JOURNAL OF CATALYSIS 59, 382–394 (1979)

Activation of Hydrogen on Fe/MgO Catalysts Studied by Magnetic Methods and Mössbauer Spectroscopy

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Received October 21, 1977; revised July 25, 1978

Fe/MgO catalysts with large metallic particles were prepared by coprecipitation, and studied with the help of Mössbauer spectroscopy and magnetic techniques. Two activation processes of H_2 were observed. At room temperature, H_2 was adsorbed on metallic particles with a small decrease in saturation magnetization, as previously reported in the literature. Above 470 K, adsorbed hydrogen was activated according the reversible redox scheme $Fe^{n+} + nH_{ads} \rightleftharpoons Fe + nH^+$, with n probably equal to 2. Protons are trapped on basic sites of the catalyst giving OH groups.

INTRODUCTION

Iron-based catalysts are commonly used in ammonia synthesis ($N_2 + H_2$) and in the Fischer–Tropsch reaction ($CO + H_2$). However, the activation process of hydrogen which is involved in both reactions has not been clearly elucidated: Artyuk *et al.* (*1*, *2*) reported two adsorbed states of H_2 on Fe/SiO_2 and Fe/Al_2O_3 catalysts giving opposite magnetic effects on the ferromagnetic iron phase. Selwood (*3*) questioned the validity of these results owing to the fact that they were obtained at low magnetic fields and that iron particles were not shown to be superparamagnetic. In our laboratory the adsorption of H_2 was studied on unsupported iron powders (*4*): by high field techniques one state was detected corresponding to an increase of ca. 3.7 Bohr magnetons (B.M.) per adsorbed H_2 molecule. Boudart *et al.* (*5–8*) have also given evidence for one species on Fe/MgO catalysts, but in their case the observed saturation magnetization decrease was very small (ca. 0.2 Bohr magneton per adsorbed molecule). In addition, these authors have observed a large change in magnetic anisotropy upon chemisorption as seen from nuclear gamma resonance (Mössbauer spectroscopy).

This apparently conflicting situation has prompted us to study again hydrogen activation on new iron-based catalysts, over a large range of temperatures with the help of magnetic methods and Mössbauer spectroscopy.

EXPERIMENTAL METHODS

Most of the experiments reported here were performed on Fe/MgO catalysts. The starting material was obtained by coprecipitation: A solution of ammonia (100 ml H_2O and 25 ml of ammonia; density, 0.9) was added into a solution of 500 ml containing 25.4 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 2.83 g of $Fe(NO_3)_3 \cdot 9H_2O$. After filtering and washing, the slurry thus obtained was dried and then calcined for

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TABLE 1

NGR Parameters of the Precursor at 300 K

Component	IS (mm s^{-1})	Γ_{exp} (mm s^{-1})	QS (mm s^{-1})	Area in the spectrum (%)
A	0.60	0.45	0.65	70
B	0.55	0.40	1.10	30

24 hr at 770 K. The iron weight percentage varies from one preparation to another between ca. 4 and 8%. It should be noted that this method of preparation gives catalysts whose properties change with the age of precursors.

MgO blanks were also prepared in a similar way but the iron salt was not added.

The magnetization was measured in an electromagnet (21 kOe) at 300, 77, and 4.2 K and in a superconductive coil (70 kOe) at 4.2 K using the Weiss extraction method. The systems were calibrated using a Ni monocrystalline sphere with the 111 axis in the direction of magnetic field.

Nuclear gamma resonance (NGR) absorption spectra were obtained using a constant acceleration driving unit (Numelec), operated in the triangular mode, slaved to an 800-channel analyzer (Intertechnique). γ-Rays from a 10-mCi $^{57}Co/Cr$ or a 50-mCi $^{57}Co/Pd$ source (Amersham) were detected by a 0.1-mm-thick NaI (Tl) scintillation probe (Harshaw). Calibration was done from the Fe metal absorption spectrum. After computer folding the decomposition of the spectra and determination of the Mössbauer parameters were achieved using the program MOSFIT, assuming a Lorentzian shape of the lines, built by F. Varret. Isomer shifts (IS) in this paper refer to sodium nitroprusside, with a precision $\pm$ 0.05 mm s^{-1} as for quadrupole splitting (QS) and experimental linewidth (Γ_{exp}). Due to the iron content of the samples, the latter cannot be smaller than 0.3 mm s^{-1}, a value which very pure and perfect components of any spectrum cannot greatly exceed. These requirements were taken into account in computer calculations and subsequent discussions.

Thermal treatments in different atmospheres or *in vacuo* and NGR spectroscopy without removing the sample were performed using a furnace (designed by J. Moulin, Grenoble Nuclear Center) equipped with two beryllium windows (Kawecki Berylco Industries, Inc.) resulting in a 0.15% resonant absorption at 0.4 mm s^{-1}. Samples were introduced as pellets made by pressing the powders at 2 tons cm^{-2}. Low temperature spectroscopy used a cryostat (C.T.L.), the windows of which gave a resonant absorption smaller than 0.1% at 0.4 mm s^{-1}.

