the dissociation pressure. The reaction, however, is not zero order with respect to surface reacted, but more nearly 0.33 to 0.50. This might possibly represent a variation of equation 6 in which the function of $1 - \theta$ does not enter into the rate-controlling step. The decrease in rate is probably best attributed to a retardation process rather than explained on the basis of a fractional order for the Gibbs-type expression. From Fig. 8 for the two cases, $\theta = 0$ and $\theta = 1$, the ratios of the extrapolated values $(\theta = 0)/(\theta = 1)$, for the formation of the ammoniate of urea are 1.96, 2.23, 2.30, 1.96 or 2.36, and 2.40 corresponding to the pressures 150, 186, 281, 375 and 471 mm. As the pressure approaches the dissociation pressure it may be concluded that, within experimental error, the ratio approaches 2.00. In the equations[12] for processes retarded by a species A, the denominator of the expression for the differential rate is of the form $1 + K_2A$. If $K_2 = 1$, which is realistic in the present case, the effect of retardation may be incorporated into equation 7 as

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_{-1}(p - p_0)/p_0(1 + \theta) \quad (8)$$

On the basis of this expression the differential rate should diminish to one-half of its original value as the fraction of surface ammoniated increases from $\theta = 0$ to $\theta = 1$. Thus, equation 8 is most likely the general form of the rate equation for reactions of this type in which *all of the solid present represents available surface.* This is apparently true in the case of the conditioned samples of urea and thiourea. By analogy, the rate equation for the initial ammoniation would be

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_{-1}(p - p_0)(S)/p_0 \quad (9)$$

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[12] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 327 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thermomagnetic Analysis of Catalytically Active Nickel[1]

BY JEAN A. SABATKA AND P. W. SELWOOD

RECEIVED JUNE 16, 1955

The method of thermomagnetic analysis previously described has been improved by the construction of apparatus for *in situ* reduction and study of catalyst samples. It has been shown that massive and disperse nickel have the same magnetic moment at 0°K. The method has also been used for an investigation of several commercial nickel catalysts.

Introduction

In this article we describe apparatus developed for convenient measurement of specific magnetization over a wide range of temperature and for observing the effect of adsorbed gases on the magnetization. All chemical reactions on the catalyst samples are carried out *in situ*. There are also presented data relating to particle size distribution and to the influence of chemisorbed hydrogen for several different nickel catalyst preparations.

Experimental Part

Magnetic Balance.—A Faraday balance, similar to that previously described,[2] was adapted for use with ferromagnetic substances. The silica spiral spring was replaced with a beryllium bronze spring. The sample bucket and surrounding tubes were all made of silica to permit heat treatment and measurements to be carried out up to 1100°. The silica envelope was arranged so that hydrogen and other gases could be allowed to flow over the sample during heat treatment and during measurement. The upper end of the spring was supported through a metal bellows so that the sample could be moved in the magnetic field without access of air. The magnet was mounted on tracks so as to facilitate changing samples and replacement of a small furnace by appropriate shaped Dewar flasks. Higher temperatures were provided by a small sleeve furnace automatically controlled, while Dry Ice, liquid nitrogen and liquid hydrogen could be used for low temperatures. The fields used were about 6000 oersteds, which is more than adequate for saturation of massive nickel. The sample weight was such as to contain about 1 mg. of nickel. Pure massive nickel was used for calibration. All gases, such as hydrogen and helium, were purified before use. Helium was purified by passing it over supported reduced copper on asbestos at 600°, and then over silica gel at −190°. It was possible to maintain a high vacuum over the sample indefinitely, although less convenient to make actual magnetic measurements in vacuum.

Preparation of Samples.—The following commercial catalysts were studied: Girdler G-12 nickel catalyst, Harshaw Catalyst Ni-0107, Universal Oil Products Co. nickel hydrogenation catalyst, and Raney (W-6) nickel. Results also are given for a sample of nickel–silica co-precipitated catalyst prepared as described by Van Eijk Van Voorthuijsen and Franzen,[3] and designated by them CLA-5421, but here referred to as "Coprecipitate." Measurements were also made on a reduced mechanical mixture of coprecipitate and pure nickel oxide. This mixture, which was prepared before *in situ* reduction, contained equal weights of nickel from each of the two sources.

