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Magnetic Field Effects on the Catalyzed Nondissociative Parahydrogen Conversion Rate

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Explanations based on simple classical induction and diamagnetic shielding are given for some of the changes in parahydrogen conversion rates found for catalysts in a magnetic field at the 10-kOe range. Effects found on the rare earths as catalysts in extrinsic fields not much larger than terrestial magnetism are shown to have no direct relation to the 4f electrons. A proposed explanation for the field effects in this range is based on the very low energy differences between 4f, 5d, and 6s electrons in these elements and on possible selection rules.

INTRODUCTION

The nondissociative parahydrogen conversion rate may be changed by placing the catalyst in a magnetic field generated externally (*1*, *2*). The purpose of this paper is to present a phenomenological analysis for some of the extrinsic field effects that have been observed. The analysis is limited to catalysts that are known, or assumed, to be in the paramagnetic phase.

All extrinsic field observations on catalysts within the selected group fall into one or more of three categories. For one category the conversion rate suffers no change until the field exceeds about 150 Oe. The rate then rises until at 18 kOe it may be nearly threefold greater than at zero field. This behavior will be referred to as the "high field positive" effect. For another category the rate suffers little change below 150 Oe but then decreases moderately as the field is raised to 18 kOe. This is referred to as the "high field negative" effect. The third category involves no change of rate below about 2 Oe, then a decrease of 40% or more followed by no further change above about 100 Oe. This is called the "low field negative" effect. The three effects are illustrated in Fig. 1. "High field positive" has been observed over Cr_2O_3, CoO, MnO, the paramagnetic rare earths, dilute solid solutions of Cr_2O_3–Al_2O_3, and over supported Cr_2O_3/Al_2O_3. "High field negative" has been observed over Gd_2O_3 supported at low surface concentration over La_2O_3. "Low field negative" is shown over the nominally diamagnetic oxides Y_2O_3 and Lu_2O_3 after pretreatment above 823 K in hydrogen. This effect is also shown by Pr_2O_3, Nd_2O_3, Sm_2O_3, Yb_2O_3, and by the paramagnetic rare earths supported on La_2O_3 with the exception of Gd_2O_3/La_2O_3. In all that follows k_0 is the specific conversion rate ($mol \cdot m^{-2} \cdot s^{-1}$) in zero field and k_H is the rate in a field of strength $\boldsymbol{H}$. The fractional change of rate

$$\Delta k_H = (k_H - k_0)/k_0.$$

THE HIGH FIELD POSITIVE EFFECT

The field gradient normally present at or near the surface of a paramagnetic solid is augmented during application of a magnetic

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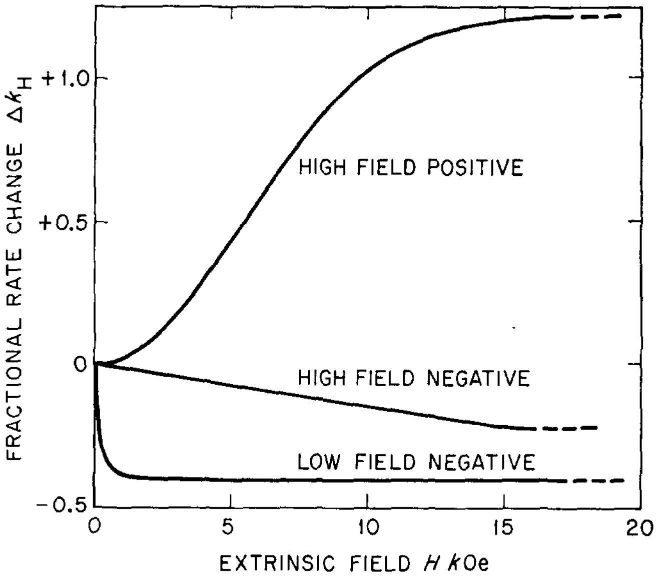

Fig. 1. Illustrative fractional parahydrogen conversion rate changes (Δk_H) over paramagnetic catalysts in an applied magnetic field.