EXPERIMENTAL RESULTS

Precursor

Only the MgO diffraction pattern is observed from X-ray analysis. The magnetic susceptibility χ is described by the Curie–Weiss law: $\chi(T + \Theta) = C$ with $\Theta = 3.3$ K. The magnetic moment calculated from the constant C is nearly equal to 4.9 Bohr magnetons, a value which is a little smaller than that generally encountered for Fe^{2+} or Fe^{3+} ions (5 or 6 Bohr magnetons). Chemical analysis indicates that iron is mainly present as Fe^{3+} ions. Mössbauer spectra are in agreement with this result and give further information as stated and illustrated in a previous note (*9*), which this study extended. At room temperature the precursor of the catalyst exhibits a doublet with a rather large linewidth (0.60 mm s^{-1}), which can be resolved into two components with NGR parameters reported in Table 1. Decreasing the temperature to 77 K does not significantly change the main shape of this spectrum. At liquid helium temperature a complex magnetic structure appears, with six very broad and asymmetric lines, probably due to the smallest particles, resulting in difficulty in computing any

TABLE 2

NGR Parameters of the Precursor at 4.2 K

Component	IS (mm s^{-1})	Γ_{exp} (mm s^{-1})	QS (mm s^{-1})	*H* (kOe)	Area in the spectrum (%)
A	0.50	Broad	—	420–460	65
B	0.50	0.50	0.60	0	35

quadrupole interaction. This situation is illustrated in Table 2.

The NGR parameters in the tables and magnetic ordering below 77 K indicate that at least a large amount of the product giving component A is not an iron oxide in small particles, which would result in a sextet associated with an internal field of 500 kOe by splitting at low temperature, with some intensity even at 77 K. The only species possible is γ-FeOOH, with a Curie temperature lower than the last one and for which a bulk hyperfine field of 460 kOe at 4.2 K is reported (*10*). Small particle sizes could account for unusual intensities and widths, arising either from changes of hyperfine field at surface layers or from processes involved in superparamegnetic relaxation (*23*). This is clear in the case of another preparation, exhibiting a similar spectrum at 4.2 K, shown in Fig. 1, where component B is 20% of the total area; component A is better described as the number of hyperfine fields is increased. The best computer fit was obtained using hyperfine fields in the 420- to 460-kOe range.

The components B could be ascribed to one or more species which can occur in this system. Discussion of this point is difficult without further characterization.

It should be noted that bulky γ-FeOOH is known to decompose at ca. 670 K, and our solids were heated to 780 K. However, in our case the iron compound is in contact with MgO, and such a situation induces a stabilization of the hydroxy-oxide.

Reduced Catalyst

The reduction was performed in a gas stream (3 liters/hr) of very pure hydrogen (99.995%) for 15 hr at various temperatures, and the sample was cooled in hydrogen. Magnetic measurements were performed to obtain information on the morphology of the reduced catalyst. As an example, curves obtained on the

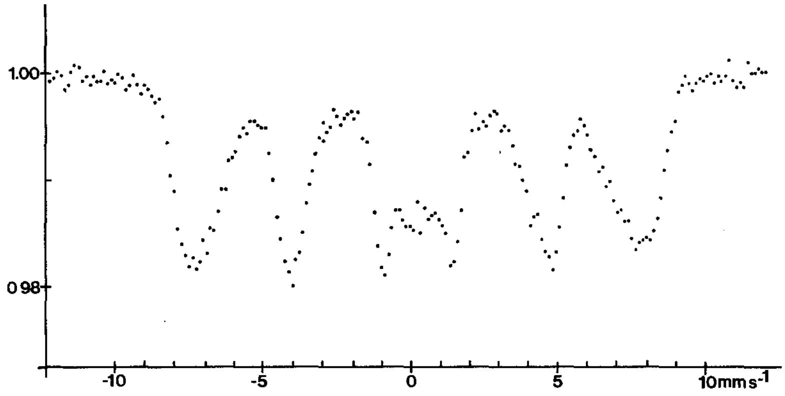

FIG. 1. NGR spectrum at 4.2 K of a precursor of the catalyst. Source, ^{57}Co/Pd.

