Templeton and Dauben[11] used the lattice parameters of rare earth cubic sesquioxides and tetragonal oxychlorides to obtain a table of crystal radii for the trivalent rare earth ions. Their values show the same general smooth contraction as found here for the tetraborides, and the rate of contraction is the same. Post, *et al.*,[6] have pointed out the similarity in the contraction, which is confirmed here, and they have suggested an "ionic" type of binding for the tetraborides.

Spedding, Daane and Hermann[12] have measured precise lattice parameters of the rare earth metals. The atomic volumes show a general decrease with abnormally high values for Eu and Yb and slightly high values for La, Gd and Lu. The slightly high value for GdB_4 may be associated with the slightly larger value of the parameter for Gd metal. The high value of the lattice parameter for YbB_6 when related to these results for the metals, supports the view of Post, *et al.*,[6] that the hexaborides exhibit some of the characteristics of metallic binding. The hexaborides are known to be good conductors also.[2]

As Table I indicates, several preparations of some of the samples were made. The lattice parameter was not found to change significantly with the conditions of preparation, the crucible material or the B/M ratio of the sample. For example, the three GdB_6 samples were analyzed and were found to have $B/Gd = 5.39$, 5.89 and 7.70. Thus, the limits of solid solution for these phases apparently are small.

Acknowledgments.—The authors wish to thank the Atomic Energy Commission for partial support of this work; Professor Charles A. Reynolds, Jr., and Mr. Frederick J. Luedders for the analytical work; Miss Diane Kerr for measuring the films; and Professor F. H. Spedding and the Ames Laboratory for some of the samples.

LAWRENCE, KANSAS

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[11] D. H. Templeton and C. H. Dauben, THIS JOURNAL, **76**, 5237 (1954).

[12] F. H. Spedding, A. H. Daane and K. W. Herrman, *Acta Cryst.*, **9**, 559 (1956).

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY]

The Role of Hydrogen in Raney Nickel Catalysts

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RECEIVED JANUARY 10, 1959

The physical properties of two samples of Raney nickel catalysts have been studied. It was found that the hydrogen content was 45 to 100 cc./g. catalyst. The evolution of hydrogen was an exothermic reaction but involved no phase changes and was substantially complete at 400°. X-Ray measurements indicated the predominant phase was face-centered-cubic and was presumably an aluminum–nickel alloy containing for one preparation 3% and for the second 8% aluminum by weight. The surface area of these two catalysts was 76 and 63 $m.^2/g.$ and was not reduced by heat treatment below 250 to 300°. Measurements of density and magnetic susceptibility were carried out at room temperature as a function of hydrogen content. These data led to the picture that the hydrogen in Raney nickel is present as atoms in a substitutional solid solution.

Introduction

Raney nickel catalysts prepared by leaching out with alkali the Al in NiAl alloys[1,2] are substantially different from those prepared by the reduction of nickel oxides. For example, Raney nickel catalysts contain hydrogen in quantities too great to be ascribable to either adsorption or solution.[3,4,5] This hydrogen participates to an extent in hydrogenations[6] over this catalyst and although it is lost on aging it can be partially restored at high pressures.[7] In addition, removal of this hydrogen is accompanied by a decline in the catalytic activity.[3,4] Clearly, to understand the nature of Raney nickel we must first understand the role of this hydrogen. In this research we have attempted to shed some light on this question through studies, employing surface area measurement, differential thermal analysis, X-ray diffraction and magnetic and density measurements as a function of the amount of hydrogen evolved.

Experimental

Two samples of Raney nickel were studied. The first of these was a commercial sample, Davison sponge nickel, supplied by the Davison Chemical Company. This sample, D-1 was stored under water for about one year prior to the studies reported here and, consequently, was probably fairly stable during the course of the experiments. The other sample of Raney nickel was prepared according to the W-6 procedure of Adkins and Billica[2] as modified by Smith, *et al*,[3] except that it was stored under water after its preparation.

