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ESR Evidence of Hydrogen Migration on Supported Metal Catalysts

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The ESR investigation has provided evidence that the resonance at $g = 2.10$, developed upon heating of noble-metal-supported catalysts in hydrogen, results from the reduction of iron oxide to metallic iron also present on the supported catalyst. The mechanism of the oxide reduction evidently occurs by a sequence of events including hydrogen chemisorption on a metal such as palladium, hydrogen atom transfer to the support and then to iron oxide sites, and subsequent coalescing of iron to form ferromagnetic domains. The relative effectiveness of iron oxide reduction resulting from the presence of various supported metals and supports appears to depend on the relative heats of hydrogen atom sorption compared with the activation energy required for the atom transfer from the metal to the support.

INTRODUCTION

During a study of the mechanism of heterogeneous catalytic reactions involving hydrogen, we observed that some catalysts containing both palladium and iron oxide when heated in hydrogen developed an intense electron spin resonance (ESR) line with a g value of about 2.10. In this paper we focus on the evidence that the resonance is caused by iron, and that the iron is produced by reduction of iron oxide on the support by a process including hydrogen transport from a supported metal such as palladium. We also discuss the relative effects on the reduction resulting from the presence of different kinds of metals and supports, and from the several methods of metal application to the supports.

Evidence of hydrogen atom transport from the supported metal to the support surface has been reported in various studies (*1–9*). In the present study, ESR is used to provide such information. It should be possible to extend the ESR approach by employing a reducible or oxidizable substance as a local probe at the surface, where one form of the study substance is paramagnetic, or ferromagnetic as in the present study.

EXPERIMENTAL

Catalyst preparation. Metals were applied to the solid supports by impregnation (I), mechanical grinding (G), and ion exchange (X) (the symbols in parentheses refer to Tables 1 and 2).

Impregnation with solutions of noble metal ions was carried out by dissolving the metals (Pt, Pd, and Au) in aqua regia, and by applying aliquots of these solutions to the alumina. Also a series of Pd-Au alloy samples were prepared to contain 2.2×10^{-4} g atom of total metal (Pd and Au) per gram of support, with compositions of 100, 80, and 40 atom % palladium. The impregnated powders were dried in air at 400°K, reduced by heating in a stream of hydrogen (760 torr)—first at 675°K for 4 hr, then at 970°K for 4 hr—and for most samples (except the pure Al_2O_3 and SiO_2 samples) finally evacuated at 1170°K for 2 hr. In the X-ray analysis of these samples (those heated to 1170°K), the line-broadening indicated an

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average metal particle diameter of about 400 Å and the lattice spacing (*10*) showed that the Pd-Au had alloyed completely. Samples of alumina without impregnated metal were prepared in a similar way. Impregnation with iron was carried out by applying aliquots of ferric nitrate solution (Mallinckrodt, reagent crystals) at pH 1 to the supports and then drying in vacuum at 400°K for several hours. Iron was always applied after palladium had been added to the support, except when iron was a natural (N) impurity of the support.

Mechanical mixing of palladium, platinum, or Fe_3O_4 (Fischer, purified magnetite) with alumina or silica was carried out by grinding together weighed amounts of the materials. The metals were prepared by hydrazine reduction of the aqueous solution of the salts (*11*). From X-ray examination the average crystallite diameter was estimated to be about 850 Å. Alumina and silica of two purities were used. Al_2O_3(a) and SiO_2(a) were obtained from Gallard Schlesinger, New York, and the purities are reported to be 99.9999%. Al_2O_3(b) was obtained from Kaiser Aluminum and Chemical Corp.: it is reported to be 65% alpha, and the remainder largely delta and theta, with a surface area 20 m^2/g and an average particle diameter of 50 μ; emission spectroscopy indicated 0.025% Fe_2O_3. SiO_2(c) was obtained from the Ottawa Silica Co., designated as No. 395, and reported to contain 99.75% SiO_2, 0.08% Al_2O_3, 0.02% CaO, 0.092% MgO, and 0.014% TiO_2; emission spectroscopy indicated 0.008% Fe_2O_3.

