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The Chemisorptive Bonding of Hydrogen on Nickel

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Published experimental results plus a limited amount of new data show that chemisorbed hydrogen on nickel must consist of an atom carrying a negative charge. The nickel atom most affected retains a magnetic moment but loses its ability to participate in ferromagnetic exchange interaction. It retains most of its other properties as part of the metal particle. The stoichiometry is one hydrogen to one nickel with minor peripheral effects. There is no change of stoichiometry, or of bonding mode, over the whole range of surface coverage or, within limits, of temperature change. The bonding is quite different from that in nickel hydride.

INTRODUCTION

The purpose of this paper is to present the bonding mode most nearly consistent with published experimental data for hydrogen chemisorbed on nickel. To do this it has been necessary to resolve some anomalies and a few apparent contradictions. Attention has been directed chiefly to two areas, first, the poisoning of the nondissociative orthohydrogen conversion and, second, the loss of magnetic moment. Both of these occur when hydrogen is chemisorbed on nickel. The mode of bonding in the one case must be the same as that in the other.

Adsorbates other than hydrogen are not considered, except as they may contribute to the main objective, and no attempt has been made to compare the conclusions reached with those derived from theoretical studies. Rather the purpose has been to collect, evaluate, and correlate the available experimental data with the hope of being able to present the facts with which any theoretical treatment must be consistent. Few of the ideas presented are new but some of the relationships between them have not heretofore received attention.

THE CATALYST POISONING REACTION

Pure Nickel

There is much evidence that chemisorbed hydrogen poisons nickel for the nondissociative orthohydrogen conversion. For instance, Harkness and Emmett (*1*) studied pure nickel oxide reduced in flowing hydrogen at a temperature of 573 K, then cooled in hydrogen to 77 K. (Hereafter procedures such as this will be abbreviated as follows: $H_2573 \rightarrow 77$). The conversion activity at 77 K was almost two orders less than that for the same sample pretreated ($H_2573He77H_2$). Singleton (*2*) obtained similar results on nickel films. It might be thought that some of the activity in these experiments may have been due to a dissociative conversion mechanism. It is true that many reports have been made of hydrogen–deuterium equilibration over similar catalysts at 77 K, but in every case the specific rates reported have been much less than the conversion rates referred to here.

Supported Nickel

There appear to be no reports of nickel supported on high-area silica behaving much differently than pure nickel as described in the preceding paragraph. But nickel–alumina presents some anomalies. If nickel oxide supported on alumina is pretreated ($H_2700 \rightarrow 77$) it may exhibit specific catalytic activity much in excess of that predictable from the magnetic moment of the nickel metal. Attention to this was drawn by Weitzel *et al.* (*3*). The catalyst contained 5.3% Ni, prepared by impregnation of high-area alumina and pretreated ($H_2673 \rightarrow 20$). This observation was confirmed by Wakao *et al.* (*4, 5*) who also found that a 0.5% nickel–alumina pretreated ($H_2673 \rightarrow 77$) had an activity only 40% less than after the alternative pretreatment ($H_2673He77H_2$). In new experimental work by the author (unpublished data) it was found that a 5.0% nickel–alumina pretreated ($H_2673 \rightarrow 77$) had the same activity as after the pretreatment ($H_2763evac77H_2$). But if the same sample was reduced at a higher temperature ($H_2873evac77H_2$) the specific activity was not only diminished by over two orders but the effect of changing the pretreatment to ($H_2873 \rightarrow 77$) lowered the activity by an additional 50%. It may therefore be said that if nickel oxide is supported on alumina and is not completely reduced to metal there is a surprisingly large conversion activity at low temperatures and, also, this activity is not strongly poisoned by chemisorbed hydrogen.

The reason for the high activity shown by incompletely reduced nickel–alumina catalyst is almost certainly that suggested by Reinen and Selwood (*6*) namely that during reduction the Ni^{3+} (*7*) becomes, first, Ni^{2+} with the loss of O^{2-}. This leaves the Ni^{2+} with its Bohr magneton number $\beta(Ni^{2+}) = 2.9$ or higher and directly accessible to molecular hydrogen. There is abundant evidence in the literature that, as shown by Wigner (*8*), the nondissociative conversion rate is proportional to β^2. For a stage at which half the nickel has been reduced to metal, for which $\beta(Ni) = 0.6$, and the remainder only to Ni^{2+}, the metal will contribute only 7% to the catalytic activity if it is assumed that the distance of nearest approach is about the same. The high activity of the partially reduced catalyst has, therefore, a simple explanation. The "activated" nickel oxide contributes most of the activity until it is about 90% reduced to metal.

The cause of the anomalous lack of effective hydrogen poisoning in partially reduced samples is obvious from the considerations presented above. Molecular hydrogen is chemisorbed to a limited extent only on nickel oxide, and then only at moderately elevated temperatures. Unless nearly all the nickel oxide is reduced to metal the poisoning effect of chemisorbed hydrogen is difficult to observe. It might be thought that the antiferromagnetism of nickel oxide would complicate this explanation but actually nickel oxide supported at relatively low concentration on alumina is paramagnetic (*7*) and, in any event, the nondissociative orthohydrogen rate is greater at temperatures moderately below the Néel point for Cr_2O_3, CoO and MnO (*9, 10*). This surprising result is apparently related to a change of the rate-determining process from diffusional to spin–wave interaction at T_N (*11, 12*).

In summary it may be said that there are no unexplained exceptions to the statement that the nondissociative conversion process over nickel metal is strongly, if not completely, poisoned by chemisorbed hydrogen. This poisoning can only occur through lowering, to near zero, of the magnetic moment of the surface nickel atoms most closely affected, or by steric blocking of those atoms by the adsorbed species.