Both samples were analyzed for Ni and Al[8] after drying *in vacuo* at about 400°. The D-1 sample contained 0.8% acid (HCl) insoluble material, 91.0% Ni and 8.0% Al. The W-6 sample contained 0.3% acid insoluble (HCl) material, 77.3% Ni and 13.24% Al, the remaining 9.2% presumably being combined oxygen. In the case of the D-1 sample it is apparent that the Al is essentially all present as metallic Al and that the analysis as stated is substantially correct. In the W-6 sample it appears that a large fraction of the Al is not present as metallic Al but as the oxide. If it is assumed that the W-6 catalyst consists only of Ni, Al and Al_2O_3 the values 77.3% Ni, 19.8% Al_2O_3 and 3.0% Al are consistent with the above analysis and in reasonable agreement with those reported by Ipatieff and Pines.[9,10]

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[1] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[2] H. Adkins and H. Billica, THIS JOURNAL, **70**, 695 (1948).

[3] H. A. Smith, H. J. Chadwell and S. S. Kirdis, *J. Phys. Chem.*, **59**, 820 (1955).

[4] L. K. Freidlein and N. I. Ziminova, *C. A.*, **45**, 1836^{n}, 5029^{e}, 6031^{a} (1951).

[5] E. Lieber and F. L. Morritz, *Advances in Catalysis*, **5**, 417 (1953).

[6] N. A. Khan, THIS JOURNAL, **74**, 3018 (1952).

[7] H. L. Littman and B. Dew-Hughes, Paper presented at the 132nd meeting of the ACS at New York, September 1957.

[8] H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1957).

[9] V. N. Ipatieff and H. Pines, THIS JOURNAL, **72**, 5320 (1950).

[10] G. W. Watt and S. G. Parker (*ibid.*, **74**, 1103 (1952)), have

The H_2 content of these catalysts was studied on a system similar to that described by Smith, *et al.*[3] Samples were initially covered with water.[11] The standard procedure adopted was to use a sample tube equipped with a thermocouple well buried in the wet catalyst. The catalyst was degassed at room temperature until no endothermic reaction was occurring in the catalyst. At this point the catalyst was heated in an oven to remove the rest of the hydrogen.

The surface areas of these catalysts were determined as a function of hydrogen content by the standard BET method[12] with N_2 as the adsorbate.

Differential thermal analysis of the D-1 catalyst was made with a 3″ × 1″ copper cylinder in the top of which were drilled two 1/4″ holes. These holes contained, respectively, a 0.5-g. sample of iron powder and a 0.5-g. sample of Raney nickel. The block was placed in a sample tube sealed to the gas collection apparatus. The heating rate was about 10° per minute. Two procedures were used in the analysis. In the first, the sample was heated with continual pumping, the gas being discharged into a buret, in the second procedure, a small amount of helium was added to the sample chamber and the hydrogen evolution was followed manometrically in a closed system.

All the magnetic measurements cited herein were made at the ambient temperature, *i.e.*, about 25°. The magnet was a 6″ magnet with tapered pole pieces manufactured by Varian Brothers, Inc. The Faraday balance, similar to that used by Selwood, *et al.*,[13] consisted of a McBain–Bakr type of balance in which the sample tube and sample were between the tapered poles of an electromagnet. The McBain–Bakr balance was connected to a standard type of vacuum system containing traps, Pirani and McLeod gauges and also a Puddington[14] type Sprengel pump which discharged into a calibrated volume. The moist sample (about 0.010 g.) was put in the sample tube cooled to −78° and thoroughly evacuated. The system was then shut off from the diffusion pump and the Puddington gas collection pump was cut in. The catalyst was warmed to room temperature and thoroughly degassed. The volume of dried gas collected was measured (to about 0.001 cc. S.T.P.) and the magnetization of the sample was determined. The room temperature magnetization of this sample then was measured with successively higher degassing temperatures until at 400 to 500° the degassing rate was negligible.

Samples for X-ray analysis were obtained by pretreating the catalyst as desired in a sample tube. A small amount was then transferred *in vacuo* to a side tube connected to the sample tube and sealed off. The tube then was broken under water and the wet sample was mixed with Duco cement to form a paste and rolled into cylinders 0.2 to 0.5 mm. in diameter in order to obtain X-ray powder patterns. The X-ray photographs were obtained on an 11.5 cm. Debye camera. Exposures were for two to eight hours with Cu Kα radiation at a current of 15 milliamperes and 45,000 volts.

All density measurements were made in duplicate, as a function of hydrogen content on a helium densitometer of a type which will be described shortly in the literature.[15] On the basis of check measurements with massive nickel the error was thought to be about ±0.001 cc. in volume, and since samples weighing 2-3 g. were used, this meant an error of about ±0.02 g./cc. in density measurements.