The following Linde molecular sieves (zeolites) were studied as provided: Pd(0.5) CaY [SK-310], Pd(0.5)NaY [SK-300], Pt(0.5) CaY [SK-200], Ni(1.0) NaY [SK-400], Cu(1.0) NaY[SK-410], and NaY[SK-40]. The weight percent of the exchanged metal (i.e., Pd, Pt, Ni, or Cu) in a calcium or sodium type Y molecular sieve is indicated by the number in parentheses, and the number in brackets is Linde's designation. Pellets were crushed to coarse particles. In addition, a sample of Pd(0.0025)NaY was prepared from NaY by ion exchange using a palladium salt solution at pH 5. The average iron oxide content of the sieves is reported to be about 0.01%.

Procedures. The supported metal samples were situated in a vacuum apparatus so that ESR measurements could be made as the temperature and the ambient gas were independently varied. All samples were degassed by evacuating at 770°K for at least 1 hr with a vacuum apparatus employing an oil diffusion pump and traps cooled in liquid nitrogen. While the samples were at 770°K, they were exposed to hydrogen (Matheson Co.) that was passed through a Deoxo purifier and a trap cooled in liquid nitrogen.

ESR measurements were made at room temperature, except as specified, with a Varian V-4502 X-band spectrometer with a 12-inch magnet and a dual cavity accessory operated from a low power bridge. The sample cavity employed 100-kc/sec field modulation, and the reference cavity employed 200-cps field modulation. A sample of 0.1% pitch in KCl (Varian) was used in the reference cavity to monitor the instrumental sensitivity and in the sample cavity to provide a standard for calculating spin densities.

RESULTS

The ESR results for palladium and iron on various solids are tabulated in Table 1, and the results for various other metals and iron on solids are in Table 2. Quantitative evaluation of the ESR signal at $g = 2.10$ in terms of the absolute spin density is complicated if the resonance originates from ferromagnetic iron. There is in fact evidence of ferromagnetism from the exceedingly high values of spin densities determined from a first-moment analysis of the ESR lines of some samples, for example, 10^{22} spins/g for Pd(2.0)CaY (Run 11) and more than 10^{23} spins/g for Ni(1.0)NaY (Run 18). The spin density will therefore depend on two factors: the paramagnetism arising from the number of iron atoms, and the dimensions of the ferromagnetic domains. Since the contributions of these factors cannot be evaluated separately without some difficulty, only relative values of spin density are used in the tables and figures, and the highest

TABLE 1
ESR OF SOLIDS WITH SUPPORTED PALLADIUM AND IRON

	Solid			Time	ESR		
Run	Support[a]	Pd[b] (wt %)	Fe[b] (wt %)	770°K, 760 torr H_2 (hr)	Relative spin density	g value	Linewidth (gauss)
1	Al_2O_3(a)	2.2 I	—	15	1	—	—
2	Al_2O_3(a)	—	0.05 I	0	1000	4.4	2000
				1	1000	2.4	1700
				20	1000	2.3	1700
				3 (1020°K)	1000	2.13	1300
3	Al_2O_3(a)	2.2 I	0.05 I	0	1000	2.5	—
				16	1000	2.10	260
4	Al_2O_3(a)	2.2 I	0.17 G Fe_3O_4	15	1000	2.05	170
5	SiO_2(a)	4.1 G	—	20	1	—	—
6	SiO_2(c)	—	0.008 N	20	10	Complex	—
7	SiO_2(c)	2.0 G	0.008 N	1	100	2.10	175
8	NaY(d)	—	0.01 N	20	10	2.2	630
9	NaY(d)	0.0025 X	0.01 N	13	1000	2.10	210
10	NaY(d)	0.5 X	0.01 N	20	1000	2.10	155
11	CaY(d)	0.5 X	0.01 N	16	1000	2.10	160

[a] Supports: (a) Gallard Schlesinger 99.9999%; (b) Kaiser; (c) Ottawa Silica No. 395; (d) Linde Air Products Co., zeolite.

[b] Application of metals: N, native; I, impregnation; G, mechanically ground; and X, ion-exchanged.

relative spin density, 10 000, corresponds to a calculated value of about 10^{23} spins/g.

A concerted and pronounced effect of iron and palladium was observed when supports containing *both* these metals were heated in hydrogen. In all such cases an intense resonance at a g value of about 2.10 appeared, e.g., Run 3 for alumina, and Run 7 for silica. Although the palladium was applied by impregnation on alumina and by grinding, for expediency, on silica, the same concerted effect occurs with both supports.