field generated externally. The flux density $\boldsymbol{B}$ in the sample in a field of strength $\boldsymbol{H}$ is $\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M}$ where $\boldsymbol{M}$ is the magnetization. As $\boldsymbol{M} = \kappa\boldsymbol{H}$, where κ is the susceptibility, the change in flux density, as the catalyst surface is crossed, is easily determined. Standard tables for Dy_2O_3 at 290 K give $\chi = \kappa d$, where d is the density, equal to 230×10^{-6} $cm^{-3}\cdot g^{-1}$. Hence in a field of 10 kOe the term $4\pi\chi = 0.23$ kOe. It is obvious that the applied field can cause an increase of effective gradient at the surface of a paramagnetic solid and a small decrease for one with a negative susceptibility.

It is firmly established (*3*) that, in accordance with the Wigner treatment (*4*), the nondissociative conversion rate is proportional to the square of the Bohr magneton number, β, of the catalytic site. If $k_0 = \alpha\beta^2$ then in a field $\boldsymbol{H}$ a first approximation gives:

$$k_H = \alpha(\beta^2 + \gamma \boldsymbol{H}\chi d) \qquad (1)$$

where α is approximately constant for any similar group of catalysts such as the paramagnetic lanthanide sesquioxides, and γ is a constant for any particular sample. It follows that:

$$\Delta k_H = [\alpha(\beta^2 + \gamma \boldsymbol{H}\chi d) - \alpha\beta^2]/\alpha\beta^2 = \gamma \boldsymbol{H}\chi d/\beta^2. \qquad (2)$$

Equation (2) shows that at a given temperature Δk_H is proportional to the applied field. It also shows that Δk_H varies with temperature to the degree that the susceptibility is influenced. Experimentally it is not easy to find catalysts that are free from phase transitions and chemical reactivity in hydrogen. But MnO is satisfactory for testing the field strength dependence of Δk_H (*5*). At 298 K Δk_H rises almost linearly with $\boldsymbol{H}$ up to about 10 kOe. There is then a slowly decreasing dependence of Δk_H on $\boldsymbol{H}$. No case has been found in which Δk_H increases by significantly more than the first power of $\boldsymbol{H}$.

The effect of temperature and thus of susceptibility on Δk_H is shown in Fig. 2 derived from data (*6*) on a dilute Cr_2O_3–Al_2O_3 solid solution over the range 173–373 K. The relationship between χ and Δk_H deviates somewhat from linearity but there is no question that as the susceptibility rises Δk_H also rises.

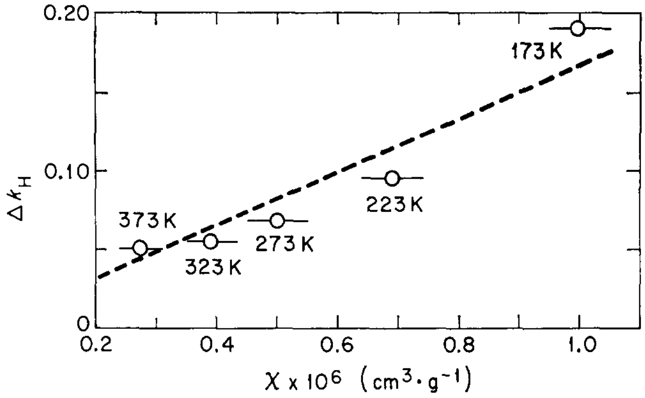

FIG. 2. Fractional rate change in a field of 7.5 kOe vs κ/d (magnetic susceptibility/density) over 1% Cr_2O_3–Al_2O_3.