THE LOSS OF MAGNETIC MOMENT

Definition of $\epsilon_{Ni}(H)$

We define a number ϵ, for the system under consideration, as follows:

$$\epsilon_{Ni}(H) = (\Delta M_0/M_0)n(Ni)\beta(Ni)/n(H),$$

where $\Delta M_0 = M_0' - M_0$ is the change of saturation magnetization at absolute zero, n(Ni) the moles of nickel present, β(Ni) the Bohr magneton number of nickel metal, and $n(H)$ the moles of hydrogen atoms adsorbed. It will be noted that ϵ is dimensionless. The experimental determination, properties, and applications of ϵ to hydrogen and to other adsorbates and adsorbents have been described by the author (*13*).

Determinations of ϵ_{Ni}(H) have been made by several groups including Dietz and Selwood (*14*), Hahn and Löckenhoff (*15*), and Martin *et al.* (*16*). For many reduced nickel–silica preparations and other samples, such as are commonly used in catalytic hydrogenation, the values of ϵ_{Ni}(H) are in excellent agreement at -0.70 ± 0.02. It is to be noted that Martin *et al.* used α instead of ϵ and that their definition refers to $n(H_2)$ instead of n(H). Consequently their $\alpha = 2\epsilon$ as defined in this paper for hydrogen as adsorbate although not necessarily so for other adsorbates [Ref. (*13*) p. 120]. The number ϵ_{Ni}(H) has been found to be independent of surface coverage and of metal particle size over a wide range. On these samples the adsorption and desorption magnetization–volume isotherms are identical, ϵ_{Ni}(H) is independent of the temperature of adsorption provided that this is not so low that appreciable physical adsorption takes place, and it is independent of preadsorbed molecules provided that, under the conditions, no chemical reaction takes place.

Anomalous Values of ϵ_{Ni}(H)

Reinen and Selwood (*6*) have reported that, under some circumstances, $-\epsilon_{Ni}$(H) is considerably less than 0.70. Their results, subject to various uncertainties described in the original paper, are summarized in Table 1. These anomalous results have been confirmed and extended by Martin *et al.* (*16*) who have also found that the magnetization–volume isotherm is not always reversible. A few of the many results obtained by Martin *et al.*, from the adsorption part of the cycle only, are also shown in Table 1. The general appearance of the adsorption–desorption cycle reported by Martin *et al.* is shown in Fig. 1 (this does not refer to any particular sample). It is important to note that while the adsorption is carried out at room temperature, and that while

TABLE 1

Comparison of ϵ_{Ni}(H)[a]

Sample:	Ni–SiO$_2$			Ni–Al$_2$O$_3$			Ni–MgO
Ref.:	(*6*)	(*6*)	(*16*)	(*6*)	(*6*)	(*16*)	(*16*)
Preparation:	Coppt.	Impreg.	Impreg.	Impreg.	Impreg.[b]	Coppt.	Impreg.
Surface ($m^2 \cdot g^{-1}$)	275	483	324[c]	281[d]	175	261[c]	46[c]
Ni content (%)	48	13.5	12.6	13.5	13.5	14	12.9
Reduction T in H_2 (K)	700	673	703	723	673	923	773
% Ni reduced	~100	~90	90	~80	~90	87.5	47
Particle diam (nm)	4.6[e]	8.8[e]	—	5.2[e]	11.6[e]	—	—
ϵ_{Ni} (H)[f]	−0.67	−0.57	−0.60	−0.34	−0.67	−0.3	−0.22

[a] Adsorption at 298 K.

[b] After sintering at 873 K.

[c] Prior to reduction.

[d] Al_2O_3 prior to impregnation.

[e] Obtained by the Langevin low field method, Ref. (*13*), p. 46.

[f] α, used by Martin *et al.* (*16*) equals 2ϵ.

some of the hydrogen may be desorbed at room temperature, yet a large fraction of the hydrogen may only be desorbed at substantially elevated temperature. An indication of this is given in Fig. 1. It will also be seen from Fig. 1 that a sample giving $-\epsilon_{Ni}(H) = 0.3$ for adsorption yields a value of 0.6 for the earlier stage of desorption. But later, as the temperature must be raised to remove the remaining hydrogen, the magnetization actually rises above that found before the admission of any hydrogen. (It is repeated that the magnetization measurements were all made at liquid helium temperature.) The adsorption–desorption hysteresis found by Martin *et al.* was observed for all samples for which $-\epsilon_{Ni}(H) < 0.6$. Even for some samples of nickel–silica there was an indication of hysteresis and this was especially true of less well-reduced samples. A very large hysteresis loop was found for nickel supported on magnesia.

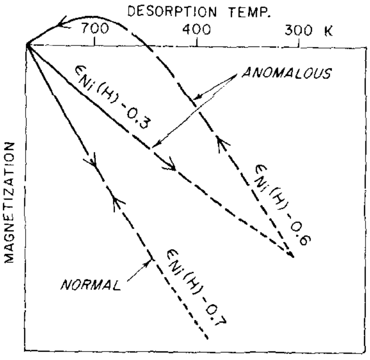

FIG. 1. Representative adsorption–desorption magnetization–volume plot for H_2 on Ni/Al_2O_3 [based in part on Martin *et al.* Ref. (*16*)].