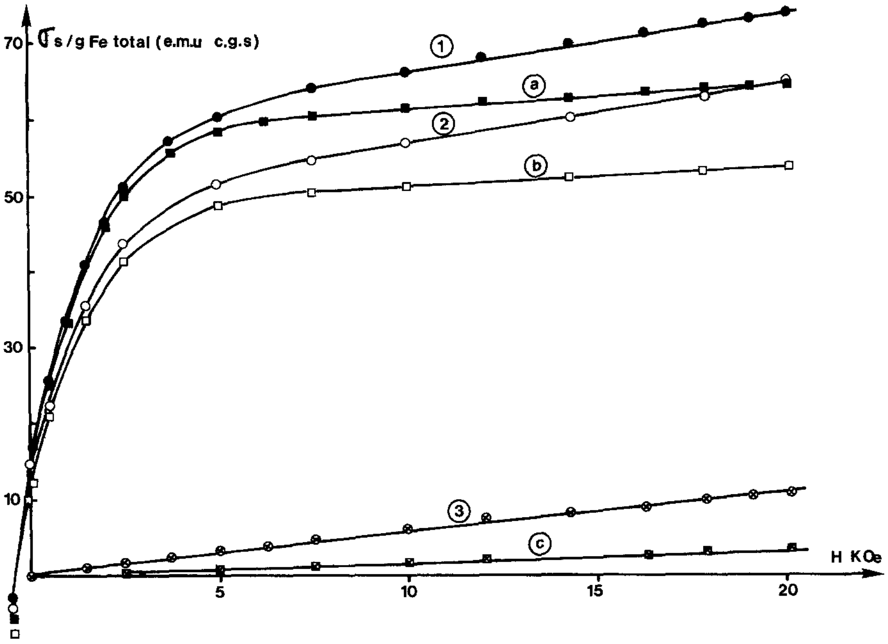

FIG. 2. Magnetization vs field strength. Precursor: Measurement at 77 K, curve 3; at 300 K, curve c. After reduction at 950 K: Measurement at 77 K, curve 1; at 300 K, curve a. After reduction at 950 K and outgassing at 770 K: Measurement at 77 K, curve 2; at 300 K, curve b.

sample reduced at 950 K are shown in Figs. 2 and 3. The degree of reduction is calculated from the saturation magnetization which is deduced from a linear extrapolation at zero field (it is assumed that the specific saturation magnetization is the same as that of bulk iron, σ_s = 217.7 emu cgs at 300 K). Curves obtained at 4.2 K do not allow such an extrapolation because of the large contribution of the unreduced

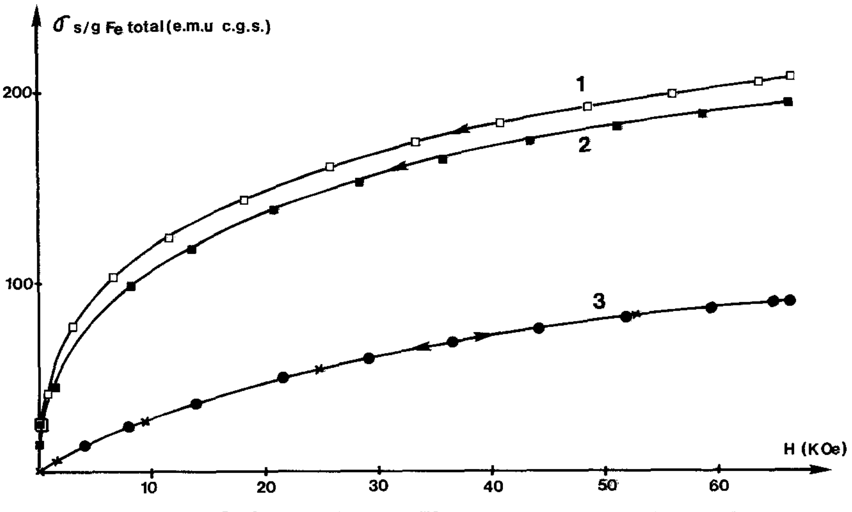

FIG. 3. Magnetization vs field strength at 4.2 K. Precursor, curve 3. After reduction at 950 K, curve 1. After reduction at 950 K and outgassing at 770 K, curve 2.

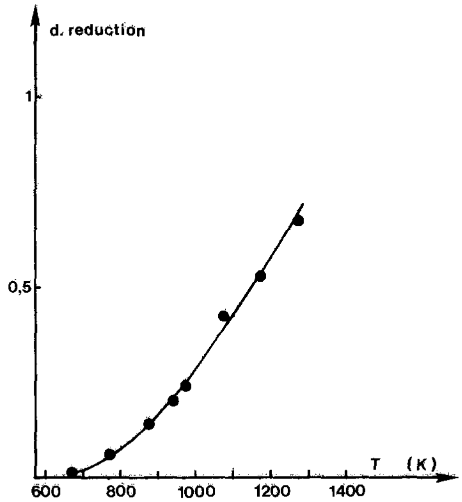

Fig. 4. Variation of the degree of reduction of Fe/MgO catalyst containing 8.45% Fe by weight, against reduction temperature.

TABLE 3

Coercive Field as a Function of the Temperature of Measurements for Sample Reduced at ca. 950 K[a]

$T_{\text{meas.}}$ (K)	H_c (Oe)
300	375
77	435
4.2	490
2	520

[a] Outgassing does not change the above results.

iron to the total magnetization. Variations of the thus calculated degree of reduction against the reduction temperatures for a sample containing 8.45% Fe by weight are shown in Fig. 4. It can be seen that reduction starts only beyond 670 K and that at 1270 K the degree of reduction is only 0.7. Hence, this type of catalyst should be considered as a complex mixture of metallic and unreduced iron.

After Néel (*12*) and Weil (*13*), some idea of particle size may be found from the variations of the remanence with the temperatures of measurement. The application of the method fails, however, to give coherent results in our case, probably because particle sizes are larger than the critical diameter of the single domain particles (ca. 30 nm).

The coercive fields, H_c, of the previous sample are given in Table 3. The relatively high value observed for H_c shows that anisotropy does not arise from strain or crystal anisotropy (*14*). It should instead be attributed to shape anisotropy which may theoretically push H_c as high as 5200 Oe in long particles randomly oriented.