Results

Hydrogen Evolution.—Data for the evolution of hydrogen as a function of temperature are shown in Fig. 1 and 2. Figure 1 shows the results of two runs (1 and 2) in which the aged catalyst D-1 was heated at successively higher temperatures until the evolution of hydrogen at each temperature became negligible. The agreement for the two runs illustrates the stability of this catalyst since run 2 was obtained several months after run 1. One rather interesting feature of these curves is the fact that there is an inflection point at about 160°. The feature is more clearly brought out in run 3. In this case the catalyst was heated at the rate of about 10°/min. and the hydrogen evolution was observed continuously. This curve is shifted to the right from the curves for the static measurements (runs 1 and 2) simply because the quasi-stable equilibrium obtained in these runs was not attained instantaneously. In run 3 the rate of hydrogen evolution is essentially zero below 150° increases

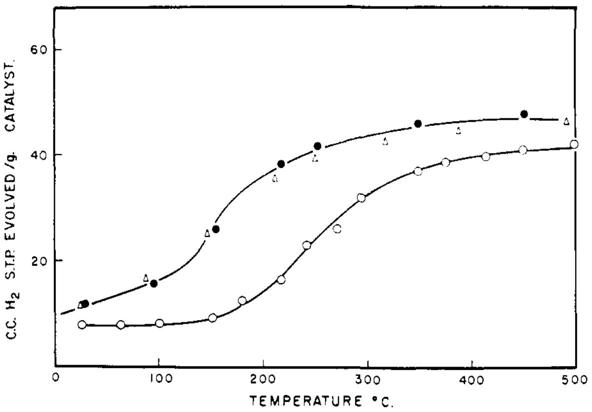

Fig. 1.—Hydrogen evolution from a Raney nickel catalyst (D-1). The symbols △, ● and ○ stand for runs 1, 2 and 3. Runs 1 and 2 were those carried out concurrently with surface area and density measurements. Run 3 was carried out with continuous heating at a rate of about 10°/min.

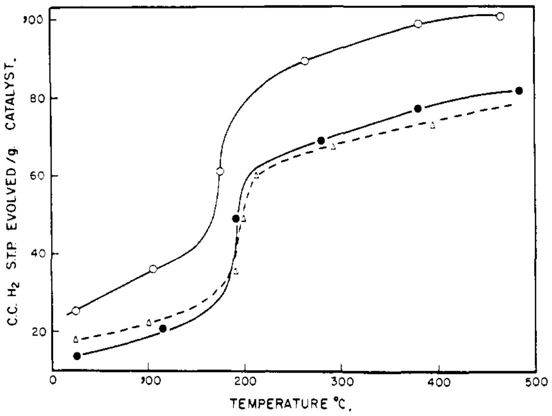

Fig. 2.—Hydrogen evolution from a Raney nickel catalyst (W-6). The symbols ○, ● and △ stand for runs 1, 2 and 3 which were carried out 3, 33 and 85 days after preparation of the catalyst.

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contended that the W-6 catalyst contains no alumina as such, but consists of 80.2% nickel, 13.0% metallic aluminum and 6.8% hydrogen, oxygen and other impurities. Their conclusion was based largely on the assumption that any aluminum(III) oxide would be insoluble in the nitric acid used to dissolve their sample, and they found that only 1% of the sample was insoluble. In the procedure we used, the sample was dissolved in hydrochloric acid. The analysis for the D-1 sample (91.0% nickel and 8.0% aluminum) clearly suggests that the amount of metallic impurities in this activated nickel-aluminum alloy was far less than 6.8%. The same alloy was used to prepare the W-6 sample and we feel that the component which accounts for 9.2% of the weight of our W-6 catalyst (77.3% nickel, 13.24% aluminum and 0.3% acid insoluble material) cannot be metallic impurities but must be oxygen combined with aluminum.

(11) Preliminary runs showed that samples stored under CH_3OH or C_2H_5OH yielded large amounts of methane when degassed and heated to evolve hydrogen.

(12) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(13) P. E. Jacobson and P. W. Selwood, *ibid.*, **76**, 2641 (1954).

(14) I. E. Puddington, *Ind. Eng. Chem., Anal. Ed.*, **16**, 592 (1944).

(15) R. J. Kokes, unpublished work.

rapidly to a maximum at about 220–240°, and then falls again becoming quite low above about 350°. These results suggest a rather sudden onset of lability on the part of the hydrogen between 200 and 300°.