The pure alumina and silica supports

TABLE 2
ESR OF SOLIDS WITH VARIOUS SUPPORTED METALS[a]

	Solid		Time	ESR		
Run	Metal (wt %)	Support[b]	770°K at 760 torr H_2 (hr)	Relative spin density	g value	Linewidth (gauss)
12	0.5 Pt I	Al_2O_3(b)	20	1	—	—
13	4.2 Pt G	SiO_2(c)	20	10	2.09	280
14	0.5 Pt X	CaY(d)	16	100	2.10	840[d]
15	2.2 Pd I	Al_2O_3(b)	14	1000	2.08	480
16	80Pd/20Au[c] I	Al_2O_3(b)	20	10	2.08	—
17	40Pd/60Au[c] I	Al_2O_3(b)	20	1	—	—
18	1.0 Ni X	NaY(d)	0.2	10 000	2.26	1000
19	1.0 Cu X	NaY(d)	2	10	2.10	500

[a] Al_2O_3(b) contains 0.025 wt % iron; the iron contents of other supports are in Table 1.

[b] See footnote *a* in Table 1.

[c] Total atom percent equivalent to 2.2 wt % Pd.

[d] Strongly asymmetric resonance.

which contained palladium but no iron did not exhibit any resonances either before or after heating in hydrogen (Runs 1 and 5).

The supports which contained iron but no palladium or platinum, exhibited broad intense resonances whose line shapes were complex. Before heating in hydrogen a *g* value as high as 4.4 was observed; after heating in hydrogen the *g* values were in the range of 2.2 to 2.5, and the linewidths were of the order of 1000 gauss. These broad resonances are probably caused by ferric ion, and partial reduction may have occurred when the solids were heated at 770°K in hydrogen, as evidenced in Run 2 by the decrease of the *g* value and linewidth. The continued decrease of *g* value and linewidth which occurred in Run 2 when heating was continued at 1020°K suggests that reduction may then have proceeded partially to iron. The Al_2O_3(b) sample exhibited not only a broad resonance, but also several weak, asymmetric, and relatively sharp resonances (30 to 100 gauss), which are probably due to impurities since these lines were not present in the pure sample, Al_2O_3(a).

The relative spin densities of the 2.10 resonance for several solids with supported palladium after various periods of heating at 770°K in 760 torr H_2 are shown in Fig. 1. The curves show a rapid initial increase in spin density which approach a limiting value.

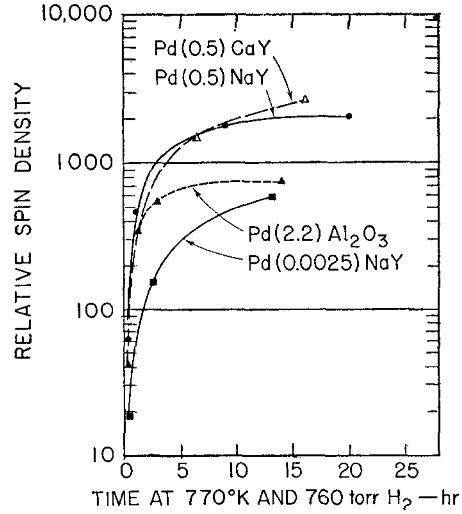

FIG. 1. Relative spin density of 2.10 line for supported palladium catalysts as a function of exposure time at 770°K to hydrogen at 760 torr.

Among the factors which determine the limiting value of the spin density are the concentration of iron; the type, concentration, and method of application of the noble metal; and the nature of the support. As the iron concentration was increased from 0.05 to 0.25 wt %, by impregnating Pd(2.2) Al_2O_3 with $Fe(NO_3)_3$ solution, an approximately proportional increase was observed in the spin density of the resonance. However, increasing the palladium concentration by a factor of 200 caused only a fourfold increase in the spin density (Fig. 1).