The low values of $-\epsilon_{Ni}(H)$ found for some samples of nickel–alumina have been thought (*6*) to be related to incompletely reduced nickel oxide and it is certain that a parallelism exists. The explanation proposed by Martin *et al.* (*16*) is essentially as follows. There are two modes of chemisorption. For one mode $\epsilon_{Ni}(H) = -0.70$ and for the other $+0.65$. For samples such as completely reduced nickel–silica the former value is the only one found. For samples such as partially reduced nickel–alumina both values are found. The positive ϵ is related to adsorption on the unreduced oxide and especially near the metal–oxide boundary. The exact nature of the bonding leading to a positive ϵ is not clear. Two additional pieces of experimental information will be mentioned. First, although it is difficult to compare two different samples, yet it seems clear that those samples yielding an adsorption $\epsilon_{Ni}(H)$ of -0.3 take up more hydrogen than do those samples yielding $\epsilon_{Ni}(H) = -0.7$. And, second, chemisorbed oxygen yields the normal $\epsilon_{Ni}(O_2) = -1.5$ for all samples (*13, 16*).

The explanation of Martin *et al.* (*16*) may be extended in a logical manner that includes all available experimental data. This explanation does not invoke a positive ϵ. Since the initial observation of Khoobiar (*17*) it has become clear that "activated" hydrogen may migrate over alumina and various other oxides. The subject has been reviewed by Sermon and Bond (*18*). Evidence for migration on the nickel–alumina system is less extensive than that on platinum–alumina but there seems little doubt that on the latter the ratio of hydrogen atoms chemisorbed to surface metal atoms can rise to two or higher. There is also no doubt that such hydrogen, at appropriate temperature, is capable of migrating to, and of reducing, pure nickel oxide at an accelerated rate. It is proposed that a partially reduced nickel–alumina sample interacts with hydrogen in the following manner. The hydrogen is chemisorbed virtually instantaneously on the nickel metal at room temperature but, as surface coverage increases, some of the hydrogen migrates over the alumina and to the nickel oxide. As a result of this migration the quantity of hydrogen remaining chemisorbed on the nickel metal is overestimated by a factor that may approach two. Consequently $\epsilon_{Ni}(H)$ appears to be about -0.3 instead of about -0.7. At, or near, complete surface coverage of the metal a portion of the hydrogen is held by weak bonding and it may be removed by evacuation at room temperature. The magnetization then rises and, before much hydrogen has had time to migrate back to the metal it is found (Fig. 1) that $\epsilon_{Ni}(H)$ is about -0.6. But, as desorption proceeds it is necessary to raise the temperature. Finally, above 673 K, the reaction by which the nickel metal was originally generated begins to occur at a measurable rate and this gives rise to a slight increase in the proportion of nickel present as metal. This would cause an increase of the saturation magnetization, M_0. For the case illustrated in Fig. 1, and for a nickel particle containing 100 atoms, this could occur by an increase of only 2 atoms/particle. But, as evacuation and desorption continue at 723 K there is soon no hydrogen left, except perhaps in the form of OH^-, and the fraction of nickel present as metal reverts to its original value. The anomalous rise and fall of M_0 during desorption thus has a simple explanation.

It appears to be, therefore, possible to confirm that the apparent contradictions in values for $\epsilon_{Ni}(H)$ are due to a special situation, namely, the presence of unreduced nickel oxide. This is, of course, the same situation that leads to the activity and poisoning anomalies for the orthohydrogen conversion. It may be said that in the absence of this complication an atom of chemisorbed hydrogen lowers the Bohr magneton number of nickel by 0.70. This loss can only occur through one of the following three mechanisms: loss of the magnetic moment of the nickel atom most strongly affected (this is identical with one of the possible mechanisms listed for conversion poisoning), or partial filling of the collective *d* band of the metal, or loss of participation in ferromagnetic (parallel) exchange interaction by the nickel atom affected (a local magnetic moment being retained). The saturation magnetization measurements are made with increments of chemisorbed hydrogen although experimental difficulties prevent carrying the pressure up to atmospheric. It is true that low field magnetizations at room temperature have been extended to well above atmospheric and the results show a continuing, but small, linear decrease. What confidence may be placed in the low field work is discussed in Ref. (*13*), pp. 82, 85, and 92. For the purposes of the present paper it will be assumed that $\epsilon_{Ni}(H)$ has been proved to be constant over at least two-thirds of complete coverage and that there is strong evidence it remains the same over the remaining third.

Some Bonding Considerations

Any proposed mechanism to explain the nondissociative orthohydrogen conversion poisoning must be capable of explaining the change of magnetic moment. But there is an important difference in what is measured by the two experiments. The conversion experiment is related to the magnetic moment of the nickel atom most closely approached by a hydrogen molecule (and to the distance between them). The Bohr magneton number of this nickel atom, which must be on the surface, will be designated $\beta(Ni_s)$. But determination of $\epsilon_{Ni}(H)$ involves the average magneton number for all nickel atoms in the sample. This will, as before, be designated $\beta(Ni)$. The proof that, in the absence of an adsorbate, $\beta(Ni_s)$ and $\beta(Ni)$ are the same is presented in Ref. (*13*), p. 24. It may also be asked if the conversion rate measured over a ferromagnetic solid could be dependent on a spin–wave mechanism involving, in this case, many nickel atoms. But at 77 K it is more probable that the rate is diffusion controlled (*19*).

The four different mechanisms derived from conversion poisoning and magnetization results, as developed in preceding sections, are summarized in Table 2. Some additional comments will be made. Mechanism 1 involves, of necessity, a loss of exchange interaction because the atom no longer has unpaired electrons. In a sense, the nickel atom is physically removed or, alternatively, it is replaced by a diamagnetic atom such as copper. Mechanism 2 has no effect on $\beta(\mathrm{Ni})$ or on $\beta(\mathrm{Ni_s})$. It could be achieved by a hydrogen atom carrying appreciable negative charge. Mechanism 3 is the collective *d* band model that has undergone much change since it was proposed many years ago. A more recent view is given by Dowden (*20*). Mechanism 4 involves loss of parallel Heisenberg exchange interaction by the nickel atom involved, but a magnetic moment is retained. (If the moment were lost Mechanisms 1 and 4 would be identical.) It will be noted that some of the mechanisms are mutually exclusive as indicated in Table 2 and that some could not alone account for all the facts.