Figure 2 shows the data for the rate of hydrogen evolution for the W-6 catalyst. Qualitatively, the features of the curves are similar to those for the D-1 catalyst; one additional feature is, however, evident. The data for run 1 were obtained 3 days after preparation of the catalyst. It was noted that for at least one month after its preparation, the catalyst while stored in water was degassing as evidenced by gas bubbling up from the catalyst. Comparison of run 1 to 2 and 3 in Fig. 2 shows clearly that during the first month of the life of the catalyst about one-fifth of the hydrogen is lost. Moreover, it appears that a large part of the hydrogen lost is that labile portion removed from a fresh catalyst below 100 to 120°. On the basis of runs 2 and 3 which were run 33 and 85 days after the preparation of the catalyst, it is evident that the catalyst reaches a more or less steady state after about one month.

On the basis of some 9 runs with the D-1 catalyst the hydrogen evolution was 43.6 ± 1.8 cc./g. The maximum temperatures to which the catalyst was heated to remove hydrogen ranged from 400° to about 1000°. These results show not only the reproducibility of these experiments but also suggest that substantially all the hydrogen is removed at or below 400°.

Surface Area.—The surface area of the 200 mesh 50–50 Ni–Al alloy used as a starting material for catalyst studied herein was 0.13 m.^{2}/g. The area of the D-1 catalyst vacuum dried at room temperature was 76 m.^{2}/g.; it did not change appreciably when heat-treated below 250° where 80 to 90% of the hydrogen was removed. Even after removal of substantially all of the hydrogen by heating the sample to 480° the area was still appreciable (35 m.^{2}/g.). This catalyst is apparently more stable thermally than pure metal catalysts.[16] Probably, the trace of alumina in the D-1 catalyst promotes thermal stability.

Similar results were obtained with the W-6 catalyst, but in this case the thermal stability was somewhat greater. The area (initially 63 m.^{2}/g.) did not change with heat treatment below 350°. In addition, when the W-6 sample was heated to 500° it lost only one-fourth of its area. It seems reasonable to suppose that this enhanced stability of the W-6 catalyst is connected with its large alumina content.

Both of the catalysts used in the present studies have areas appreciably larger than those (18.6 to 50 m.^{2}/g.) reported by Smith and co-workers for a variety of Raney nickel catalysts.[17] However, our results for the W-6 catalyst are in fair agreement with the value 87 m.^{2}/g. reported by Watt, Roper and Parker.[18] It is also of interest to note that these authors obtained values of about 59 cc./g. (average value), for the hydrogen content of the aged W-6 catalyst in fair agreement with our data.

X-Ray Measurements.—X-Ray powder patterns for the unactivated 50–50 NiAl alloy are those expected for a mixture of Ni_2Al_3 and $NiAl_3$. These phases would be expected for an equilibrium alloy of this composition.[19]

X-Ray powder patterns were obtained for the D-1 catalyst as a function of hydrogen content. In every case the only detectable phase had a face-centered cubic structure with an a_0 between 3.532 ± 0.004 Å. (initial) and 3.535 ± 0.002 Å. (degassed). No attempt was made to determine crystallite size but, of course, the lines which were initially quite broad became sharper as the catalyst was heated to successively higher temperatures. The a_0 values are greater than those found for a sample of pure nickel (3.524 ± 0.001 Å.), but this is to be expected for samples in which there is a solid solution with Al. The a_0 value should be 3.546 Å. for a Ni–Al alloy containing 8 wt. % or 16 atom % Al.[16]

A sample of the W-6 catalyst was also examined with X-ray to determine what phases were present. In addition to the face centered phase (a_0 = 3.53 A.) there were faint but sharp lines characteristic of β $Al_2O_3{\cdot}3H_2O$. This material was apparently present only in small amounts since the weight loss after heating the sample of W-6 catalyst *in vacuo* from room temperature to about 500° was only about 1%. It is clear, therefore, that the bulk of the aluminum present was not present as β $Al_2O_3{\cdot}3H_2O$ but as poorly crystallized alumina whose water of hydration is largely removed by prolonged evacuation at room temperature.[21]

Differential Thermal Analysis.—Figure 3 shows the results of differential thermal analysis carried out *in vacuo* on about 0.5 g. of D-1 catalyst together with data obtained simultaneously for the evolution of hydrogen and the rate of evolution of hydrogen. It is apparent from these data that the evolution of hydrogen is an exothermic reaction as indicated originally by the work of Raney.[20] This reaction takes place most rapidly slightly below 200°. Similar results were obtained when the sample was heated in a closed system with helium, but in this case the peak in the differential thermocouple reading occurred at 220–230°.