The Mössbauer spectrum at 300 K of the reduced catalyst is shown in Fig. 5. The majority of Fe° gives the sextet of ferromagnetic metallic iron. The arrow

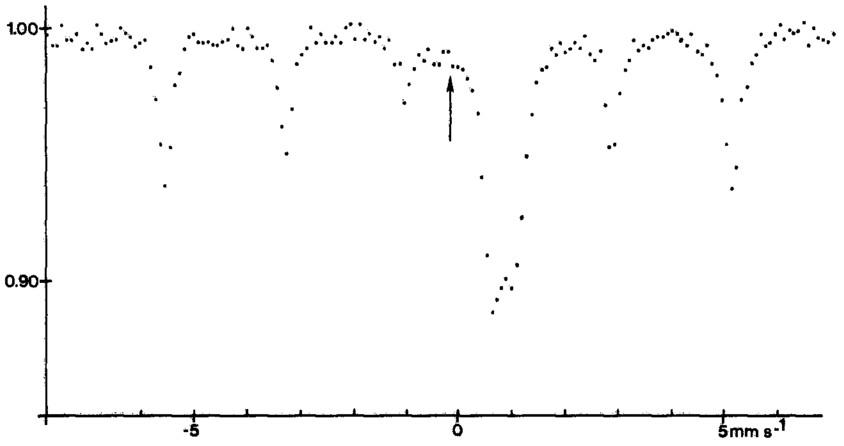

Fig. 5. NGR spectrum at 300 K of reduced catalyst No. 2. Source, ^{57}Co/Pd.

TABLE 4

Metallic Iron in NGR Spectra at Room Temperature in Hydrogen of Reduced Catalysts

Catalyst No.	Fe content (%)	Reduction treatment	IS (mm s^{-1})	Γ_{exp} (mm s^{-1})	Area in the spectrum (%)	Fe° content from magnetic data (%)
1	4.15	15 hr at 870 K +1.5 hr at 950 K	0.23	0.45	42	25
2	8.45	15 hr at 950 K	0.26	0.30	54	30

indicates the position where a line of superparamagnetic metal could appear: There is clearly no signal, and computation cannot allow for it to be more that 3% of the ferromagnetic species. Table 4 gives NGR parameters of such spectra.

The fact that no superparamagnetic iron is present indicates that there are no metallic iron particles smaller than the critical diameter corresponding to an equilibrium time of 10^{-8} s, the Larmor precession frequency (*15*). This critical diameter can be calculated from the Néel formula (*12*):

$$1/\tau = 1/\tau_0 \exp[-(vH_cI/2kT)].$$

τ = equilibrium time,

I = magnetization per unit volume,

v = volume of the iron particle corresponding to the critical diameter,

τ_0 = the frequency factor, depending slightly upon H_c and T, and calculated from data collected in (*10*). The calculated value for this critical diameter is 74 nm.

Average crystallite sizes calculated from X-ray line broadening are equal to ca. 35 nm. The fact that crystallite sizes are smaller than particles sizes deduced from Mössbauer spectroscopy indicates that iron particles are polycrystalline.

The metallic surface area determined by selective chemisorption of CO at 195 K (*16*) is equal to 11 m^2/g Fe. The corresponding diameter is 68 nm, a value which is roughly in agreement with the Mössbauer results.

It can be concluded from this study that our catalyst contains rather large metallic iron particles (ca. 70 nm).

Table 4 also shows that the part of the NGR spectra attributed to Fe° is ca. 1.7 times larger than the amount of Fe° deduced from magnetic measurements, probably due to differences in Lamb–Mössbauer factors of metallic and ionic species.

The other iron species are reduced ions, resulting in a large absorption at the center of the NGR spectrum. This part can be fitted to the sum of two lines, with parameters reported in Table 5. They

TABLE 5

Ionic Iron in Reduced Catalysts from NGR Spectra at Room Temperature in Hydrogen

Catalyst No.	1st line			2nd line		
	IS (mm s^{-1})	Γ_{exp} (mm s^{-1})	Area in the spectrum (%)	IS (mm s^{-1})	Γ_{exp} (mm s^{-1})	Area in the spectrum (%)
1	1.15	0.95	48	1.55	0.43	10
2	1.11	0.50	24	1.55	0.41	22

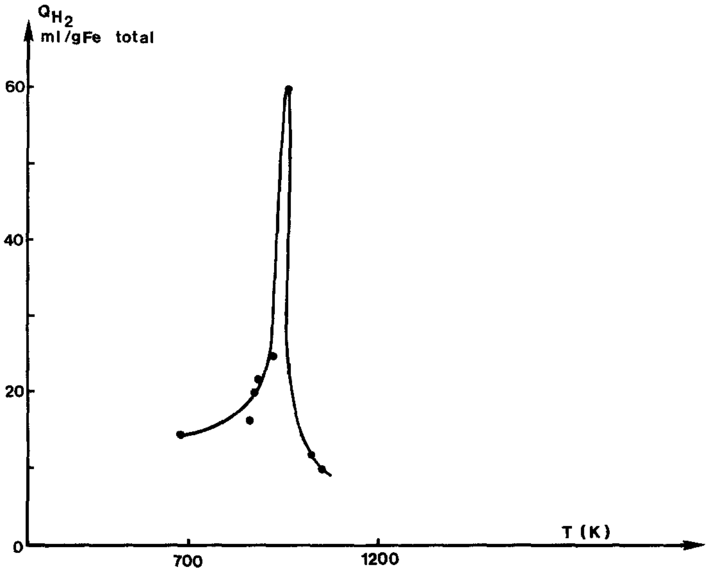

FIG. 6. Quantity of evolved hydrogen at 770 K (Q_{H_2} in ml NTP/g Fe total) against the reduction temperature, for Fe/MgO catalyst.

belong to Fe^{2+} and perhaps Fe^{+} which will be discussed later.