All samples except the Raney nickel were analyzed for nickel before reduction in the magnetic balance. The nickel weight per cent. found for the several samples was as follows: Girdler, 55.6; Harshaw, 67.9; U. O. P., 52.8; and coprecipitate, 42.2.

All samples except the Raney nickel were heated at 350° in flowing hydrogen for 24 hours. Some samples were further subjected to sintering as described below. After the samples were reduced the atmosphere was changed to purified helium and the specific magnetization was measured down to liquid nitrogen or liquid hydrogen temperatures as desired. The effect of chemisorbed hydrogen was determined by flushing the system with hydrogen at room temperature before the magnetization was measured.

A sample of coprecipitate was progressively sintered in flowing hydrogen up to 650° to determine whether the magnetization extrapolated to absolute zero is independent of particle size. This procedure is believed to be justified since the initial reduction is virtually certain to be complete[4] and it prevents reoxidation by traces of air or water vapor.

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[1] This is the second paper (other than a brief Communication) to be published on this topic. The first appeared in THIS JOURNAL, **77**, 1462 (1955). This work was supported under contract with the Office of Naval Research.

[2] P. E. Jacobson and P. W. Selwood, THIS JOURNAL, **76**, 2641 (1954).

[3] J. J. B. Van Eijk Van Voorthuijsen and P. Franzen, *Rev. trav. chim.*, **70**, 793 (1951).

[4] W. Heukelom, J. J. Broeder and L. L. Van Reijen, *J. chim. phys.* **51**, 473 (1954).

In the case of the Harshaw catalyst a sample was sintered at 650° for 1 hour in purified helium.

Raney nickel was treated quite differently. The sample was prepared according to the directions of Covert and Adkins.[5] Samples were washed with toluene by decantation and placed in the balance suspended in toluene, evacuation then being carried out for 10 minutes to remove the toluene. Measurements were then taken from room temperature down to liquid nitrogen temperature. Additional measurements were made on a sample which had been evacuated for 2 hours at room temperature in an attempt to remove chemisorbed hydrogen, and on one which had been heated in helium at 400° for one hour.[6] The effect of hydrogen at room temperature also was determined.

The mechanical mixture of coprecipitate and of pure nickel oxide was reduced at 350° for 24 hours to ensure complete reduction of the nickel–silica part of the mixture. This sample and a sample of coprecipitate were also measured at two field strengths, as indicated below, to determine to what degree magnetic saturation might or might not be achieved.

Results

Figure 1 shows reduced specific magnetization, σ/σ_0 *vs.* temperature for coprecipitate (42.2% Ni) at three stages of sintering, namely: (1) reduction at 350° for 24 hours, (2) the same plus heating in hydrogen for 2 hours at 426°, then 2 hours at 451°, and (3) the same plus heating in hydrogen for 2 hours at 562° then 2 hours at 682°. The reduced (or relative) magnetization σ/σ_0 is obtained by dividing the observed deflection per g. of nickel for a given temperature and field strength by the deflection produced by the same weight of massive nickel at 0°K. as found by extrapolation and, of course, at the same field.

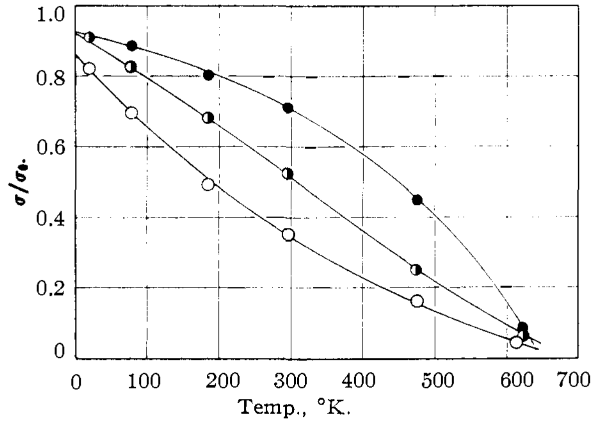

Fig. 1.—Thermomagnetic curves for: O, reduced; ◑, partially sintered; and ●, strongly sintered 42.4% Ni–SiO_2 coprecipitate.