Magnetic Measurements.—Magnetic measurements were made on the original alloy and on the two activated catalysts. The original alloy showed no ferromagnetism; hence, no free nickel was present initially. Figure 4 shows the room temperature magnetization of the D-1 and the W-6 catalyst as a function of the hydrogen removed. The data for the D-1 catalyst indicate the reproducibility of these measurements. (In two of the runs the dehydrogenation of the catalyst was not carried to completion owing to a possible leak in the system.) These data clearly show that the magnetization increases more or less linearly with the amount of hydrogen removed until about 90% is removed. Removal of the last traces of

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(16) A. P. Franklin and R. B. Campbell, *J. Phys. Chem.*, **59**, 65 (1955).

(17) H. A. Smith, W. C. Bedoit and J. F. Fuzek, THIS JOURNAL, **71**, 3769 (1949).

(18) G. W. Watt, W. F. Roper and S. G. Parker, *ibid.*, **73**, 5791 (1951).

(19) A. J. Bradley and A. Taylor, *Proc. Roy. Soc.* (*London*), **159**, 56 (1937).

(20) M. Raney, *Ind. Eng. Chem.*, **32**, 1199 (1940).

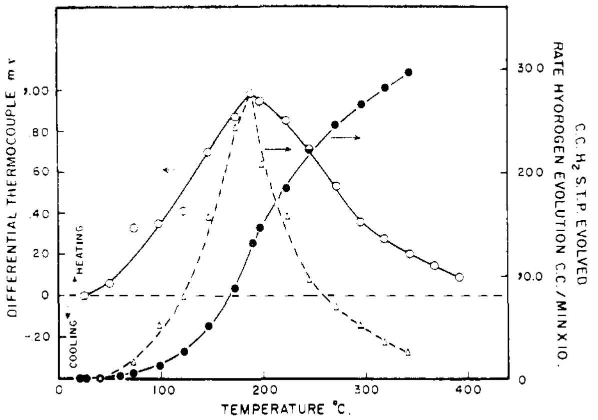

Fig. 3.—Differential thermal analysis of a Raney nickel catalyst (D-1) (about 0.5 g.). The symbols ● and △ refer to hydrogen evolution and rate of hydrogen evolution, respectively. The symbol ○ refers to differential thermocouple readings.

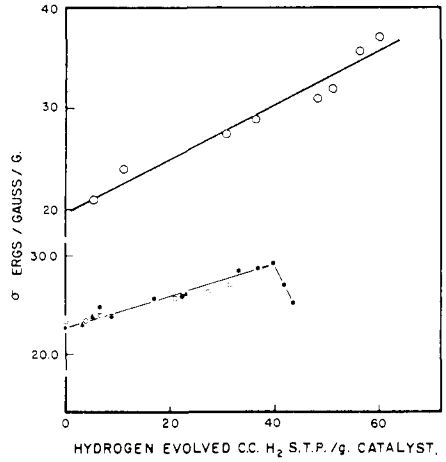

Fig. 4.—Specific magnetization of a Raney nickel catalyst as a function of its hydrogen content. The upper curve is for the W-6 catalyst and the lower curve is for the D-1 catalyst. The different symbols denote duplicate runs on different samples. Note broken scale.

hydrogen from the D-1 catalyst causes an abrupt drop in the magnetization. This occurs at about 250°, the temperature at which the surface area starts to decrease. For the W-6 catalyst no marked departure from linearity is apparent. The slope of the linear part of these plots is greater by a factor of two for the W-6 catalyst.

The total amount of hydrogen evolved for the D-1 catalyst in the magnetic studies, 44 cc./g., is in good agreement with the amount found in the runs shown in Fig. 1, but the amount found for the W-6 catalyst is only 60 cc./g. compared to the value of 72 cc./g. found for the aged catalyst (Fig. 2). It is believed that this result follows from the fact that the hydrogen in the W-6 catalyst is in a somewhat more labile form than in the D-1 catalyst. Thus, the rather rigorous degassing condition used in the magnetic studies might very easily have removed some hydrogen from the W-6 catalyst but none from the D-1 catalyst. If this is the case, the origin indicated in Fig. 4 for the W-6 catalyst might correspond to a catalyst which has already lost about 10 cc. of hydrogen/g. catalyst.