The type of supported metal determines the limiting value of the spin density. Nickel is a special case because the intense resonance at a *g* value of 2.26 is probably caused by rapid formation of ferromagnetic nickel, and a 2.10 resonance if it were present would be obscured. The somewhat greater effectiveness of palladium over platinum can be seen by comparing the results on similar supports. The most direct comparison can be made for silica, Runs 7 and 13, for which the concentrations of palladium and platinum are on an equi-atom percent basis. For alumina, Runs 12 and 15, the concentration on an atom percent basis is greater for palladium than for platinum by a factor of 8, but the spin density was greater for palladium by a factor of about 10^3. Such a large effect on spin density by metal concentration alone was not expected because of the results quoted above for 0.0025 and 0.5 wt % Pd on NaY. For CaY as a support a somewhat greater spin density was produced in the presence of palladium than platinum, greater by a factor of 10 on a weight percent basis and by a factor of 5 on an atom percent basis (Runs 11 and 14).

Alloying palladium with small amounts of gold decreased the spin density by a factor much greater than that corresponding to the amount of gold. For example, for the alloys containing 0, 20, and 60 atom % gold supported on alumina, the relative spin densities are estimated to be 1000, 10, and 1, respectively (Runs 15–17).

The method of application of a metal to a support is also a controlling factor in attaining high spin densities, but this effect was not examined in detail. In the case of palladium on alumina, application by impregnation is much more effective than mechanical grinding, but for palladium on silica grinding was quite effective. For iron on alumina, application by either impregnation with ferric nitrate solution or mechanical grinding with magnetite appears to be effective.

In an effort to learn more about the origin of the 2.10 resonance, we determined the temperature dependence of spin density and linewidth for the Pd(0.5)CaY sample used in Run 11. The measurements were made on the sample after it was sealed in the quartz tube and heated at 770°K in 760 torr hydrogen. The results in Fig. 2 show that spin density and linewidth increased as the temperature was decreased, and approached limiting values below about 50°K. These results are reversible with temperature. The 2.10 resonance did not exhibit microwave power saturation, and at 133° and 288°K the line shape was Lorentzian.

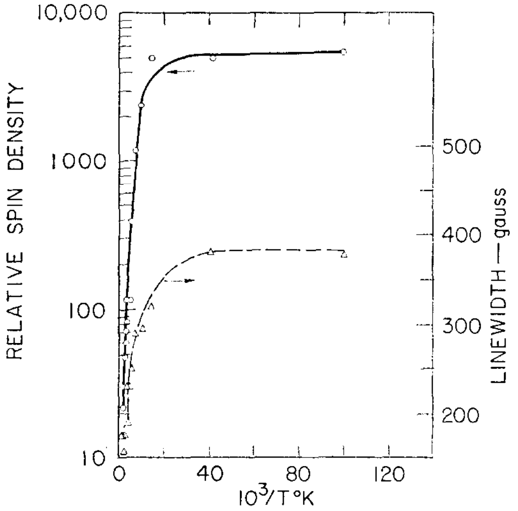

FIG. 2. Effect of temperature on relative spin density and linewidth for Pd(0.5)CaY heated for 20 hr in hydrogen at 760 torr and 770°K.

The spin density of the 2.10 resonance decreased rapidly when samples were heated in oxygen, and more slowly when samples were heated during evacuation. For example, when a sample of Pd(0.5)CaY, which had been heated at 770°K in 760 torr hydrogen for 33 hr, was heated in vacuum, the spin density measured at room temperature was essentially unaffected at temperatures below 670°K, but at 770°K there was a significant decrease in the spin density accompanied by an increase in linewidth. The original spin density and linewidth could then be restored by heating at 770°K in 760 torr hydrogen for only 15 min. This rate is much faster than that required to originally produce the resonance for the first time (Fig. 1). In addition, this alternate heating in vacuum and in hydrogen could be repeated several times without loss of spin density.

In order to determine whether the 2.10 resonance is produced by metallic iron, the amount of hydrogen gas evolved was measured when acid was added to a supported metal solid which had been heated in hydrogen. One-gram samples of two solids were tested: Fe(0.0025)Pd(2.0)Al_2O_3(a) made by impregnating the sample from Run 1 with ferric nitrate solution, and Fe(0.25)Al_2O_3(a) made in a similar way but in the absence of palladium. These solids were individually evacuated at 770°K for 2 hr, heated at 770°K in 760 torr hydrogen for 10 hr, and evacuated at room temperature for 1.5 hr. Then 1.5 ml of 6*N* HCl, which had previously been frozen, evacuated, and thawed three times, was transferred under vacuum conditions to the solid. Finally the hydrogen pressure in a fixed volume (51 cc) was measured by a bellows-type pressure gauge with liquid nitrogen around the solid and around a trap leading to the gauge. The amount of H_2 gas evolved after heating to 470°K was greatest for the sample containing both iron and palladium. The results indicate that at least 40% of the iron oxide in Fe(0.25)Pd(2.0)Al_2O_3(a) had been reduced to metallic iron.