THE HIGH FIELD NEGATIVE EFFECT

The only catalyst sample showing this effect to the exclusion of any other is lanthana-supported gadolinia (*7*). For Gd_2O_3/La_2O_3 the effect is a gradual decrease of k_H with increasing field. At 18 kOe $\Delta k_H = -0.23$ with some indication of saturation above 10 kOe. This effect appears to be related to diamagnetic shielding of the 4f electrons by action of the applied field on the $5d^25p^6$ electrons. The effect is negative because the field reaching the hydrogen molecule from the 4f electrons is less than that predictable from the Bohr magneton number of the rare earth ion. Equation (1) may be modified to include a diamagnetic shielding term δ:

$$k_H = \alpha(\beta^2 + \gamma H \chi d - \delta H), \quad (3)$$

and this yields:

$$\Delta k_H = H(\gamma \chi d - \delta)/\beta^2. \quad (4)$$

Equation (4) shows that Δk_H should be proportional to H as is actually the case for Gd_2O_3/La_2O_3. But Eq. (4) also shows that the sign of Δk_H depends on the relative magnitudes of $\gamma \chi d$ and δ. Observation of the high field negative effect obviously depends on having a relatively high concentration of active sites supported on a diamagnetic substrate. This is in contrast to the self-supported rare earths that may be regarded as having a high surface concentration of active sites supported on a strongly paramagnetic substrate. There is also the complication that all the rare earths other than Gd_2O_3 show the low field negative effect.

THE LOW FIELD NEGATIVE EFFECT

The only catalysts known to show this effect and none other are yttria and lutetia (*8*). The effect, shown for Lu_2O_3 in Fig. 4, consists of an abrupt negative change at about 2 Oe and reaching saturation below 100 Oe. The maximum Δk_H for Lu_2O_3 is -0.42 and for Y_2O_3 -0.28. No further change occurs up to 18 kOe. In a flow reactor at atmospheric pressure the specific conversion rate in zero field is less than 1×10^{-7} mol·m^{-2}·s^{-1} at 298 K. But as the pretreatment temperature in hydrogen

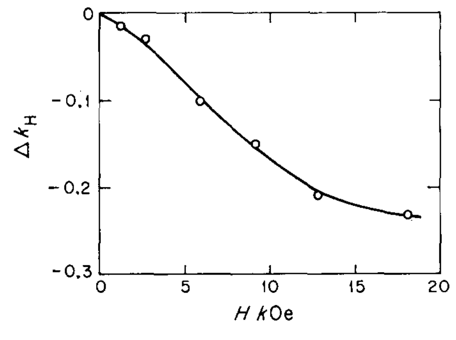

FIG. 3. Fractional rate change vs field over Gd_2O_3/La_2O_3 at 298 K.

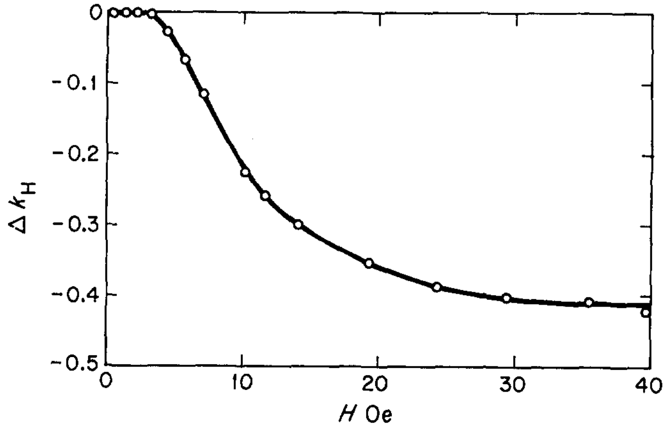

FIG. 4. Fractional rate change vs field (in Oe) over Lu_2O_3 at 298 K.

rises, k_0 also rises, reaching 1.4×10^{-6} $mol \cdot m^{-2} \cdot s^{-1}$ for pretreatment at 973 K. There is no significant change of Δk_H as k_0 rises.

The low field effect is also found over all the paramagnetic rare earths of relatively low susceptibility (7) of which Yb_2O_3 is one example. From these results it appears possible for some paramagnetic solids to have two different sources of nondissociative conversion activity and for these sources to act independently of each other. To facilitate further consideration of this possibility the following symbols will be used:

k_H^{obs}	conversion rate observed in a field H kOe
k_{sat}	rate in a field sufficient to saturate an effect
$k_H^{\pm}$	rate attributable to sites responsive to one or to both positive and negative high field effects
k_H^{-}	rate attributable to sites responsive to the low field negative effect
Δk_H^{obs}	fractional rate change observed in a field H kOe.