Density.—Figure 5 shows the density of the D-1 catalyst and the W-6 catalyst as a function of hydrogen content. To a first approximation, the density increases linearly with the amount of hydrogen removed. The most surprising feature of these data is that the density is abnormally low. For example, if we assume that the aluminum in the D-1 catalyst is present as a solid solution with nickel on the basis of our analysis the density should be about 8.0 g./cc. It is apparent from Fig. 5 that this value is not attained even after all of the hydrogen is removed. Similar computations for the W-6 catalyst are subject to a greater uncertainty owing to the presence of the alumina phase. Since the over-all weight loss in this treatment was about 1% and, since almost all of the weight loss occurred in the early stages of dehydrogenation, it seems likely that the alumina, at least in the later stages of the dehydrogenation, was essentially anhydrous. In this event the density of the alumina was probably 3.5 g./cc. or at worst 3.0 g./cc.[21] Using these values, we find the calculated density of the W-6 catalyst to be 6.6 to 6.2 g./cc. These values once again are considerably greater than those found experimentally and suggest the catalyst has a highly defective structure.

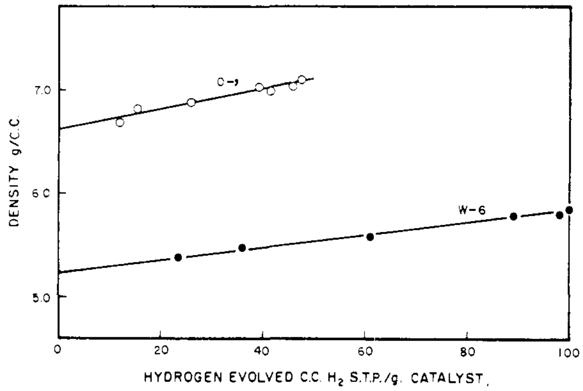

Fig. 5.—Helium density of Raney nickel catalysts as a function of their hydrogen contents.

Discussion

At the start of this investigation, answers to the following three questions concerning the nature and properties of the hydrogen content of Raney nickel catalysts were sought: (1) how is the hydrogen held by the nickel; (2) what influence does the hydrogen have on the magnetic properties of the catalyst and (3) what influence, if any, does the original hydrogen in the Raney nickel have on catalytic activity? The work in the present paper appears to have yielded a satisfactory answer to the first two of these questions. The third one will be the subject of a second paper.

Nature of the Hydrogen in Raney Nickel Catalysts.—The data presented above can, it appears, be best interpreted by concluding that the hydrogen is held in the nickel in the form of substitutional replacement of nickel atoms in the lattice.

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[21] Alumina Properties, Aluminum Company of America (1946), Pittsburgh, Pa.

It does not appear to be present as adsorbed hydrogen or as dissolved hydrogen; neither does it appear to be formed by the reaction of residual aluminum during the process of heating the sample to remove the hydrogen. The evidence for these conclusions may be summarized.

1. The density of the samples is much lower than would be expected for bulk nickel or for nickel–aluminum alloys of the compositions of the samples of D-1 and W-6 catalysts here studied. A reasonable interpretation of these low densities is the existence of the nickel as a defective structure[22] involving a large number of lattice vacancies. The initial density of the D-1 sample would correspond to the presence of 18.2% lattice vacancies. The calculation for the W-6 catalyst is a little less certain than that for the D-1 sample because an assumption has to be made for the density of the aluminum oxide present. Using the reasonable value 3.5 for the density of the alumina, one obtains an estimate of 30.4% lattice vacancies.

2. The lattice vacancies in the nickel are sufficient in number to account for substantially all the hydrogen that can be removed from the samples by careful heating and thorough evacuation. For example, the 18.2 and 30.4% lattice vacancies calculated for the D-1 and W-6 catalysts from the density data would correspond to 46 and 70 cc. of H_2, respectively, per gram of catalyst if each lattice vacancy is assumed to hold one hydrogen atom. By comparison, as shown in Fig. 1, the hydrogen evolved from the D-1 catalyst was in the range 46 to 48 cc. per gram; that evolved from the W-6 catalyst (Fig. 2) was about 100 cc. per gram for the fresh catalyst and in the range 72–81 cc. for the stable catalyst that had stood in water for 35 days or longer. The agreement is excellent for the D-1 catalyst and as good as can be expected for the W-6 catalyst in view of the assumption that had to be made in regard to the density of the 19.8% Al_2O_3 believed to be present.