In Fig. 2 we give data on Harshaw, Girdler, U. O. P. and Coprecipitate active catalysts. Data on the sintered sample of Harshaw catalyst and on massive nickel are also shown. Table I shows the influence of hydrogen chemisorbed at room temperature and measured at room temperature for each sample. The influence of hydrogen was, as expected, negative and is expressed as the percentage decrease of magnetization for each sample.

TABLE I

INFLUENCE OF CHEMISORBED HYDROGEN

Sample	Percentage decrease of magnetization
Harshaw	14
Girdler	10
U. O. P.	6
Coprecipitate	20
Sintered Harshaw	6.5
Massive nickel	0

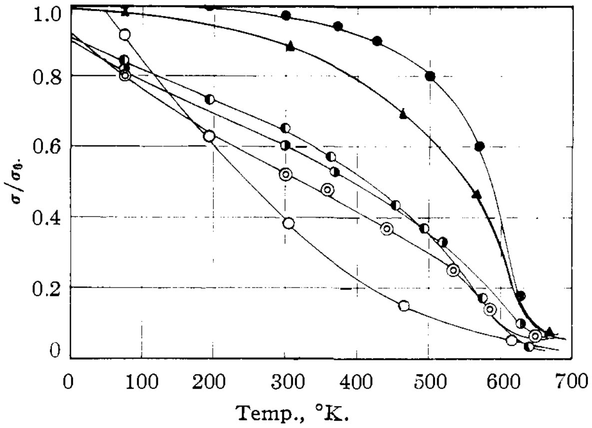

Fig. 2.—Thermomagnetic curves for: O, coprecipitate; ◎, U.O.P.; ◑, Harshaw; ◐, Girdler; ▲, sintered Harshaw; ●, massive nickel.

Figure 3 shows the magnetic data on Raney nickel. There was no influence of chemisorbed hydrogen observable on this sample, either before or after pumping at 200° or heating at 400°.

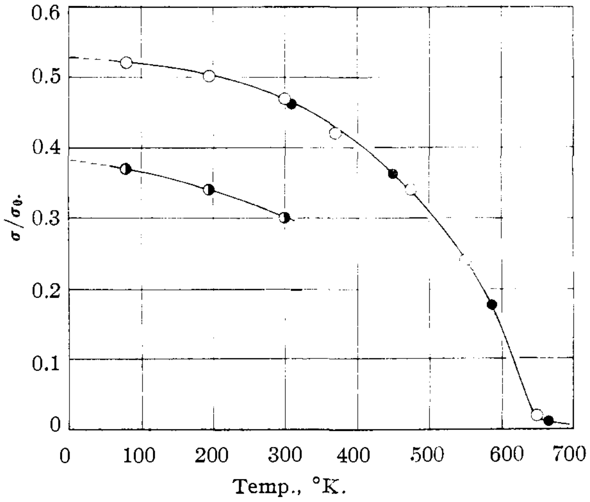

Fig. 3.—Raney nickel, ◑, evacuated at room temperature, O, heated in helium at 400° and ●, the same heated in hydrogen at 380°. The ordinate scale is based on the weight of sample rather than on the weight of metallic nickel, and hence is not very significant.

Figure 4 shows a comparison of magnetization curves for massive nickel, for coprecipitate reduced in hydrogen for 24 hours at 350° and for a 1:1 (Ni basis) mechanical mixture of the two.

Table II gives a comparison of σ/σ_0 for disperse nickel as measured at two field strengths and at several temperatures. Massive nickel is effectively saturated at all fields used.

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(5) L. W. Covert and H. Adkins, THIS JOURNAL, **54**, 4116 (1932).

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TABLE II

REDUCED SPECIFIC MAGNETIZATION, σ/σ_0 FOR SEVERAL Ni SAMPLES AT TWO FIELD STRENGTHS

Sample	Reduction conditions	Temp., °K.	σ/σ_0 at 4500 oersteds	σ/σ_0 at 6300 oersteds
Massive		298	0.97	0.97
Coprecipitate	24 hr. at 350°	298	.41	.48
Coprecipitate	sintered 1 hr. at 650°	298	.95	.95
Coprecipitate	24 hr. at 350°	77	.81	.88
Coprecipitate	24 hr. at 350°	184	.62	.71
Coprecipitate	24 hr. at 350°	297	.46	.54
1:1 mechanical mixture	24 hr.at 350°	300	.79	.78

Discussion

Earlier papers on this subject attribute anomalous thermomagnetic curves shown by supported nickel catalysts to a distribution of particle sizes[7] and relate particle diameter to Curie temperature.[8] This view is supported also by work done on thin films.[9]

Two alternative methods for the study of particle sizes in nickel catalysts have recently been published.[4,10] The method of Heukelom, *et al.*, is related to our own in that specific magnetization has been measured over a range of field strengths at one temperature in contrast to our studies at one field strength and a range of temperatures. Particle diameters calculated by Heukelom, *et al.*, give results somewhat larger than our own, but not alarmingly so in view of the approximations in both procedures.