For a sample of Yb_2O_3 pretreated in hydrogen at a maximum temperature of 823 K, hereafter designated Yb_2O_3 (823 K), and measured at 298 K, $\Delta k_{0.04}^{obs} = -0.11$ and $\Delta k_{18}^{obs} = +2.1$. It will be assumed that the surface of Yb_2O_3 (823 K) contains sites that are different from the normal $Yb^{3+}(4f^{13})$ but which cannot be the familiar diamagnetic $Yb^{2+}(4f^{14})$. Proof of this is found in the invariable increase of catalytic conversion activity after the pretreatment indicated.

If there are two independent kinds of conversion sites on the surface of Yb_2O_3 (823 K) then:

$$k_H^{obs} = k_H^{\pm} + k_H^{-}. \qquad (5)$$

In a field of 0.1 kOe, which is sufficient to saturate the low field negative effect, $k_{0.1}^{obs} = k_{0.1}^{\pm} + k_{sat}^{-}$. But $k^{\pm}$ suffers no change in such a weak field; hence:

$$k_{0.1}^{obs} = k_0^{\pm} + k_{sat}^{-}, \qquad (6)$$

$$\Delta k_{0.1}^{obs} = (k_{sat}^{-} - k_0^{-})/k_0^{obs}, \qquad (7)$$

and

$$k_0^{-} = (\Delta k_{0.1}^{obs} \times k_0^{obs})/\Delta k_{sat}^{-}. \qquad (8)$$

It is, therefore, possible to find k_0^{-}, and $k_0^{\pm}$, provided that Δk_{sat}^{-} can be found.

One method for obtaining Δk_{sat}^{-} is to assume that it is the same for Yb_2O_3 as for Lu_2O_3, namely, -0.42. On this assumption it is found that $k_0^{-} = 0.26\ k_0^{obs}$ for the sample of Yb_2O_3 (823 K) referred to above. For a typical sample of Yb_2O_3 (823 K) $k_0^{obs} = 0.22 \times 10^{-4}$ $mol \cdot m^{-2} \cdot s^{-1}$. These values depend, of course, on the uncertain precision of all conversion rates of this kind, but the ratios $k_0^{-}/k_0^{\pm} = 0.36$, and $k_0^{-}/k_0^{obs} = 0.26$ are reproducible to $\pm 10\%$ on samples of identical pretreatment.

From data such as those given in the preceding paragraph it is possible to find

$\Delta k_{sat}^{\pm}$ in a sample showing both high and low field effects. This will be illustrated for a sample of Yb_2O_3 (823 K) for which

$$k_0^{obs} = 0.094 \times 10^{-4},$$

$$k_{0.04}^{obs} = 0.085 \times 10^{-4},$$

and

$$k_{18}^{obs} = 0.290 \times 10^{-4}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}.$$

By definition, $\Delta k_H^{\pm} = (k_H^{\pm} - k_0^{\pm})/k_0^{\pm}$ and, from Eq. (5),

$$\Delta k_H^{\pm} = [(k_H^{obs} - k_H^{-}) - (k_0^{obs} - k_0^{-})]/(k_0^{obs} - k_0^{-}).$$

For this sample $k_0^{-} = 0.24\ k_0^{obs}$, so that

$$\Delta k_H^{\pm} = [(k_H^{obs} - k_H^{-}) - 0.76 k_0^{obs}]/0.76 k_0^{obs}.$$

As

$$k_{0.04}^{obs} = k_0^{\pm} + k_{sat}^{-} = 0.90 k_0^{obs},$$

and as

$$k_{sat}^{-} = 0.90 k_0^{obs} - k_0^{\pm} = 0.90 k_0^{obs} - 0.76 k_0^{obs} = 0.14 k_0^{obs},$$

it follows that

$$\Delta k_{sat}^{\pm} = (k_{sat}^{obs} - 0.90 k_0^{obs})/0.76 k_0^{obs} = [0.29 - (0.90 \times 0.094)]/(0.76 \times 0.094) = 2.9.$$

Results for $\Delta k_{sat}^{\pm}$ on a few other rare earths are: Pr_2O_3, 1.5; Nd_2O_3, ~1.7; and Sm_2O_3, 0.7.