It would not be possible for a chemisorptive bond between hydrogen and nickel to influence one, and only one, metal atom. There must always be some peripheral effect on neighboring atoms. The fact that $-\epsilon_{\mathrm{Ni}}(\mathrm{H})$ is almost always larger than $\beta(\mathrm{Ni})$ by about 14% may be related to this effect. For an average exposed atom with from 3 to 11 nearest metal atom neighbors this is not a large change. But to this degree we cannot make a sharp distinction between "local" and "collective" interactions. For the sake of this discussion we shall define "local" interaction as that in which only a few of the neighboring atoms suffer a measurable effect.

From the information in Table 2 it is possible to conclude that the bonding of hydrogen to nickel must involve one of the following: Mechanism 1, or 1 plus 2, or 2 plus 3, or 2 plus 4. But Mechanism 3 (collective *d* band) is easily eliminated. If an electron from the hydrogen were to enter the collective *d* band of the metal there is little doubt that $\beta(\mathrm{Ni})$ would decrease and that $\epsilon_{\mathrm{Ni}}(\mathrm{H})$ would equal -1.0 But this change would be spread over all the nickel atoms in the particle so that the change in $\beta(\mathrm{Ni_s})$ would be small, the effect on the conversion activity would be marginal and steric blocking would be required. But if the collective *d* band yielded an electron to the hydrogen, forming $\mathrm{H}^{\delta-}$, then $\beta(\mathrm{Ni})$ would increase. This does not occur. This leaves the choice of mechanisms as 1, or 1 plus 2, or 2 plus 4.

TABLE 2

Possible Bonding Mechanisms

No.	Mechanism	$-\epsilon_{\mathrm{Ni}}(\mathrm{H})$	$\beta(\mathrm{Ni_s})$	*o*–*p* H_2 poisoning	Excludes No.
1	Local moment lost	0.7	0	Yes	3
2	Steric blocking	—	0.6	Yes	—
3	Collective *d*-filling	1.0	~0.6	Slight	1 and 4
4	Local exchange lost	0.7	0.6	No	1 and 3

CHEMISORPTION ON COPPER–NICKEL ALLOYS

Cu–Ni Complexities

Additional information concerning nickel–hydrogen bonding may be obtained by the use of copper–nickel alloys. Not only do the nickel atoms become more dispersed but, as is well known, $\beta(\mathrm{Ni})$ decreases as the copper concentration increases and becomes zero at the critical concentration corresponding to about 56 at.% Cu. But copper–nickel alloy is far from being a simple solid solution. It is necessary to consider to what degree published results of adsorption phenomena may have been influenced, intentionally or otherwise, by these complications.

One complexity is that described by Kadota and Ikeda (*21*). Certain copper–nickel concentrations are thermodynamically unstable and, below about 500 K, may separate into two phases of approximate composition $\mathrm{Cu_{0.8}Ni_{0.2}}$ and $\mathrm{Cu_{0.02}}$-

$Ni_{0.98}$ (the metastable compositions may be obtained by appropriate heat treatment). Furthermore, as reported by Sachtler and Dorgelo (*22*), the higher diffusion rate of copper may cause each particle of alloy to become covered with a surface layer of $Cu_{0.8}Ni_{0.2}$. While X-ray diffraction and magnetization measurements may be used to establish bulk alloy composition this is not always true of surface composition. Auger electron spectroscopy may be used (*23*) for some preparations. Adsorption and catalytic activity data often provide useful clues.

Another complexity appears in the neighborhood of, and above, the critical copper concentration. The nickel atoms tend to form clusters and, above a certain size, these clusters have a magnetic moment. The probability of cluster formation decreases, as expected, with increasing copper concentration. This situation was noted by Goldman (*24*). Among the numerous papers on this topic the experiments of Kouvel and Comly (*25*) and the theory of Dvey-Aharoni and Fibich (*26*) are especially useful. Nickel clusters concern us to a degree because of their possible influence on the interpretation of adsorption and catalytic activity data at copper concentrations moderately above 56 at.%.

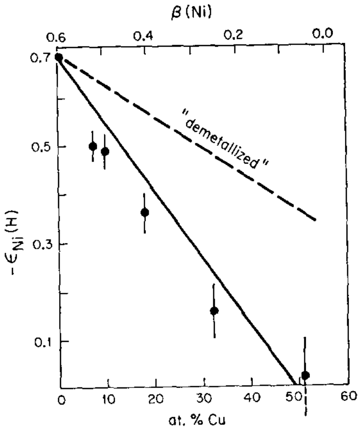

FIG. 2. Effect on the Bohr magneton number per unit quantity of chemisorbed hydrogen versus atomic percentage of copper in Cu–Ni alloys [based on Dalmon *et al.* Refs. (*31* and *32*)]. The rather large probable error is characteristic of all adsorption measurements on this alloy system.

The third complexity involves the possibility that in copper–nickel alloy there is a depletion of nickel in the surface layer. The changes of concentration predicted by Williams and Nason (*27*) are not inconsequential and, if true, they could pose a serious problem for the interpretation of adsorption data. Some experimental data related to this prediction are mentioned below. If, as shown by Ollis (*28*), particles under 20 nm diameter are less susceptible to forming concentration inhomogeneities we may, perhaps, neglect this particular complexity. But still another complexity related to this one and mentioned by Moss and Whalley (*29*) is the possibility that chemisorbed hydrogen may attract nickel atoms to the surface, thus enriching the surface layer. This is also treated theoretically by Williams and Nason (*27*).