It will be clear that all these methods depend on the fact that extremely small particles are subject to thermal agitation and hence less readily orientate in a magnetic field than do normal single ferromagnetic domains. Effective orientation may be achieved by a very long mathematical extrapolation to saturating field as done by Heukelom, *et al.*, or by an extrapolation to absolute zero as shown in the present paper.

The conclusions which may be drawn from the new data presented in this paper will now be presented.

First, it has been shown experimentally as in Fig. 1 that the specific magnetization extrapolated to absolute zero is independent of particle size. This shows that all the nickel in a catalyst sample may be accounted for provided that reduction is complete, and it serves as a convenient measure of extent of reduction where reduction may be less than complete.

Second, it has been shown that there is actually considerable dependence of magnetization on field strength for supported nickel catalysts in comparison with massive nickel. This field strength dependence vanishes at 0°K.

Third, a mechanical mixture containing small (supported) particles of nickel and large, massive, nickel shows the thermomagnetic curve expected on the basis of the interpretation previously given and thus supports the conclusions given below on the several commercial catalysts.

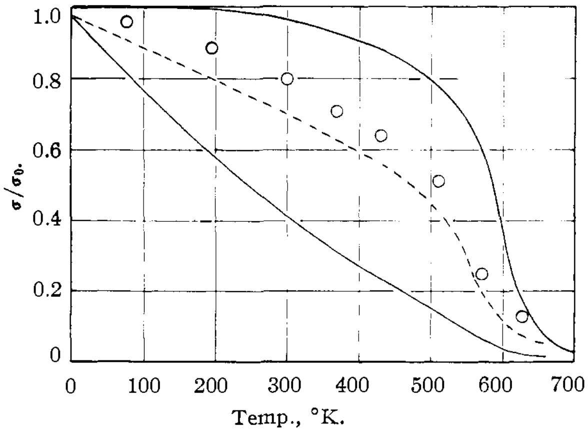

Fig. 4.—Thermomagnetic curve (O) for a 1:1 mixture of coprecipitate and massive nickel. The failure of the experimental points to agree exactly with the average (---) of coprecipitate and massive is probably due to the poor reproducibility of the curve for coprecipitate, in different samples and under slightly different conditions of reduction.

Fourth, inspection of the thermomagnetic curves for the various commercial supported catalysts shows that each contains nickel in a fairly large particle size together with a very small particle size. The samples differ somewhat in the detailed distribution of particle size but all samples show approximately complete reduction to nickel metal and no appreciable alloying with components which might reduce the effective magnetic moment by dissolving in the nickel with consequent partial filling of the d-band.

Some moderate differences in the effect of chemisorbed hydrogen probably reflect minor differences in the distribution of particle sizes. It will be clear that those nickel particles which will show the largest effect of chemisorbed hydrogen are those which become ferromagnetic just above the temperature of measurement which, in the present case, was room temperature. It will be noted that when the Harshaw sample was sintered it showed the expected growth of particles and diminished influence of hydrogen, but the effect of hydrogen was still appreciable. This is doubtless due to the fact that the smallest particles which are swept up, so to speak, in the sintering do not in any event contribute much to the magnetism at room temperature.

The results on Raney nickel are preliminary only and are difficult to interpret. Raney nickel is an unusually complex mixture believed to contain aluminum, aluminum oxide and hydrogen, in addition to nickel itself. The sample prepared by evacuation at room temperature showed a rather low magnetization which was not appreciably altered by evacuation at 200°. This result seems to indicate that removal of hydrogen in itself produces no marked effect and this was confirmed by the absence of any decrease in magnetization when hydro-

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(7) A. Michel, R. Bernier and G. Le Clerc, *J. chim. phys.*, **47**, 269 (1950).