Collected results on these self-supported rare earths are shown in Table 1 for convenient comparison with related data on several lanthana-supported samples to be given below. Additional information on the relationship between $k_0^{\pm}$ and k_0^{-} may be obtained by pretreating Yb_2O_3 at progressively higher temperatures. It is well known that specific conversion rates over the paramagnetic rare earths are increased by raising the pretreatment temperature. This increase has been shown (*9*) to be due chiefly to progressive dehydroxylation as, for instance, by the reaction $2\ OH^- \rightarrow O^{2-} + H_2O$, thus providing improved access to the catalyst by the hydrogen molecule. It has been found (*10*) that Yb_2O_3 (973 K) shows a 6.5-fold increase of k_0^{obs} as compared with Yb_2O_3 (823 K). But during this increase $\Delta k_{0.1}^{obs}$ falls to -0.01 which is near the limit of detectability. For this sample, then, k_0^{-} is only $0.02 k_0^{obs}$ and the ratio $k_0^{-}/k_0^{\pm} \simeq 0.02$. Regardless of the true value of Δk_{sat}^{-}, it is clear that the large increase in k_0^{obs} for Yb_2O_3 (973 K) is due almost entirely to an increase in $k_0^{\pm}$ and not to any appreciable change in k_0^{-}. The low field negative effect observed on Yb_2O_3 has obviously reached its maximum after pretreatment at 823 K. The k_0^{-} activity thus reached is comparable with that reached by Lu_2O_3 but only at a much higher pretreatment temperature.

Some additional clues concerning the source of k^{-} activity may be obtained from supported rare earths (*7*). With one exception, the catalyst support was La_2O_3 of surface 2.0 $m^2 \cdot g^{-1}$. For Tb_2O_3/Al_2O_3 the surface of the finished catalyst was 160 $m^2 \cdot g^{-1}$. Pretreatment was in hydrogen at 823 K and measurement at 298 K for all samples. All calculations were made with the assumption that $\Delta k_{sat}^{-} = -0.42$ as previously described for Yb_2O_3. Data on several supported catalysts are shown in Table 2 which may be compared with Table 1. The effect of the diamagnetic support is, except for Gd_2O_3/La_2O_3, to cause a large increase in the ratio $k_0^{-}/k_0^{\pm}$. For Dy_2O_3 $k_0^{-} < 0.01 k_0^{obs}$, while for Dy_2O_3/La_2O_3 k_0^{-}

TABLE 1

k_0^{obs} and $k_0^{-}/k_0^{\pm}$ for Several[a] Self-Supported Rare Earths at 298 K after Pretreatment in H_2 at 823 K

Sample	$k_0^{obs} \times 10^4$ ($\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$)	$k_0^{-}/k_0^{\pm}$
Pr_2O_3	0.36	0.32
Nd_2O_3	0.18	0.05
Sm_2O_3	0.025	0.2
Yb_2O_3	0.22	0.36

[a] For other self-supported paramagnetic rare earths $k_0^{-}/k_0^{\pm} < 0.01$.

TABLE 2

k_0^{obs} and $k_0^-/k_0^\pm$ for Several Supported Rare Earths at 298 K after Pretreatment at 823 K

Sample	$k^{obs} \times 10^4$ ($mol \cdot m^{-2} \cdot s^{-1}$)	$k_0^-/k_0^\pm$
Eu_2O_3/La_2O_3	1.15	1.4
Gd_2O_3/La_2O_3	1.83	<0.05
Tb_2O_3/La_2O_3	1.48	2.9
Tb_2O_3/Al_2O_3	1	1.0
Dy_2O_3/La_2O_3	1.71	1.2
Er_2O_3/La_2O_3	1.36	2.0
Yb_2O_3/La_2O_3	0.91	1.6

$= 0.53k_0^{obs}$. For $Yb_2O_3/La_2O_3 k_0^\pm$ is twice that in Yb_2O_3, but k_0^- has increased by a factor of 12.