DISCUSSION

It is concluded that metallic iron gives rise to the 2.10 resonance. First of all, only when iron is present does heating a solid in hydrogen produce this resonance. Also, ferromagnetic iron is a material with a very high magnetic susceptibility, which can account for the extraordinarily high spin densities. Further, evidence that the resonance center is due to metallic iron is provided by the observed *g* value of the resonance, which is in agreement with that reported (*12*) for dispersed iron, and by the experiment in which hydrogen was evolved by the acid. Although the Curie temperature of bulk iron is 1043°K, it would probably be less for small particles (*13*) and may indeed be as low as 520°K because we did not observe the 2.10 resonance above this temperature. In addition, the iron oxide–noble metal case is probably analogous to that of nickel oxide, which is reduced at lower temperatures in the presence of palladium or platinum on the support (*1*).

It is unlikely that any center other than iron could give rise to the 2.10 resonance. That is, since the *g* value is essentially independent of the supports, the center must be a common element in all the supports, e.g., hydrogen, oxygen, and iron. Hydrogen atoms can be ruled out because the observed *g* value is too high. Furthermore, the high observed spin densities almost certainly rule out ordinary paramagnetic centers produced by atoms or defects. Also, the presence on the support of a metal such as palladium or platinum is apparently not required to reduce the iron if the support is heated to a high enough temperature (Run 2).

It is improbable that the 2.10 resonance is produced by an oxide of iron. That is, before the hydrogen treatment, the iron was certainly present as an oxide, such as Fe_2O_3 or Fe_3O_4, which exhibited much broader resonances and higher *g* values than the 2.10 resonance. However, there is evidence of a partial reduction, or change of crystal morphology, of the oxides. This was determined from the decrease of the *g* value and linewidth which occurred when the supported oxides were heated in hydrogen in the absence of palladium or platinum, for example, during the first hour of heating at 670°K in hydrogen of Run 2. The subsequent changes that occurred on heating at 1020°K are probably related to the partial formation of metallic iron. Broad resonances with *g* values in the range of 2.49 to 2.09 have been ascribed to ferromagnetic oxide impurities in alumina (*14*) and zeolites (*15*). However, in ESR studies of alumina and zeolite heated in hydrogen, a resonance analogous to that which we observed at 2.10 has not been reported (*3,16*).

The observed temperature dependence of the spin density of the 2.10 resonance is consistent with the presence of a ferromagnetic, but not a paramagnetic, center. That is, the temperature decrease from 500° to 50°K resulted in an increase of spin density by a factor of about 100, whereas an increase of about 10 would be expected for a paramagnetic center. The observed temperature dependence is consistent with the behavior of a ferromagnetic material, in a magnetic field, whose susceptibility increases at low temperatures to a saturation value as the domains become completely ordered. The temperature dependence of the linewidth may be accounted for in two ways. On the one hand, the temperature dependence is that predicted for pure ferromagnetic metals on the basis that the microwave skin depth is reduced at low temperatures and that line-broadening results (*17*). On the other hand, it may be argued that local magnetic field inhomogenities prevail at low temperatures, and line-narrowing results when the inhomogenities are averaged out at higher temperatures. The smaller linewidths observed at higher spin densities may be expected of a ferromagnetic substance where an exchange interaction occurs.

We believe that the decrease of the spin density resulting from heating in vacuum is caused by reoxidation of the iron by either residual sorbed oxygen or water. The rapid restoration of the spin density by heating this sample in hydrogen can be accounted for by the reduction of the oxidized iron, probably present as small oxide crystallites which no longer require migration and coalescing of iron atoms. This consideration leads to the conclusion that the rate-limiting process for the increase of the 2.10 resonance, Fig. 1, depends on migration and coalescing of iron atoms.

Heating of the Ni(1.0)NaY sample (Run 18) in hydrogen apparently produced metallic nickel. Evidence of this reduction to ferromagnetic nickel is provided by the observed *g* value which is consistent with that reported (*12*, *18*) for dispersed nickel and by the very high spin density.