Interaction of H_2 on Fe/MgO Catalysts

After reduction, gas which was evolved by heating the sample *in vacuo* (10^{-6} Torr) was collected in the rough vacuum volume of the pumping system where the pressure increase was measured (*17, 18*). Mass spectrometer analysis showed that the evolved gas was H_2.

In Fig. 6 the volume of evolved hydrogen at 770 K is plotted against the reduction temperature. A maximum is observed at reduction temperatures between 920 and 1000 K with a corresponding volume nearly equal to 60 ml/g of total iron (300 ml/g of metallic reduced iron). In Fig. 7 is shown the volume of evolved hydrogen plotted against the treatment temperature for the Fe/MgO catalyst reduced at a temperature corresponding approximately to the maximum of the curve of Fig. 6. The volume of H_2 evolved from an unreduced precursor is very small compared to that evolved from a reduced sample, indicating that reduced iron is involved in this evolution. However, the total evolved volume at 1220 K (650 ml/g of reduced metallic iron) is not compatible with a desorption of surface chemisorbed hydrogen.

These preliminary experiments suggested to us that evolved hydrogen could originate from hydroxyl groups on (or in) the

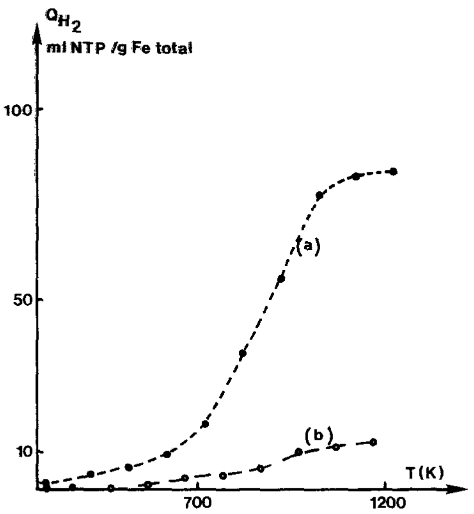

FIG. 7. Quantity of evolved hydrogen against treatment temperature for Fe/MgO catalyst reduced at 960 K, curve a; and unreduced Fe/MgO precursor, curve b.

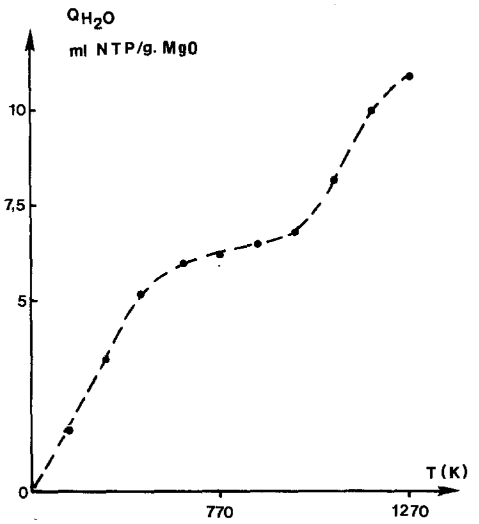

Fig. 8. Quantity of evolved H_2O against treatment temperature for MgO blank pretreated in H_2 at ca. 960 K.

catalyst: As can be seen from infrared spectroscopy (*19*) and from Fig. 8, there is a large concentration of OH groups on (or in) the MgO blank. In Fig. 8 is shown the volume of evolved water from MgO pretreated in H_2 at ca. 960 K as a function of the outgassing temperature. The two parts of the curve observed in Fig. 8 probably correspond to surface and bulk hydroxyl groups of the magnesia blank. The presence of large amounts of OH groups in the Fe/MgO catalyst, particularly after reduction, is also quite plausible, as confirmed by infrared spectroscopy (*19*).

The magnetic study of H_2 evolution is expected to shed some light on the nature of H_2 activation. When H_2 is evolved by pumping at temperatures up to 770 K a decrease of the saturation magnetization is observed. The average variation per evolved H_2 molecule is 1.5 B.M./H_2 when magnetic measurements are performed at 300 K; the corresponding values at 77 and 4.2 K are, respectively, 1.4 and 1.9 B.M./H_2 (Figs. 2 and 3). We will consider to a first approximation that these three measurements are in agreement, indicating that the error due to a lack of saturation at 300 and 77 K is rather small (this is in accordance with the fact that iron particles are large). This is the reason why most of

