation of carbon monoxide and the decomposition of nitrous oxide over a series of catalysts made by heating equimolar mixtures of zinc oxide and iron oxide at several elevated temperatures to produce differing degrees of reaction to form zinc ferrite. Bupp and Scott[3] reported upon the decomposition of nitrous oxide over the same series of catalysts and did not confirm the existence of a catalytically active phase intermediate in structure between the mixture and the compound, as reported by Hüttig.

All of these results were complicated by the fact that the reaction used as a test of catalytic activity had to be carried out at temperatures around 500°, at which temperature the catalyst itself undergoes considerable change in surface area and magnetic properties during the course of a single measurement of catalytic efficiency.

In the present investigation, the conversion of normal hydrogen to the equilibrium form (49.73% parahydrogen)[4] at −195° was used as a test of catalytic activity. This reaction has the advantage of taking place rapidly at low temperature

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[1] Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955. From a thesis submitted by R. Eldo Svadlenak in partial fulfillment of the requirements for the Ph.D. degree, Oregon State College. Published with the approval of the Oregon State College Monographs Committee as Research Paper No. 320, Department of Chemistry, School of Science.

[2] G. Hüttig, *Sitzber. Akad. Wiss. Wien, math.-nat. Kl.*, **7**, 648 (1936).

[3] L. P. Bupp and A. B. Scott, THIS JOURNAL, **73**, 4422 (1951).

[4] A. Farkas, "Light and Heavy Hydrogen," Cambridge, London, 1935, p. 14.

over such catalysts, and further is expected to be quite strongly influenced by the magnetic properties of the catalyst. γ-Fe_2O_3, α-Fe_2O_3, and a series of ZnO–Fe_2O_3 mixtures heat-treated as before[2,3] were the catalysts used.

Experimental

Apparatus.—The apparatus previously described[3] was used, with certain modifications. The reaction chamber was altered in order to eliminate leakage around the catalyst bed. Gas entering the reaction chamber passed downward and out through a fixed vial at the bottom which contained the catalyst supported on a coarse grade fritted glass disc. The volume of the vial per unit height was 0.318 ml./cm. Suspended above the fixed vial, by means of a thermostated copper–beryllium spring having a sensitivity of 20.8 mg./mm., was a reference vial constructed by flattening the bottom of a 3 inch Pyrex test-tube. Measurements of surface area and magnetic susceptibility were made upon catalyst samples contained in the reference vial. The reaction chamber either could be heated by a removable tubular electric furnace or cooled with a dewar flask of liquid nitrogen, with the assurance that both the catalyst in the fixed vial and in the reference vial had the same treatment at all times.

The amount of conversion of normal hydrogen (25% para) to 50% parahydrogen was estimated by the thermal conductivity method. The conductivity cell was similar to that of Bolland and Melville[5] and contained a tungsten filament from a 7.5 watt G.E. light bulb as the resistance wire, enclosed by an 8 mm. capillary tubing. The cell was attached to the system so that a constant volume of gas extracted from the reaction chamber could in turn be expanded into the previously evacuated cell. When the cell was immersed in liquid nitrogen, its resistance was 2.2 ohms less when the filament was surrounded by 50% parahydrogen than when it was surrounded by normal hydrogen.

Only one flowmeter was required for these experiments.

Reagents.—The α-Fe_2O_3 and the ZnO were prepared as before.[3] The γ-Fe_2O_3 was made by oxidizing magnetite prepared by the Lefort method[6] with nitrous oxide at 500°.[7]

The nitrogen and normal hydrogen were of commercial tank stock purified by passing through 10% pyrogallic acid to remove oxygen, through copper turnings at 400° to remove the last traces of oxygen, and finally through a calcium chloride tower and a liquid nitrogen trap to remove moisture and condensable gases. Equilibrium hydrogen at −195° was prepared by the desorption of hydrogen adsorbed at −195° on a previously well outgassed charcoal column.

Experimental Procedure.—A weighed amount of catalyst was placed in each vial in the reaction chamber, covered with glass wool and the volume of catalyst was ascertained from the height to which the vial was filled.

The system was then evacuated and the magnetic susceptibility determined at room temperature. A Styro-foam container filled with liquid nitrogen was then placed around the reaction chamber and the magnetic susceptibility was determined at −195°. The catalyst was degassed by heating at 200° while evacuated to a pressure less than 5 μ until the sample in the reference vial showed no further change in weight.[8] The surface area of the sample was then measured, using the B.E.T. method based upon the adsorption of nitrogen.

Following the surface area determination the samples were again degassed and a dewar flask filled with liquid nitrogen was placed around the reaction chamber. The system was filled with normal hydrogen at 1.00 atm. which was allowed to pass through the catalyst bed at a fixed rate as measured by the mercury slug flowmeter.

The resistance of the cell was determined when surrounded by normal hydrogen, by hydrogen which had just passed through the catalyst bed, and then by equilibrium hydrogen. The amount of conversion was obtained by linear interpolation. Several flow rates were used for each catalyst sample. The time of contact of the gas with the catalyst was calculated from the flow rate and the gas volume within the catalyst bed. The latter readily was obtained as the difference between the total volume occupied by the catalyst and the volume of the catalyst itself calculated from the mass and density. For the zinc oxide–iron oxide mixtures, the density was taken as 5.24 g./ml., a weighted average of the densities of the two components.