In order to account for the reduction of the supported iron oxide in the presence of palladium or platinum, it is necessary to postulate a hydrogen transport mechanism in which supported iron oxide is reduced to iron by hydrogen atoms that are provided by chemisorption on palladium or platinum and transported, presumably by the support, to the iron oxide sites. It is reported that hydrogen is sorbed by the support when palladium or platinum are present (*1–9*), and hydrogen transport from metal to support has already been referred to in connection with the hydrogen reduction of oxides (*2*).

The factors which control the overall mechanism of hydrogen migration resulting in iron oxide reduction can be qualitatively interpreted in terms of energy considerations involving the following processes: (a) hydrogen chemisorption on the noble metal crystallites, (b) desorption from the noble metal crystallites, (c) surface transport across the metal–support interface, (d) reduction of the iron oxide, and (e) agglomeration of iron. One determining factor is the type of metal, and for the various metals we tested the order of decreasing effectiveness for reduction of iron oxide is Pd > Pt > Cu ~ Pd/Au. For palladium and platinum dissociative hydrogen chemisorption occurs with a low activation energy, while for gold a large activation energy is involved. For the supports, chemisorption of hydrogen occurs with an activation energy, which is larger relative to that of the metal. However the hydrogen atoms evidently can migrate on the surface of a support, indicating a moderately strong bonding of the hydrogen to the support. Accordingly, it is possible to offer an explanation of why hydrogen transport occurs in the case of palladium and platinum and does not occur in the case of gold. We propose that the process of hydrogen atom transfer from palladium or platinum to the support occurs with an activation energy which is low compared to the activation energy of hydrogen desorption from these solids. The differences in the effectiveness of hydrogen atom transfer may then depend on the activation energies of the transfer at the various metal–support interfaces. However, in the case of gold, hydrogen desorption is less activated than for the other metals and proceeds on the potential surface which leads to hydrogen molecule formation. Therefore, there is a low probability that hydrogen atoms will transfer to the support. The effect observed by alloying palladium with gold may be accounted for in two ways. In the first it is postulated that the gold concentration at the surface of the alloy is richer than in the bulk, although our X-ray analysis indicated satisfactory alloy formation for the bulk. Such a high gold concentration at the surface would presumably inhibit hydrogen transfer to the support because desorption is favored. In the second, gold and palladium crystallites may be in contact, permitting hydrogen transport to the gold and desorption of hydrogen molecules from the gold.

The character of the contact between the metal and the support and/or the degree of metal dispersion evidently influences the effectiveness of hydrogen transfer to the support and oxide reduction. Oxide reduction was greater when the metal was applied in a highly dispersed state (by impregnation or by ion exchange) than when it was applied by mechanical grinding. A similar requirement for an intimate contact between metal and support has been shown in a catalytic study in which hydrogen migration occurred between Pt/SiO_2 and Al_2O_3 when these solids were ground; but less migration occurred when the solids were simply mixed (*8*).

Finally, the slow rise of spin density shown for all the solids in Fig. 1 indicates the presence of a common rate-limiting process, for example, one or more of the following: hydrogen atom transport, the iron oxide reduction step, or agglomeration of iron atoms. The agglomeration step may indeed be the rate-limiting step since, as was mentioned earlier, the spin density built up rapidly when the oxidized iron was heated in hydrogen after the iron had had an opportunity to agglomerate. In the present study of nickel supported on zeolite all three processes evidently proceeded rapidly.

Although we have not yet correlated information from the ESR studies with that from heterogeneous catalytic reactions, results have been reported which suggest that such a correlation may be found. For example, the isomerization yield of cyclohexane to methylcyclopentane on Pt/Al_2O_3 was markedly enhanced when the catalyst was pretreated by heating in hydrogen at 770-820°K, but insignificant isomerization occurred after pretreatment at temperatures as low as 720°K or after the pretreated catalyst was heated in oxygen (*19*). These pretreatment conditions are similar to those used in our study, the first leading to the 2.10 resonance, and the others leading to its elimination.

In the present study ESR was used to help identify the reduced iron and to deduce that hydrogen transport had occurred. It is feasible to use ESR to study hydrogen transport by using reducible supported impurities, such as oxides of iron or nickel, as an indicator of the transport. We are exploring this approach to evaluate the influence of different supported metals and supports on hydrogen transport properties.

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