The final complexity to be mentioned is the possibility, implied in work by Shallcross and Russell (*30*) that, at high copper concentrations the magnetic moment of the surface nickel atoms, $\beta(Ni_s)$, may not be zero. This too is referred to below although it has less possible significance for the chief purpose of this paper.

ϵ_{Ni}(H) *over Cu–Ni*

Dalmon *et al.* (*21*, *32*) have measured ϵ_{Ni}(H) on copper–nickel alloy supported on silica. The copper concentration range was 0–46 at.%. Particle diameters were from 5 to 20 nm (*33*). Magnetization and X-ray diffraction measurements provided evidence of freedom from bulk segregation. A typical result for a sample containing a total metal loading of 15 wt%, and 33 at.% Cu, was $\beta(Ni) = 0.38$ and $\epsilon_{Ni}(H) = -0.41$. Equality of $-\epsilon$ with β was found throughout the whole range of decreasing β(Ni), with increasing percentage of Cu, that occurs in this alloy system, as shown in Fig. 2.

In view of the importance of these results we shall consider what effects, if any, may have been caused by the several complexities described in the preceding section. According to Robertson *et al.* (*34*) the preparative procedure used by Dalmon *et al.* (*31*) should have been adequate to insure bulk homogeneity. Let us suppose, however, that, as shown by Sachtler and Dorgelo (*22*) each particle had become covered with a layer of $Cu_{0.8}Ni_{0.2}$. Then, regardless of whether or not the surface nickel atoms had retained a magnetic moment, they could not have contributed to $\beta(Ni)$, and $\epsilon_{Ni}(H)$ would have been zero throughout the range of copper concentration. This, obviously, did not occur. Also, the possibility of nickel clusters is of concern only at moderately above the critical copper concentration, 56 at.%. The possibility, predicted by Williams and Nason (*27*), is that the surface nickel concentration is depleted in all these alloys. If depletion had occurred, and was comparable to that predicted, it would have caused a decrease in the volume of hydrogen chemisorbed and this decrease would have been substantially greater than that calculated from the bulk nickel concentration. There is no indication that such an unexpectedly large decrease occurred. This evidence, taken together with the small particle sizes used, suggests that surface depletion was not sufficient to affect the results. If some nickel enrichment caused by the chemisorbed hydrogen had occurred there is no reason to believe that the values for $\epsilon_{Ni}(H)$ would have been different.

Conclusions from Alloy Results

It will be recalled that the bonding of hydrogen to nickel could involve loss of $\beta(Ni_s)$ (Mechanism 1, Table 2) and that this could be, in a sense, equivalent to physical removal of the affected nickel atom. This is the mechanism proposed by Sachtler and Van der Plank (*35*) who referred to the atom as being "demetallized," that is to say, it becomes no longer an effective part of the metal particle' ensemble.

Dalmon *et al.* (*32*) correctly point out that, according to the Sachtler and Van der Plank mechanism the ratio of copper to nickel in the particle would necessarily rise as each surface nickel atom became "demetallized." Thus, instead of $-\epsilon_{Ni}(H)$ remaining equal to $\beta(Ni)$, it would have been found that, at each alloy composition, $-\epsilon_{Ni}(H)$ would have been substantially larger than $\beta(Ni)$. This did not occur.

The alternative (to Mechanism 1) suggested by Dalmon *et al.* (*32*) is that the affected atom remains "metallized." Unfortunately the terms "metallized" and "demetallized" lack precise definition. If "metallized" means that the atom remains as an effective part of the metal ensemble and that it becomes diamagnetic like a copper atom, the result would be an even more drastic effect on $\epsilon_{Ni}(H)$. But if no change whatever occurred in the nickel atom we would have no nickel–hydrogen bond.

Our conclusion is that the nickel atom loses some, but not all, of its properties as a metal. A magnetic moment, $\beta(Ni_s)$, is retained but the atom loses its ability to participate in parallel exchange interaction. It might be thought that a change of sign to antiparallel (antiferromagnetic) interaction would be possible, but this would have the effect of doubling $\epsilon_{Ni}(H)$. Rather, the atom is paramagnetic but it can no longer contribute to the bulk moment, $\beta(Ni)$. If the atomic moment is retained it is necessary to have steric blocking to explain the conversion poisoning that occurs. It is shown below that the surface stoichiometry is almost certainly one hydrogen atom to one nickel atom. If this is true there is only one species large enough to provide steric blocking and that is a hydrogen atom carrying a negative charge, $H^{\delta-}$. Our final conclusion is, therefore, that nickel-hydrogen bonding involves Mechanism 4 plus 2 (Table 2). This conclusion is independent of the major changes proposed in recent years concerning the *d* band structure of Cu–Ni alloys. It is still true that removing one nickel atom from a copper–nickel alloy particle in the high nickel concentration range will lower the saturation magnetization.

RELATED EXPERIMENTAL DATA

More information is obtainable from other work. This is described in two subsections, first, the concept of surface coverage and, second, the stoichiometry and mode of bonding. Topics discussed are restricted to those bearing directly or indirectly on our main conclusion concerning the surface bonding of hydrogen and nickel. Both areas were covered, to 1960, by Bond (*36*).

Surface Coverage

The concept of surface coverage has no adequate definition of general applicability. This is especially true of particulate matter for which the surface may be highly irregular. In a sense the surface of a metal such as nickel in fcc structure may be defined in terms of the number of atoms present with less than 12 nearest neighbors. But for practical purposes it is best to rely on chemisorption data even if this involves some questionable assumptions.