Because $k_0^\pm$ is an appreciable fraction of k_0^{obs} for all the supported paramagnetic rare earths it may be predicted that at high fields k_H^{obs} would tend to rise, or fall, depending on the magnitude of the susceptibility in Eq. (3). Such a change has been found (*7*) for Er_2O_3/La_2O_3 over which Δk_H^{obs} rises from −0.23 at 0.1 kOe to about 0 at 18 kOe. A similar result has been reported for Tb_2O_3/Al_2O_3 (*2*). It is obvious that on these catalyst samples all three field effects are operative. The experimental data for Er_2O_3/La_2O_3 are given in detail in Fig. 5 (*7*). On Er_2O_3/La_2O_3 $\Delta k_H^{obs}/H$ over the linear field region is 0.023 kOe^{-1} and for Er_2O_3 it is 0.071 kOe^{-1}. As shown in Table 2, for Er_2O_3/La_2O_3 $k_0^-/k_0^\pm = 2.0$ and $k_0^{obs} = 1.36 \times 10^{-4}$ $mol \cdot m^{-2} \cdot s^{-1}$. Then $k_0^\pm = 0.453 \times 10^{-4}$ $mol \cdot m^{-2} \cdot s^{-1}$, and if $\Delta k_H^{obs}/H = 0.023$ kOe^{-1} then at, say 6 kOe, $k_6^\pm - k_0^\pm = k_6^{obs} - k_{0.1}^{obs} = 0.105$. Hence $\Delta k_6^\pm = 0.105/0.453 = 0.23$. For self-supported Er_2O_3 $\Delta k_6^{obs} \simeq \Delta k_6^\pm = 0.41$. It appears, therefore, that the "effective" susceptibility at the surface has been lowered by the La_2O_3 causing $\Delta k_H^\pm$ to fall to about two-thirds of that for the self-supported sample.

DISCUSSION AND CONCLUSIONS

The three magnetocatalytic effects observed over paramagnetic catalysts may be distinguished from each other by the sign and the field dependence of Δk_H. In this section conclusions concerning these effects will be summarized and consideration will be given to a possible source of the low field negative effect.

For any sample of matter in a magnetic field there must be a change of flux density at the surface. This field gradient is added

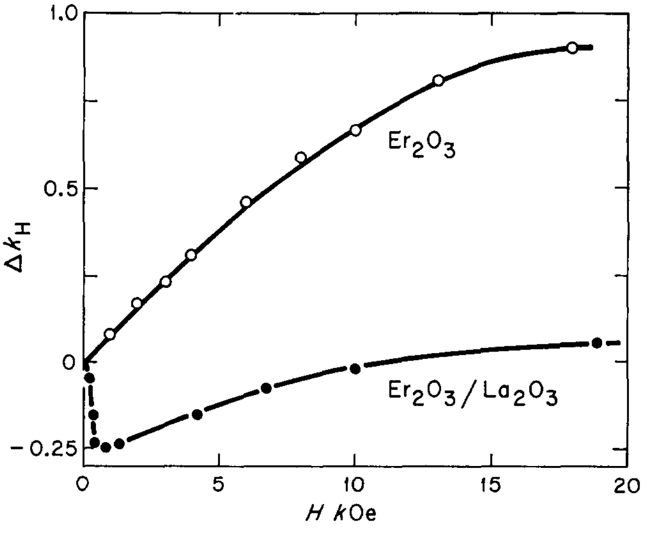

FIG. 5. Fractional rate changes vs field at 298 K over Er_2O_3 and Er_2O_3/La_2O_3.

to that produced by permanent moments at the catalytic sites. The increase of gradient is proportional to the applied field intensity and to the susceptibility of the sample. The fractional rate increase of the catalyzed parahydrogen conversion should then be proportional to $H\chi$ as shown in Eq. (2). This has been shown experimentally to be the case provided that such complications as phase transitions and chemical reactivity are avoided. To the writer's knowledge there has been only one other attempt to explain the high field positive effect (*11*), but that interpretation leads to the prediction that the conversion rate should increase as the square of the applied field.