First-order rate constants were obtained by plotting $-\log(1 - E)$, where E is the fraction of conversion to the equilibrium form, against contact time and finding the slope. In most cases a fairly straight line was obtained, as illustrated in Fig. 1b. The scatter of the experimental points is probably attributable mainly to uncertainty in the contact time, arising from the likelihood of the formation of channels through the catalyst. The thermal conductivity cell, though capricious and subject to instability, yielded satisfactorily reproducible values during stable operation, so that errors in E are believed to be small.

For comparison of the catalysts, the total surface area of each sample was divided by the gas volume within the catalyst bed; the result was designated σ.

In most instances the surface area and the magnetic properties were redetermined after the catalysis measurements. No significant changes were noted when degassing temperatures did not exceed 200°.

Experimental Results

Pure ZnO, having a surface-to-volume ratio $\sigma = 8.5$ m.²/ml., was the poorest catalyst studied. The conversion was less than 10% for contact times as great as 7.5 sec. γ-Fe_2O_3, for which $\sigma = 93$ m.²/ml., was found to be a very effective catalyst. Complete conversion resulted during a contact time of 0.38 sec. Indeed, the rate was too great to allow the determination of a rate constant. α-Fe_2O_3 also was an efficient catalyst. The degree of conversion over a sample of $\sigma = 107$ m.²/ml. is shown in Fig. 1a. The rate constant was 2.8 sec.$^{-1}$.

Equimolar mixtures of ZnO and α-Fe_2O_3 were heated in Alundum boats for six hours at 410, 500, 600, 650, 700 and 900°. These catalysts gave the results shown in Fig. 1. The efficiency of the catalysts falls off with increasing pre-treatment temperatures. Simultaneously with this decrease in catalytic activity there is a general decrease in surface area coupled with a very definite increase in magnetic susceptibility at −195° for pretreatment temperatures above 500°. There is no evidence of a catalytically active phase intermediate between the mixture and the compound zinc ferrite, as reported by Hüttig.[3]

In Fig. 2 is presented the relation between the rate constant, k, and σ for each of the iron oxide-zinc oxide catalysts. For several of the catalysts, namely, those pretreated at temperatures of 500° and below, the rate constant is nearly independent of the catalyst surface per unit volume of reacting gas.

Table I gives the magnetic susceptibilities, per gram of mixture, of the catalysts at room temperature and at −195°.

Discussion

Magnetic Properties.—Neutron diffraction measurements[9] show that α-Fe_2O_3 is undoubtedly anti-

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(5) J. L. Bolland and H. W. Melville, *Trans. Faraday Soc.*, **33**, 1316 (1937).

(6) L. A. Welo and O. Baudisch, *Chem. Revs.*, **15**, 45 (1934).

(7) L. P. Bupp, Thesis, Oregon State College, 1950.

(8) When higher temperatures were used, *e.g.*, 300°, the upper portions of the catalyst frequently became quite magnetic. The reason for this is unknown. The dissociation pressure of Fe_2O_3 to form Fe_3O_4 is about 10^{-24} mm. at 300° while that of ZnO is estimated as 10^{-54} mm. [A. C. Halferdahl, *J. Ind. Eng. Chem.*, **22**, 956 (1930); W. Stahl, *Met.*, **4**, 686 (1907)] so that thermal decomposition does not occur under these conditions.

(9) R. P. Ozerov, *Uspekhi Fiz. Nauk*, **47**, 445 (1951).

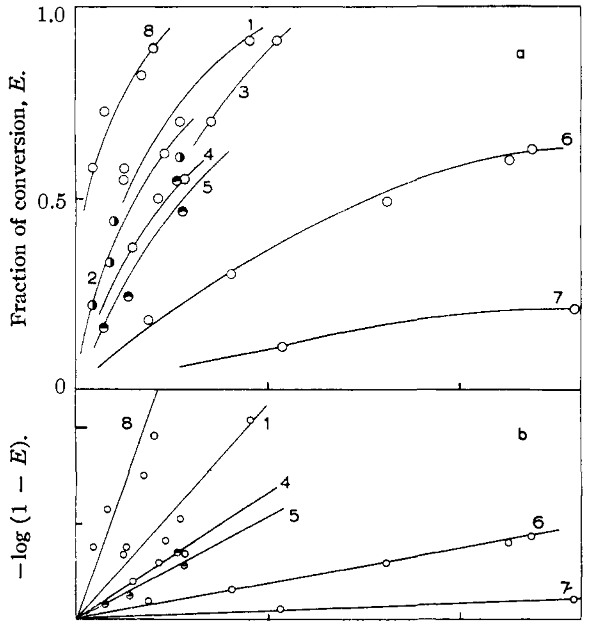

Fig. 1.—(a) rate of conversion of normal hydrogen to the equilibrium form at −195°; (b) first-order rate law curves: Curve 8, over α-Fe_2O_3; others, ZnO–Fe_2O_3 heated at: 1, 25°; 2, (half-shaded circles) 410°; 3, 500°; 4, 600°; 5, 650°; 6, 700°; 7, 900°. The first order curves for 2 and 3 very nearly coincided with curve 1.