For nickel it is possible to use the maximum change of saturation magnetization observed for a sample exposed to hydrogen. Because of the peripheral effect previously mentioned it is necessary to make a moderate correction to $\Delta \boldsymbol{M}_0$ so that for a sample showing, say, a 20% decrease of $\boldsymbol{M}_0$, at what appears to be maximum coverage, we have $0.86\Delta \boldsymbol{M}_0/\boldsymbol{M}_0 = 17\%$. This is the fraction of nickel atoms present in the sample and accessible to hydrogen for chemisorption. It may not have a very close relationship to the geometric area or to the BET area. The "magnetic" area is not dependent on the bonding stoichiometry. It is also true that all nickel atoms accessible to hydrogen chemisorption may not be accessible to other adsorbate molecules. It is sometimes stated that the number of surface atoms may be titrated from the volume of hydrogen chemisorbed under stated conditions. This method is obviously unsatisfactory unless full coverage has actually been achieved.

A better understanding of this problem may be obtained by combining the results of several earlier studies, with considerable reinterpretation. First, it is now firmly established from magnetic saturation studies by Dalmon *et al.* (*31*) that $\epsilon_{Ni}(O_2) = -1.5$ for silica-supported samples, over a considerable range of surface coverage. (In all such measurements with oxygen great care must be taken that oxidation below the surface is minimized.) This result shows that one atom of chemisorbed oxygen has the same effect on the magnetic moment of the nickel particle as does one atom of hydrogen. Furthermore, Klemperer and Stone (*37*) showed that, on nickel film, complete irreversible monolayer coverage with oxygen at room temperature is achieved at 0.1 mm Hg pressure, but coverage with hydrogen under identical conditions is only 40%. This difference is attributable to the large difference between heats of adsorption of oxygen and of hydrogen, and also to the fact that for oxygen the heat does not diminish appreciably over most of the coverage. Vaska and Selwood (*38*) showed that complete coverage of hydrogen over nickel–silica was not reached, at room temperature, below about 100 atm, as estimated from the change of magnetization. It was found, for instance, that after appropriate corrections, 17.9 cm^3 H_2 (STP) at 71 atm lowered the magnetization by 14% from which we conclude that the fraction of nickel on the surface is 12%, corresponding to 1.2×10^{21}

Ni atoms g^{-1} from $\Delta \boldsymbol{M}$ and 1.0×10^{21} from the volume of H_2 taken up. According to Klemperer and Stone a reasonable average number of nickel atoms in a sample of unit surface area is 1.54×10^{19} atoms g^{-1} Ni. Hence the specific surface calculated from $\Delta \boldsymbol{M}$ is 78 $m^2 \cdot g^{-1}$ which is certainly not unreasonable for a sample of nickel–silica containing 52.8 wt% Ni and an overall surface (BET, N_2) of 175 $m^2 \cdot g^{-1}$.

Our conclusions concerning full surface coverage on nickel are that it may be determined by measuring the change of $\boldsymbol{M}_0$ produced by covering the surface with hydrogen or with oxygen until no further change takes place. The hydrogen method requires pressures approaching 100 atm and the experimental difficulties are formidable. Oxygen is preferable but it must involve the slow addition of dilute oxygen in helium or of nitrous oxide (*37*). Room temperature is satisfactory. It must be emphasized that the use of hydrogen even at 1 atm is in no way satisfactory for this purpose. An estimate from Vaska and Selwood (*38*) is that coverage of nickel by hydrogen at 1 atm and 300 K is about 80% complete. This is in satisfactory agreement with the coverage reported by Klemperer and Stone (*37*) under rather different conditions. Fractional coverages may, of course, be determined quite conveniently by the use of hydrogen. Some of the many problems arising with other adsorbates are described in Ref. (*13*), pp. 103–148.

In a recent paper Rudajevová and Pour (*39*) gave surface area estimates obtained from magnetization–volume isotherms for hydrogen, oxygen and other gases on nickel. The conclusion is that hydrogen is preferable to oxygen, which is the reverse of that given in the present paper. Their conclusion was based chiefly on their finding that the volume of oxygen taken up per unit mass of nickel was much greater than that of hydrogen, and that the fractional change of magnetization per unit volume of oxygen was twice that of hydrogen. Both the experimental data and the reasoning are open to question. The samples consisted of nickel–alumina reduced at a maximum temperature of 698 K and, therefore, almost certainly capable of showing the complexities described by Martin *et al.* (*16*). In fact, if we assume, for the moment, that the results of Rudajevová and Pour show a 1:1 bonding for oxygen atoms then their value for hydrogen is exactly the subnormal one reported by Martin *et al.* for the same system. Second, the experimental method was the low field permeameter and this is subject to various limitations [Ref. (*3*) p. 92]. If these limitations are ignored any results obtained in this way may be meaningless. Furthermore, Rudajevová and Pour assumed that full coverage with hydrogen was obtained by the "irreversible" hydrogen which was defined as that not removable by evacuation at room temperature. This is arbitrary and it ignores the work of Klemperer and Stone (*37*) and of Vaska and Selwood (*38*). And finally, the conclusion that the fractional change of magnetization per molecule of oxygen is twice that produced by hydrogen and hence indicates that one molecule of oxygen forms bonds to four nickel atoms is directly contrary to the careful saturation magnetization study of Dalmon *et al.* (*31*).