(8) P. W. Selwood, T. R. Phillips and S. Adler, THIS JOURNAL, **76**, 2281 (1954).

(9) E. C. Crittenden and R. W. Hoffman, *Rev. Mod. Phys.*, **25**, 310 (1953).

(10) L. Weil, *J. chim. phys.*, **51**, 715 (1954).

gen was re-admitted at room temperature. This result suggests that most of the nickel is effectively "massive" nickel in the catalyst as normally prepared.

When the sample is heated at 400° in helium a substantial increase of magnetization takes place. The thermomagnetic curve then becomes near that expected for massive nickel. Such a process could occur through some degree of sintering, by some reduction of nickel oxide, or by a precipitation process involving dissolved aluminum. The mixture is obviously so complex as to require much more work before any definite conclusion may be drawn. There is no indication of a substantial fraction of the nickel being in extremely small particles as found by Weil,[10] but such particles might have been revealed if we had extended our measurements to lower temperatures. It should also be pointed out that Raney nickel prepared in different ways doubtless has quite different particle size distribution curves.

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[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Reactions of Atomic Hydrogen with Ozone and with Oxygen[1]

BY J. D. MCKINLEY, JR., AND DAVID GARVIN

RECEIVED JUNE 29, 1955

The reactions of oxygen and ozone with atomic hydrogen at room temperature have been studied in a low pressure flow system and the products (trapped at liquid nitrogen temperature) have been determined. The yields of water, hydrogen peroxide and "evolved" oxygen under various operating conditions are compatible with the view that product formation occurs primarily by radical recombination reactions in the cold trap. Hydroxyl is the immediate precursor of all water formed (and of a small amount of peroxide) while the fate of perhydroxyl is the formation of hydrogen peroxide (in the cold trap) and either hydroxyl or molecular oxygen in the pre-trap phase.

Introduction

The important free radical reactions in the oxidation of hydrogen have been the subject of many studies in which atoms or radicals produced by the action of an electric discharge have been mixed with a variety of stable molecules. These low pressure, short contact time studies include the work of Boehm and Bonhoeffer,[2] Geib and Harteck,[3] Rodebush,[4] and Badin[5] on the molecular oxygen–atomic hydrogen reaction. Related studies of the reactions of dissociated water and peroxide vapors have been made by Rodebush,[4,6] Winkler,[7,8] Giguere[9] and Oldenberg.[10,11]

In all of these systems, the products, when trapped at liquid air or liquid nitrogen temperatures after a contact time of about 0.1 second, form a glass which, upon warming, "melts" at about −115° with considerable frothing and oxygen evolution, then freezes to a crystalline mass, and eventually melts to a concentrated aqueous peroxide solution.[3,7] When the products are trapped at higher temperatures the yields of hydrogen peroxide and evolved oxygen decrease, until, at and above −120°, only water is recovered.[2,4a,7,8] The variation with temperature of the distribution of products between peroxide and water in both the oxygen–atomic hydrogen and dissociated water vapor reactions have been shown by Winkler[7] to be very similar. Such experiments show that peroxide is formed only in the trap (at temperatures less than −115°) and that some water is also formed there.[12,13] In addition, it is generally true that the effect of an increased contact time at room temperature or above is to reduce sharply the yields of peroxide and evolved oxygen, while the water yield tends to increase slowly.[4a,5,7,8]

The results of a study of the low pressure reaction between atomic hydrogen and ozone and a reexamination of the reaction between atomic hydrogen and oxygen are reported here. The two systems are interpreted in terms of a set of reactions that may also be used to explain the behavior of dissociated peroxide and water vapors.

Experimental

Apparatus and Reagents.—A conventional kinetic vacuum system was used. Both it and the preparation and analysis of the reagents are described briefly elsewhere.[14,15] The reaction cell used for these studies was a cylinder, 60 mm. i.d. by 100 mm. long, containing a centrally located capillary nozzle, 0.27 mm. i.d. through which ozone or oxygen

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(1) This research was supported by the United States Air Force under Contract No. AF 33(038)-23976 monitored by the Office of Scientific Research and has been reported in Technical Note No. 19, OSR-TN-55-164, Chemical Kinetics Project, Princeton University (1955).

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