3. The surface area of the samples is much too small to permit the observed amounts of hydrogen to have been present principally as adsorbed hydrogen. For example, the 63 m.^{2}/g. surface area of the W-6 catalyst corresponds to a monolayer of 14.4 cc. of physically adsorbed nitrogen. Chemisorption measurements (to be reported elsewhere) showed that only 20%[23] of the surface was nickel. The remainder presumably was covered by alumina. Taking into consideration the usual ratio of about 1:2 between the volume of H_2 and CO adsorption on nickel, one would conclude that only 1.5 to 2 cc. of hydrogen would be chemisorbed on the surface if each nickel capable of holding a CO molecule was capable of holding a hydrogen atom. This is to be compared to 72 to 100 cc. of hydrogen observed on the W-6 catalyst. For the D-1 sample, no chemisorption measurements for carbon monoxide have as yet been made. Even if one assumes that all of the surface of this catalyst is available for hydrogen adsorption as atoms one would expect only 8 to 10 cc. of the observed 47 cc. of hydrogen to be capable of being accounted for as adsorbed hydrogen.

4. A second and conclusive bit of evidence which indicates that most of the hydrogen has to be accounted for by something other than adsorption is found in the differential thermal analysis. In the temperature range 180 to 230° a strong heat evolution occurred; this was accompanied by a strong evolution of hydrogen. X-Ray results showed no detectable phase changes in this region. Surface area measurements preclude the possibility that the heat evolution resulted from sintering because the surface area did not decrease appreciably below about 250°. The conclusion seems inescapable that the evolution of the hydrogen is an exothermic process. This rules out surface adsorption as a major factori n retaining the hydrogen because all large adsorptions of hydrogen on metals have proved to be exothermic in adsorption and endothermic in desorption.

5. The large amounts of hydrogen held by the catalysts cannot reasonably be interpreted as due to ordinary solution. To begin with the latter at one atmosphere pressure should amount to only 0.01 cc./g. instead of the 46 to 100 cc. observed. Some may argue that the high equivalent pressure of hydrogen formed by the reaction of sodium hydroxide with aluminum in making the catalyst might produce supersaturated solution of hydrogen in the nickel. Against this there are two bits of evidence. Littman and Dew-Hughes[7] showed that as much as 50 cc. of hydrogen per gram could be put back into a Raney nickel catalyst after the latter had been degassed at 1200°. Thus at 400° such a sample on exposure to 140 atmospheres of hydrogen picked up about half the amount it originally contained. At this pressure and temperature the true solubility is only about 0.4 cc./g., about 1% of the amount of hydrogen taken up by the sample. The second bit of evidence has to do with the rate of hydrogen evolution from the original Raney nickel catalyst. The hydrogen evolution is much slower than would be expected if it were merely dissolved in the nickel. The temperature of maximum rate of evolution (180 to 220°) is about that which one would expect on the basis of the usual rule that sintering and atom migration in a metal begins at about $^1/_3$ to $^1/_4$ the melting point.

6. The hydrogen evolved from the Raney nickel catalysts cannot be due to the reaction of water vapor with the residual aluminum content of the catalyst. For example, if all of the aluminum in the D-1 catalyst had reacted to form hydrogen, it would have resulted in the final degassed catalyst containing 14% Al_2O_3 instead of the observed 1%.

The magnetic data in Fig. 4 are interesting from several points of view. In discussing these data we shall, following Selwood,[24] assume that the change in σ relative to the value for pure nickel is the same for this catalyst at room temperature as it would be at absolute zero.

The data in Fig. 4 strongly suggest that the D-1 catalyst is not a homogeneous solution of aluminum in nickel. The value of σ increased linearly, with the amount of hydrogen removed until the

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[22] A. Taylor and J. Weiss, *Nature*, **141**, 1055 (1938).

[23] Unpublished work, R. J. Kokes and P. H. Emmett.

[24] L. E. Moore and P. W. Selwood, THIS JOURNAL, **78**, 697 (1956).

temperature of the catalyst reached 260 to 300°; it then dropped abruptly. Since the temperature at which this sudden drop occurs is about the same as that at which sintering starts, it appears to be related to and could be accounted for by the onset of intercrystalline diffusion of patches of aluminum into the catalyst.