Stoichiometry and Modes of Adsorption

The concept of surface stoichiometry is no less elusive than that of surface coverage. A definition of stoichiometry for nickel is implicit in the definition given above for $\epsilon_{Ni}(H)$. With due regard for the small peripheral effect already described it is possible to define the stoichiometry for the nickel–hydrogen system in the following manner. The Bohr magneton number for any particle of nickel is $\beta(Ni)n(Ni)L$ where $n(Ni)$ is the number of moles of nickel in the particle and L is Avogadro's constant. The stoichiometry is then the number of hydrogen atoms, $n(H)L$, necessary to lower

$\beta(\mathrm{Ni})n(\mathrm{Ni})L$ by $\beta(\mathrm{Ni})$ which is, of course, 0.60. All the experimental work shows that one hydrogen atom is sufficient to cause this change. Hence the stoichiometric ratio is Ni:H = 1, and this does not change over the full range of surface coverage.

This ratio for nickel–hydrogen has been accepted for many years [Ref. (*36*) p. 91], although not over the full coverage. A difficulty arose in comparing adsorption volume ratios of different molecules under identical conditions before it was realized that full coverage for hydrogen could only be achieved at pressures much higher than for oxygen. Similarly, the astonishing complexity of almost all chemisorbed species except hydrogen and (with precautions) oxygen makes it very difficult to compare coverages for different molecules. Some of these complexities are described in Ref. (*13*). Our conclusion with respect to the stoichiometry of nickel and hydrogen is that it is 1:1 and that this is the same as the nickel–oxygen ratio because for this system $\epsilon_{\mathrm{Ni}}(\mathrm{O}_2) = -1.5$ (*16*).

Numerous attempts have been made to gain additional information concerning coverage and stoichiometry from the chemisorption of hydrogen on copper–nickel alloys. Cadenhead and Wagner (*40*), using coprecipitated alloy powders, found that the volume of hydrogen per unit of alloy surface dropped sharply at the first 10 at.% Cu, then remained constant to 90%. This was interpreted, apparently correctly, as indicating a constant surface composition that was probably in the neighborhood of $\mathrm{Cu}_{0.8}\mathrm{Ni}_{0.2}$. Other work by Sachtler and Van der Plank (*35*) was done on alloy films deliberately pretreated to obtain a uniform, $\mathrm{Cu}_{0.8}\mathrm{Ni}_{0.2}$, surface. Here also the volume of hydrogen chemisorbed per unit of surface was proportional to the nickel surface concentration. The experimental difficulties in such work are substantial. In addition to the various uncertainties concerning actual surface concentration in all Cu–Ni alloys it is doubtful if the maximum coverage with hydrogen was reached in any of these studies. The heat of adsorption of hydrogen on Cu–Ni alloy has been shown by Takeuchi *et al.* (*41*) to be considerably lower than that on pure nickel. It might, therefore, be expected that full surface coverage would require an even higher pressure than for pure nickel.

All these uncertainties make it impossible to gain much additional information from published work on this alloy system. This is regrettable because there are several interesting unanswered questions. Molecular hydrogen is not chemisorbed on copper. Atomic hydrogen may be chemisorbed but the bonding is weak and Pritchard and Tompkins (*42*) have shown that mobile hydrogen atoms on copper will combine and desorb. But what of the isolated nickel atom on the alloy surface? Does it chemisorb hydrogen and, if so, do both atoms remain combined with one nickel atom, or does the adjacent copper participate? It is true that even at a dilution of 80 at.% Cu each nickel atom will have on the average at least one nickel nearest neighbor. Only at considerably higher dilution will the nickel atoms be truly isolated and several of the adsorption studies suggest an abrupt loss of adsorptive capacity in that range.

One additional related alloy study will be mentioned. Shallcross and Russell (*30*) measured the orthohydrogen conversion rate over a range of copper concentration and found that appreciable nondissociative activity persists up to 90 at.% Cu. This activity is poisoned by chemisorbed hydrogen. This observation suggests that such nickel atoms, at least those on the surface, might be paramagnetic. The writer (unpublished work on coprecipitated powder) was not able to confirm this reported activity and the susceptibility measurements of Kouvel and Comly (*25*) do not show any paramagnetism at this dilution. But if diamagnetic nickel atoms are capable of chemisorbing hydrogen as appears to be shown by Sachtler and Van der Plank (*35*) and others, and if nickel at very low concentration can catalyze the H_2–D_2 equilibration as shown by Byrne *et al.* (*43*), then we have to conclude that the absence of unpaired electrons in a nickel atom is no impediment to dissociative catalytic activity. This conclusion is not inconsistent with our conclusion concerning the nature of the chemisorptive bond.

A persistent suggestion is that hydrogen may be chemisorbed on nickel by two or more different mechanisms. [Discussion of so-called activated adsorption is omitted as being of minor significance, Ref. (*13*), p. 87.] Some of the evidence for this comes from desorption spectral peaks on films as described by Klemperer and Stone (*37*) and by Völter and Procop (*44*). The effects on supported metal are less obvious. The evidence suggests two or more distinct levels of bonding energy rather than qualitatively different modes. The effects may very well be real but it is doubtful if there is any conflict with the magnetization results. The change of magnetization tells us only the Bohr magneton number loss by a nickel particle on the chemisorption of one atom of hydrogen. That this is independent of bonding energy per se is shown by the constancy of $\epsilon_{Ni}(H)$ over the whole range of surface coverage and, of course, of the heat of adsorption. But the magnetic results exclude any change in stoichiometry such as H–Ni–H, Ni–H_2 or Ni–H–Ni instead of Ni–H. There is reason to believe that over many metals, including nickel, there is a weakly bonded form of hydrogen under certain conditions. This is referred to as Type C [Ref. (*34*), p. 95]. Most of the evidence is provided by adsorption–desorption equilibria, by surface potentials and by electrical conductivities. Magnetization measurements lend no support to this view for the nickel–hydrogen system. If Type C involves solely a change of bonding energy there is no conflict. It is true that for hydrogen adsorbed at 77 K the magnetization is lowered slightly, but no more so than for an equal volume of krypton. One difficulty is that there have been no attempts made to find magnetic evidence for Type C bonding under conditions identical with those for which Type C is observed.