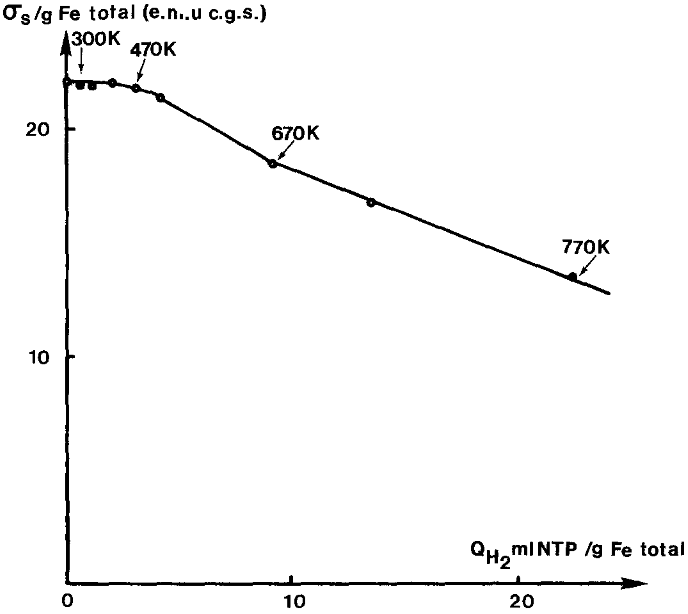

Fig. 9. Saturation magnetization measured at 300 K against the volume of evolved H_2 at different temperatures.

the magnetic measurements reported here were performed at 300 or 77 K.

In Fig. 9 the variations of saturation magnetization against the volume of evolved H_2 are shown. The system was heated stepwise up to 770 K. At evolution temperatures smaller than 470 K, no magnetization variations are observed ($\alpha \simeq 0$ B.M./H_2). A possible explanation is that H_2 originates from the support or from the ionic iron phase. However, the volume of evolved H_2 from the MgO blank or from the unreduced precursor in corresponding conditions is much smaller. This is the reason why it is believed that H_2 is coming from desorption from the metallic surface. The desorbed volume (3 ml NTP/g reduced iron) is compatible with the surface area of metallic iron. This state is probably the same as that observed by Boudart *et al.* (*5*, *8*) on Fe/MgO catalysts for which the observed magnetization decrease was very small and which was also attributed to adsorbed hydrogen.

When H_2 is evolved at temperatures between 470 and 670 K, the slope is ca. 2.2 B.M./H_2. At temperatures higher than 670 K, a linear decrease of the saturation magnetization is observed with the slope α = 1.5 B.M./H_2. When H_2 is subsequently introduced at 770 K, an increase of the saturation magnetization is observed with an average slope nearly equal to 0.9 B.M./H_2, as previously reported (*19*).

The average slope α depends on the temperature of reduction of the sample (and hence on the degree of reduction). As an example, the variation of α, measured at 300 K upon H_2 evolution at 770 K, against the degree of reduction is shown in Fig. 10. It can be seen that α lies between 1.5 and 2.5 B.M./H_2.

A similar study was carried out by infrared spectroscopy and the results were reported in a preliminary note (*19*): It can be recalled that when H_2 is evolved upon heating at 770 K, the intensity of some OH groups decreases. The introduction of H_2 (D_2) at the same temperature increases the OH(OD) band intensities. The cycle outgassing–introduction of H_2 can be repeated with the same consequences for the OH spectrum.

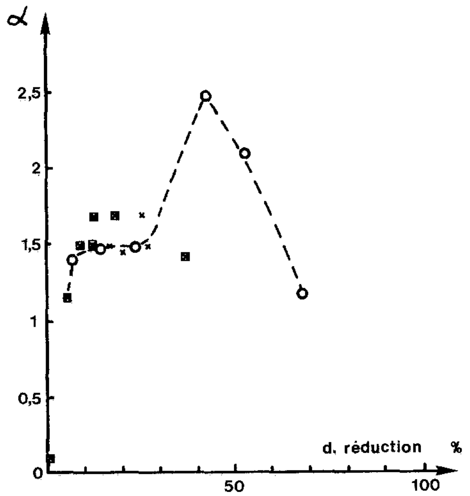

FIG. 10. Decrease of saturation magnetization for H_2 molecule measured at 300 K as a function of the degree of the reduction.

Mössbauer spectroscopy shows the changes that occurred in iron during such treatments. As previously reported (*9*), outgassing leads to the complete disappearance of the ferromagnetic component in the spectrum of catalyst No. 1 (Fig. 11). Computer analysis indicates four lines: Two are identical to those of Table 4, and two new lines are superimposed on them, equal to each other with isomeric shifts of 0.50 and 1.70 mm s^{-1}, respectively. These two lines are probably components of a doublet with IS = 1.10 and QS = 1.20 mm s^{-1}, consistent with the occurrence of a wüstite-like phase. In the case of catalyst No. 2 (Fig. 12) about 20% of the ferromagnetic component vanishes, one half giving rise to a single line of metallic iron, then behaving as superparamagnetic, and the other giving rise to an increase of the previous components at 1.15 and 1.50 mm s^{-1}. We may infer the enhancement of