The high field negative effect appears on a catalyst in which the paramagnetic sites are surrounded by $5s^25p^6$ electrons that produce diamagnetic shielding, thus diminishing the effectiveness of the active sites. The effect is almost certainly present in all the paramagnetic rare earths, but it is generally obscured by the much larger high field positive effect and, in most cases, it is complicated by the low field negative effect.

The low field negative effect is not related to the 4f electrons responsible for $k_H^\pm$ activity on all the paramagnetic rare earths. Proof of this statement is found in the following observations: On some catalysts, of which Lu_2O_3 is one, k_H^- activity only is found. On the self-supported paramagnetic rare earths k_H^- activity is always less than $k_H^\pm$ activity, but on the lanthana-supported rare earths (except Gd_2O_3/La_2O_3) the k_H^- activity is the larger. Increasing the pretreatment temperature from 823 to 973 K for a self-supported paramagnetic rare earth, of which Yb_2O_3 is an example, increases the $k_H^\pm$ activity but not the k_H^-. The $k_H^\pm$ activity tends to become independent of field above about 10 kOe but on k_H^- sites saturation occurs below 100 Oe. The k_H^- activity, unlike the $k_H^\pm$, is not proportional to β^2.

The sites providing k_H^- activity must possess a magnetic moment that is permanent in the sense of being able to catalyze the conversion over the duration of an experiment. This moment must almost certainly be situated on the surface of the catalyst. Sites involving the ion Al^{2+} have often been considered as the source of nondissociative conversion over Al_2O_3. Paramagnetic sites have been suggested for similar activity over Y_2O_3 (*12*). That this view is correct is supported by the method of preparation and by ESR evidence for Lu_2O_3 and especially for Y_2O_3 (*8*). If, for Pr_2O_3, Nd_2O_3, Sm_2O_3 and Yb_2O_3, k_0^- makes an appreciable contribution to k_0^{obs}, and if this is independent of $k_0^\pm$, then it might be surmised that the average k_0^{obs}/β^2 for these four catalysts would be larger than for the other paramagnetic rare earths. This is actually the case (*3*). The average k_0^{obs}/β^2 for these four (all pretreated at 823 K) is 20% greater than the average for the remaining seven for which data are available. It is scarcely probable that this could have been coincidence. Failure of the catalysts of higher magnetic moment to show measurable k_0^- activity (in the self-supported samples) is certainly due to the high $k_0^\pm$, and resultant very low $k_0^-/k_0^\pm$, shown by these preparations. Evidence that Nd_2O_3 may undergo surface reduction under the conditions described with, presumably, formation of the Nd^{2+} ion has been presented (*13*). If this method for forming a new paramagnetic site can occur for Nd_2O_3, then it could probably occur for at least some of the other rare earths.

Another suggestion for k_0^{obs} activity in Al_2O_3 catalyst samples is the nuclear moment (*14*). In all cases this is small compared with the electronic moment, and the distance between nucleus and hydrogen molecule is large. The nuclear moment squared for Lu^{3+} is about 600 times greater than that for Y^{3+}. Actually the parahydrogen conversion rates are about the same for Lu_2O_3 and Y_2O_3 (*8*). Similarly, k_0^- would be about 60 times greater on Pr_2O_3 than on Yb_2O_3 if the nuclear moments were controlling. Actually, k_0^- for Pr_2O_3 and Yb_2O_3 differ by a factor of only two, which is well within experimental error (7). It is unlikely that nuclear moments are significant for any of the rare earths as catalysts. A third suggestion for conversion activity on Al_2O_3 is the hydrogen molecule-ion, H_2^+, that may be formed on the surface of high area Al_2O_3 pretreated in hydrogen at 873 K (*15*). It is quite possible that H_2^+ is significant on Al_2O_3, but there is no reason why it should be formed more easily on one rare earth rather than another. There is no question that Lu_2O_3 requires a substantially higher activation temperature before it shows the same k_0^- activity as do most of the other rare earths. It seems improbable that H_2^+ contributes appreciably to the effects described, and, also, it offers no explanation for the negative field effect on Lu_2O_3 and Y_2O_3.