Surface potentials of hydrogen chemisorbed on metals have received much attention. Of necessity such measurements are made on films or single crystal surfaces. There seems little doubt that for most cases of hydrogen on nickel the surface dipole is about −0.3 V, the outer surface being negative. Not very much has been added to this area since it was reviewed by Culver and Tompkins (*45*). Some cases of sign reversal appear to be related to impurities, or, possibly, to alternate states of chemisorption but nearly all the work supports the view that the hydrogen acquires a negative charge at room temperature and over a large part of the coverage.

The electrical conductivity of nickel films and the effects of adsorbed hydrogen have been the topics of comprehensive reviews by Hayward (*46*) and by Geus (*47*). The results are complicated and they depend on the number of carriers, on reflection of conduction electrons from the surface and on other factors. A change from decrease to increase of conductivity with increasing surface coverage is not uncommon. Nevertheless, the general conclusion is that the hydrogen, over most of the coverage, may carry a negative charge.

Yet another related area is the structure and catalytic behavior of so-called nickel hydride. This form of matter, which is more like an alloy than a chemical compound, was first prepared by Baranowski and Smialowski (*48*) by electrolysis, and later by exposure of the nickel to atomic hydrogen by Palcewska and Janko (*49*). Faessler and Schmidt (*50*) found from X-ray absorption edges that filling of the nickel *d* band had occurred. Wollan *et al.* (*51*) used neutron diffraction to show that the hydrogen occupies octahedral sites in the hydride, and Wertheim and Buchanan (*52*), by Mössbauer spectroscopy, showed that ferromagnetic interaction is lost and that the electron from the hydrogen presumably goes into the nickel *d* band. It is a feature of this hydride that the hydrogen does not permeate the whole metal mass at once but progresses from the initial surface reacting with each nickel layer in turn until the final composition (about $Ni_{1.0}H_{0.6}$) is reached.

All of these results strongly suggest that the hydrogen in the hydride carries a positive charge. This, together with the concurrent loss of magnetic moment might lead to the assumption that absorbed and chemisorbed hydrogen are essentially the same. But the properties of the hydride are quite different. All of the "hydride" hydrogen may be removed by evacuation at room temperature and this is certainly not true of chemisorbed hydrogen. The electrical conductivity of the hydride is greater than that of the pure nickel while chemisorption generally causes a decrease (although sometimes followed by an increase). But the most compelling difference, for our purposes, is that presented by Frackiewicz *et al.* (*53*) who found that the *dissociative* parahydrogen conversion (and also the H_2–D_2 equilibration) in the 165–195 K temperature region was about 300-fold lower over the hydride than over the pure nickel. In other words, "hydride" hydrogen is a poison for the dissociation of molecular hydrogen over nickel, whereas chemisorbed hydrogen is a *sine qua non* for the same reaction.

Other experimental methods from which it might be hoped that comparisons might be made are not very rewarding for this purpose, although often invaluable for studies on adsorbates other than hydrogen. This is especially true of field emission spectroscopy and many of the recently developed molecular beam and other spectroscopic methods. Infrared spectroscopy yields no identifiable Ni–H bonding. This is sometimes taken, as negative evidence, for the absence of a covalent bond, or for an ionic bond distributed over three or more nickel atoms.

CONCLUSIONS

With extensive reliance on results from poisoning by hydrogen of the nondissociative orthohydrogen conversion, and from the change of magnetic moment suffered by the nickel, it has been shown that chemisorbed hydrogen causes the surface nickel atom to lose its ability to participate in ferromagnetic exchange interaction but to retain a magnetic moment. The hydrogen acquires a negative charge. These conclusions are based primarily, but not solely, on typical nickel–silica hydrogenation catalyst preparations. The conclusions are supported by various other lines of evidence and there appear to be no experimental data with which the conclusions are irreconcilable.

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Note added in proof. Martin and de Montgolfier [*J. Chim. Phys.* **72**, 405 (1975)] have concluded that hydrogen is preferable to oxygen for the surface area determination of nickel on silica. This conclusion was based on their observation that the volume ratio O_2/H_2 chemisorbed to full coverage varies from about 1.8 for a sample of surface 237 $m^2 \cdot g^{-1}$ Ni to 0.60 for a sample of 61 $m^2 \cdot g^{-1}$ Ni. Full coverage was defined for O_2 as the state at which the pressure rose rapidly at 195 K, and for H_2 as the state at pressure 10 mm Hg. The difference in behavior of O_2 and H_2 was attributed to a preferential chemisorption of O_2 on the smaller particles of nickel. It is to be noted that for a sample of nickel on alumina of surface 31 $m^2 \cdot g^{-1}$ Ni Rudajevová and Pour found the O_2/H_2 volume ratio to be 1.7. Previously Dalmon *et al.* [*Coll. Intern. CNRS*, 201 Thermochimie, Marseille, 1971, p. 593] found that $\epsilon_{Ni}(O_2) = -1.5$ and that it is independent of particle diameter over the range 3–12 nm. There cannot, therefore, be any important difference in the number of Ni atoms affected per O_2 molecule adsorbed over that size limit. It appears to the writer that the results of both Martin and de Montgolfier, and of Rudajevová and Pour, may be explained by surface penetration by O_2 of the smaller nickel particles and incomplete surface coverage by H_2 at the equilibrium pressure used.

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