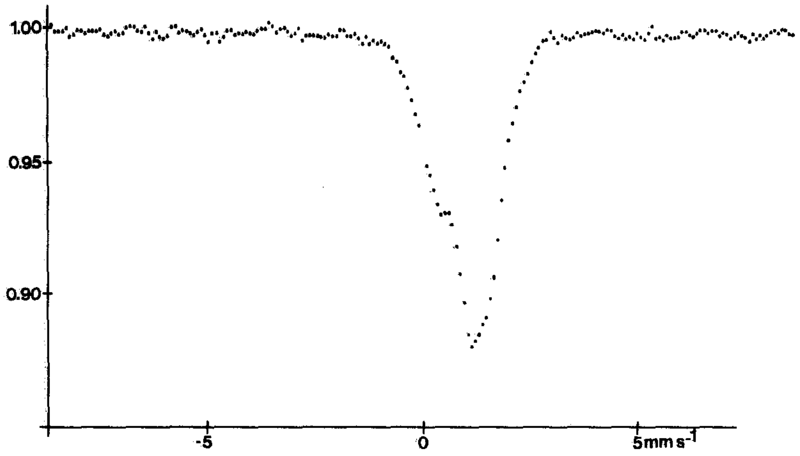

FIG. 11. NGR spectrum at 300 K of catalyst No. 1 after hydrogen desorption under vacuum. Source, ^{57}Co/Cr.

Fe^{2+}. It follows that hydrogen evolution is correlated to a total or partial oxidation of iron metal. On subsequent H_2 introduction, the spectrum of reduced catalyst is fully recovered.

DISCUSSION

The first point which deserves some discussion is the H_2 adsorption state corresponding to a very small magnetic effect ($\alpha \simeq 0$), confirming previous observations by Boudart *et al.* (*5*, *8*) which is probably to be attributed to H_2 adsorption on metallic iron. It is of interest to compare this result to magnetic effects observed on metallic Ni and Co; when H_2 is adsorbed on these metals, a decrease of saturation magnetization is observed corresponding to $\alpha = 1.7 - 1.3$ B.M. for Ni (*3*, *20*) and $\alpha = 0.4 - 0.8$ for Co (*21*). As can be seen, there is a general trend in moving from iron to nickel, $|\alpha|$ increases from left to right in the periodic table as already stated by Boudart *et al.* This trend parallels that

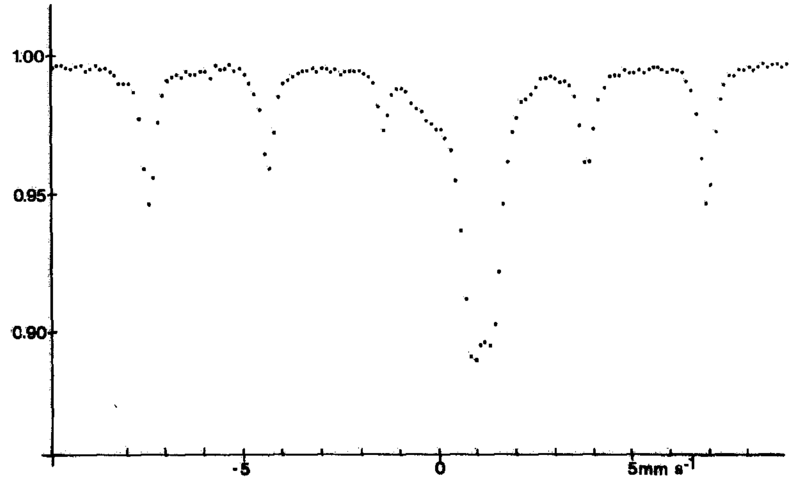

FIG. 12. NGR spectrum at 300 K of catalyst No. 2 after desorption under vacuum. Source ^{57}Co/Pd.

observed for some interstitial alloys, like NiC, CoC, and NiFeC interstitial alloys (*22*, *23*): When going from Ni ("hard" ferromagnetic) to Fe ("soft" ferromagnetic), $|\alpha|$ is decreasing. In the first case the screening charge introduced by one atom of impurity (dissolved or adsorbed) is larger in the sub-band d↓, thus leading to negative α values which approximate more or less in absolute value the difference of charge between the impurity and the host metal (four electrons for C, two electrons for H_2). In the second case ("soft" ferromagnetic), the screening charge would come from both d↓ and d↑ sub-bands, thus leading to $\alpha \geqslant 0$ (*22*, *23*).

Another point of interest is the activation of H_2 at higher temperatures which corresponds to $\alpha = 0.9 - 2.2$ B.M. H_2 evolution gives rise to a decrease of metallic iron content as seen from magnetic and NGR experiments, and to a decrease of infrared OH band intensity (*19*); introduction of H_2 in the system results in the reverse effect (increasing of the metallic iron content and of OH band intensities). Moreover, NGR indicates that when the Fe° content is decreasing, ionic iron is increasing and vice versa. These results are consistent with the following mechanism:

$$Fe^{n+} + n/2H_2 \rightleftharpoons Fe + nH^+,$$

where H^+ ions would be interacting with basic sites of the catalyst giving OH groups. During pumping, H^+ oxidizes Fe to Fe^{n+}, itself being reduced to H and desorbing as H_2. When H_2 is introduced, Fe^{n+} is reduced to metallic iron, and the protons thus formed react with basic sites of the catalyst. Fe^{n+} should be stabilized in structures, implying oxygen ions. Hence, the above reaction does require mass transfer onto the surface whose nature has not yet been clearly elucidated. As we have observed that molecular H_2 is not retained on unreduced samples at the temperatures considered (620 K, for example), it can be deduced that the presence of metallic iron is necessary for the reaction. Metallic iron would first dissociate molecular hydrogen into atomic hydrogen, which would be capable of reacting with Fe^{n+}. In fact the above equation would be the resultant of the two following equations:

$$\tfrac{1}{2}H_2 + Fe \rightleftharpoons Fe\text{–}H_{ads}$$

$$Fe^{n+} + H_{ads} \rightleftharpoons Fe + nH^+.$$

It is interesting to note that this reaction involves metallic iron, oxidized iron, and basic sites, which are present in catalysts used in ammonia and Fischer–Tropsch synthesis. This suggests that this equation could describe the activation step of hydrogen in these reactions.

It also suggests a possible mechanism for the spillover effect: Molecular hydrogen would be first adsorbed on the metal, then it would migrate onto the support in the form of OH groups. Finally, it provides a possible explanation of the well-known exchange reaction between gaseous D_2 and OH groups of the support which is catalyzed by the presence of metallic particles on the support (*24*): D_2 would be first adsorbed on the metal, then oxidized to D^+ which would give OD groups and, conversely, OH groups would give back molecular hydrogen according to the above equation.

From the data reported here it is possible to obtain some information on n, the degree of oxidation of iron involved in the above equation. We can calculate for $n = 1$, 2, or 3 assuming that ionic iron does not contribute to the overall magnetization (Fe^{n+} would be magnetically disordered, or antiferromagnetically ordered). In that case, α is, respectively, equal to 4.4, 2.2, or 1.5 B.M.; values encountered in this work lie between 0.9 and 2.5 B.M. On unsupported iron (*4*) α was 3.6 B.M. All these experimental values fall nearly in the calculated range. It is attractive to deduce from observed α values the degree of oxidation of iron involved in the equation. However, complications can arise from the fact that Fe^{n+} and Fe could be in magnetic interaction, either positive or negative. These would lead to α values different from those previously calculated (a similar effect has already been observed on Co powders). Thus, it seems hazardous to calculate n from magnetic measurements.

Mössbauer spectroscopy enables us to obtain a somewhat clearer knowledge of this point. In the reduced catalysts the two NGR lines of the ionic species (see Table 5) could be accounted for assuming either one or two forms: (I) They could be ascribed to only Fe^{2+}, partly as a doublet; the line at the right would be that with IS = 1.55 mm s^{-1}, resulting in an IS of 1.35 and a quadrupole splitting (QS) of 0.40 mm s^{-1}. For catalyst No. 1 the line at the left of the doublet would contribute the large and broad line with IS = 1.15 mm s^{-1}. Such Mössbauer parameters cannot be ascribed to separate FeO phases (*11*), so they indicate Fe^{2+} embedded in MgO, the single line corresponding to a substitutional cationic position and resulting in cancellation of even the atomic electronic field gradient due to the Jahn–Teller effect (*25*). (II) The line with IS = 1.55 mm s^{-1} would indicate Fe^{+}, as was stated in the case of Fe in ^{57}Co-doped MgO single crystals (*26*), with a dependence on the degree of reduction. Only spectra grown at low temperature without removing the samples from the cell used for the thermal treatments in hydrogen would provide a means to choose between the two hypothesis. In fact it is not necessary, because subsequent outgassing does not modify these two lines, which is further evidence for ascribing them to iron having entered the support.

As clearly seen earlier, the effect of removing hydrogen is to induce either a total or a partial transformation of iron metal into Fe^{2+}.

In the case of catalyst No. 2 the amount of metal that undergoes a chemical change, about 10% is larger than the number of surface atoms consistent with the particle sizes expected from the magnetic and CO chemisorption data and corresponds to the quantity of evolved hydrogen. The remaining metallic atoms in the smallest particles would be arranged in such small domains that they would behave as superparamagnetic, giving the observed Fe° a single NGR line. This therefore would not have the same origin as in the catalyst of Boudart *et al.* (*5*, *6*), where it appears in hydrogen chemisorption.

The behavior of catalyst No. 1, where the bulk of the metallic particles undergoes oxidation, would be expected from a more imperfect structure as suggested by the larger NGR linewidth.

Finally, all these features of the Mössbauer study are quite consistent with the mechanism deduced from magnetism and we can now give a value of n = 2 for the proposed equation.

CONCLUSION

From this work, it appears that there are at least two processes of activation of H_2 on Fe/MgO catalysts. The first one corresponds to the chemisorption of H_2 on metallic iron particles without change in the saturation magnetization, as observed by Boudart *et al.* The second one is observed at higher temperatures (470 K) and can be described by the redox equation:

$$Fe^{2+} + H_2 \rightleftharpoons Fe + 2H^{+},$$

where H^{+} ions are interacting with basic sites of the catalyst as OH groups.

It can be asked to what extent this type of H_2 activation is a general phenomenon. Some preliminary experiments on Fe/Al_2O_3 and Fe/SiO_2 catalysts show clearly that this activation process also occurs to a more or less large extent. The question now is to determine whether it can be observed on other supported metals and what is its exact role in catalytic processes.

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