If one makes the assumption that each hydrogen atom can contribute one electron and each aluminum atom can contribute 3 electrons to the d-band of the nickel atoms, the magnetic data shown in Fig. 4 seem to be explainable. For example, the W-6 catalyst on the basis of analysis and hydrogen content has about 1.8 added electrons per unit cell initially; this falls to 0.76 electron per unit cell when the hydrogen is removed. If the magnetization depends upon the number of added electrons per unit cell,[25] the value of σ would be expected to increase from 14 to 35 as the hydrogen is removed and the slope would be 0.27 per cc. of hydrogen removed. The observed values in Fig. 4 show increases from 19.5 to 35 and the slope has a value of 0.27/cc. If, as has sometimes been done,[26] one assumes that the magnetism disappears when the added electrons amount to 0.6 per gram atom, then the decrease in the number of added electrons from 0.45 to 0.22 per nickel atom as hydrogen is removed would correspond to a change in σ from 14 to 35 with a slope of 0.24 per cc. of hydrogen removed. Either of these calculations is in satisfactory agreement with the observed values and seems to suggest that each hydrogen is indeed on an average contributing one electron to the nickel.

For the D-1 catalyst similar calculations as to the total change in values of σ cannot be made because this catalyst appears to be non-homogeneous. The calculations of the slope of the magnetic susceptibility as a function of the amount of hydrogen removed might, however, be expected to be reasonable. The calculations analogous to those made for the W-6 catalyst suggest a slope of 0.28 per cc. of hydrogen removed based on the number of added electrons per unit cell and 0.16 per cc. of hydrogen based on the number of electrons per gram atom of nickel. The observed slope is 0.16 per cc. of hydrogen removed.

One final observation may be of interest. When a Raney nickel catalyst is degassed, the alloy does not wholly anneal but half of the lattice vacancies remain. It is difficult to understand why these lattice vacancies do not completely disappear when the nickel samples are heated to the 1000–1200° region. This result, however, is consistent with the observation by Littman and Dew-Hughes[7] that roughly one-half the hydrogen could be put back into a Raney nickel sample at 400° and 140 atmospheres even though the sample had first been heated to 1200°. Perhaps the small amounts of aluminum oxide tend to retard the rearrangement necessary to fill completely the vacancies in the nickel lattice.

In conclusion, it should be emphasized that the above analysis is probably over-simplified, and in fact the validity of some of the assumptions may be questionable. Nonetheless, it does give a rather detailed picture consistent with experimental data. The picture is one in which hydrogen atoms form a substitutional alloy with Raney nickel much like copper in copper-nickel alloys. This hydrogen can be removed by heating. The nickel–aluminum alloy thus created still contains a large number of lattice vacancies which can be reoccupied by hydrogen atoms by exposure to hydrogen gas at high pressures.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the W. R. Grace Company.

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[CONTRIBUTION FROM THE DEPARTMENT OF THEORETICAL CHEMISTRY, UNIVERSITY CHEMICAL LABORATORY]

Molecular Complexes and their Spectra. IX. The Relationship between the Stability of a Complex and the Intensity of its Charge-transfer Bands[1]

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RECEIVED MARCH 2, 1959

The matrix elements of the Hamiltonian and of the transition moment operator which occur in the theory of charge-transfer complexes are examined in more detail than has previously been attempted. The contribution to the intensity of the charge-transfer band arising from the interaction of the charge-transfer state with the ground state is compared with the contributions expected from the excited states of the donor and acceptor. It is shown that the donor-excited states will contribute the greatest intensity except when, for reasons of symmetry, they do not interact with the charge-transfer state. Contact charge-transfer absorption will be due almost entirely to the interaction of the charge-transfer and donor-excited states. It is proposed that in a series of related complexes, the relative behavior of the intensity of the charge-transfer band and the stability of the complex depends on the variation of the difference in energy between the most stable configuration and the configuration giving the greatest contribution to the intensity: these configurations are not usually identical. Examples are given to show that the intensity of the charge-transfer band may increase or decrease as the complex becomes more stable.

1. Introduction

Charge-transfer (c-t.) absorption bands have been observed for pairs of molecules which form crystalline molecular complexes (*e.g.*, the quinhydrones),[2] for molecules which appear to form a stable complex in solution but which give no crystalline complex (*e.g.*, iodine and benzene)[3] and for molecules

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[1] This work was initiated at the Department of Physics, The University of Chicago, whilst the author held a Fellowship from the Commonwealth Fund of New York.

[2] L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

[3] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 2832 (1948).