ferromagnetic, having plane layers of parallel spins interspersed with layers of spins directed oppositely. There is in addition some ferromagnetism, which may arise from a small proportion of included magnetite[10] or from lattice imperfections.[11] γ-Fe_2O_3 is ferromagnetic. Zinc ferrite, which has the normal spinel structure, is believed to be a nearly ideal paramagnetic material above 9° K., below which it becomes antiferromagnetic.[12]

TABLE I

MAGNETIC SUSCEPTIBILITY OF IRON OXIDE–ZINC OXIDE CATALYSTS

Pretreatment temp., °C.	Susceptibility at × 10^6, c.g.s.u./g. at 25°	−195°
25	20.2	19.9
410	22.0	21.5
500	21.7	19.1
600	25.4	52.9
650	28.9	88
700	37.5	200
900	514	...

The normal spinel structure is one in which the 16 occupied sites in the unit cell surrounded octahedrally by oxygen atoms are all filled by trivalent cations (iron in the case of zinc ferrite) and the 8 occupied sites surrounded tetrahedrally by oxygen are filled by divalent cations (*e.g.*, zinc). In case the "tetrahedral" sites are filled by trivalent cations and the "octahedral" sites are filled by 8 divalent and 8 trivalent cations the structure is said to be inverted. The ferrimagnetic spinels are generally of the latter type.[13]

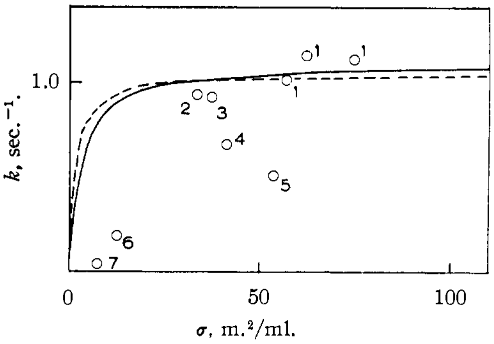

Fig. 2.—Relation between the rate constant and the surface per unit volume. Numbers have the same significance as in Fig. 1.

On quenching zinc ferrite after heating at 1400°, Brockman[14] found it to be somewhat magnetic, and supposed that some of the zinc ions interchanged positions with some of the ferric ions by thermal agitation at the high temperature giving a structure intermediate between the normal and the inverted spinel.

When the zinc oxide–iron oxide mixtures are heated at temperatures too low to cause complete conversion to the ferrite within six hours, the magnetic properties of the product may be quite complex. In particular, if the interdiffusion of the two phases results in a product having regions of the inverted spinel structure we would expect ferrimagnetism and the occurrence of a Curie temperature. Ferrimagnetism may also arise from partial destruction of the equally opposing planes of coupled spins of the Fe_2O_3. The temperature dependence of susceptibility for the samples heated at temperatures from 600 to 700° suggests the development of ferrimagnetism with the occurrence of a Curie temperature below 25°, since even if the conversion to paramagnetic zinc ferrite were complete, Curie's law would predict a considerably lower susceptibility at −195°, than that observed. Formation of Fe_3O_4 by thermal decomposition does not appear to be a possibility[8]; further, if it were formed the susceptibility at 25° would be about the same as at −195° since the Curie temperature of Fe_3O_4 is much higher than room temperature.

Effect of Surface Area.—The virtual independence of k upon σ for catalysts preheated at temperatures below 500° may be accounted for most simply in the following way. If it is assumed that the rate of adsorption and desorption of hydrogen on the catalyst surface is sufficiently high that exchange of molecules between the gas phase and the adsorbed phase occurs several times during the contact time, the fraction of time spent upon the surface by a molecule within the catalyst bed will be on the average $n_s/(n_g + n_s)$ where n_s is the number of molecules contained in the adsorbed layer and n_g is the number in the gas phase. If k_s be the rate constant for the first-order conversion of ortho- to parahydrogen for molecules actually in

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[10] L. Néel, *Ann. Phys.*, **4**, 249 (1949).

[11] J. L. Snoek, *Physica*, **16**, 333 (1950).

[12] J. M. Hastings and L. M. Corliss, *Phys. Revs.*, **102**, 1460 (1956).

[13] J. S. Smart, *Am. J. Phys.*, **23**, 356 (1955).

[14] F. G. Brockman, *Phys. Revs.*, **77**, 841 (1950).

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 σ, 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 σ 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 $\alpha\text{-Fe}_2\text{O}_3$, 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) $\gamma\text{-Fe}_2\text{O}_3$, (b) $\alpha\text{-Fe}_2\text{O}_3$, (c) $\alpha\text{-Fe}_2\text{O}_3$-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.

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

[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

RECEIVED MAY 20, 1957

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 ${}_{\rm I}H_c$ 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 ${}_{\rm I}H_c$ 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.[4] 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).