In view of the evidence discussed in the preceding three paragraphs it will be assumed that k_0^- activity has its source in an unpaired electron generated in the rare earths, including Y_2O_3. Reduction of Lu_2O_3 at appropriate temperature to form Lu^{2+} could occur by the reaction $2\ Lu^{3+}(5d^0) + O^{2-} + H_2 \rightarrow 2Lu^{2+}(5d^1) + H_2O$. A 6s electron instead of a 5d is also possible. For Y^{3+} a 4d or 5s electron could be involved. The quantity of water given up per unit surface area during catalyst activation in hydrogen between the temperatures 823 and 973 K is compatible with the conversion activity generated (*10*). This supports the view that a reductive process occurs during pretreatment.

The characterization of sites responsible for k_H^- activity over Lu_2O_3 and Y_2O_3, as described in the preceding paragraph, is complicated by the fact that Lu_2O_3, Y_2O_3, Eu_2O_3, Gd_2O_3, and Er_2O_3 heated in hydrogen between 823 and 973 K all liberate about the same quantity of water per unit surface (*10*). But the k_H^- activity developed is negligible for Eu_2O_3, Gd_2O_3, and Er_2O_3. If the pretreatment is stopped at a maximum of 823 K it is found that appreciable k_H^- activity has been generated on Pr_2O_3, Nd_2O_3, Sm_2O_3, and Yb_2O_3, but not on Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, and Tm_2O_3. As previously mentioned the maximum k_H^- activity reached by Yb_2O_3 at 823 K is comparable with that reached by Lu_2O_3 but only at a much higher pretreatment temperature. All of the above complications have a simple explanation. The reduction potential for $R^{3+} \rightarrow R^{2+}$ is larger for La^{3+}, Gd^{3+}, Lu^{3+}, and Y^{3+} than for any of the other rare earths, and much larger than for Eu^{3+} and Yb^{3+}. A pretreatment temperature of 823 K is sufficient to form the R^{2+} ion on the surfaces of all these oxides except La_2O_3, Gd_2O_3, and Lu_2O_3. But if the element has a large magnetic moment produced by its 4f electrons the ratio $k_0^-/k_0^\pm$ will be so small that no k_H^- activity can normally be detected. For Gd_2O_3 it would be necessary to raise the pretreatment temperature to at least 973 K before k_0^- became appreciable. Then, owing to progressive dehydroxylation as already described for Yb_2O_3, $k_0^\pm$ would rise to a far greater extent and no k_H^- effect would be observed.

The identification proposed above for the k_H^- sites makes it possible to consider what change could occur to produce the low field negative effect. A difficulty here is the very low interaction energy between one Bohr magneton and 1 Oe of field strength. The only explanations that seem possible involve either a change in magnetic moment of the catalytic site or a change of reaction mechanism. The latter is excluded by absolute conversion rate data on Lu_2O_3 (*16*). Let it be assumed that the state of a surface capable of showing the low field negative effect normally includes an electron in the 5d level for the rare earths, and 4d for Y_2O_3. It has been shown (*17*) that the ground state energy difference between 4f, 5d, and 6s is negligible in determination of chemical behavior. But a d electron will have both spin and orbital contributions to the magnetic moment while an s electron will have only the spin contribution. That a field of a very few oersteds could cause a change from $5d^1$ to $6s^1$ may only be attributed to a selection rule and to the non-equilibrium nature of the problem as has been mentioned (*18*). Our knowledge of conditions at the surfaces of solids such as those under consideration is insufficient to make possible an accurate estimate of the difference in moment for $5d^1$ vs $6s^1$ on Lu_2O_3. But consideration of theoretical and experimental data on related species suggests that the transition $Lu^{2+}(5d^1) \rightarrow Lu^{2+}(6s^1)$ would involve a change of Bohr magneton number from about 2.5 to 1.8. The fractional change of β^2 is then -0.48. The experimental value for Δk_{sat}^- is -0.42. It may be objected that the orbital contribution of a 5d electron would be "quenched" as is the case for many 3d compounds such as Cr_2O_3. But it seems likely that the orbital part of the moment could contribute to the parahydrogen conversion rate whether "quenched" or not, even though it could not contribute to the susceptibility.

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