The Effect of a Weak Magnetic Field on the Rare Earth Catalyzed Parahydrogen Conversion Rate

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If the catalyst is placed in a magnetic field of a few oersteds there may be observed a decrease in the parahydrogen conversion rate at room temperature over the oxides, Pr_2O_3, Nd_2O_3, Sm_2O_3, and Yb_2O_3, but not over Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, or Tm_2O_3. At 40 Oe, the rate decreases range from 5 to 20%. If the rare earth catalysts are supported at relatively low surface concentration on the diamagnetic La_2O_3, then all except Gd_2O_3 show the weak field magneto-catalytic effect. A plot of catalytic conversion rate versus extrinsic field shows an abrupt dependence of rate on field in the region of 3 to 10 Oe. It is possible, in this region, to observe the effect on the reaction rate of a change of field of less than 0.2 Oe.

INTRODUCTION

The purpose of this paper is to describe the effects, on the conversion rate of parahydrogen to orthohydrogen, of placing the catalyst in a magnetic field of from 0.1 to 40 Oe. The catalysts used were rare earths in two different forms of preparation.

In a previous paper from this laboratory (1) it was shown that chromia, in several forms, strongly catalyzes the room temperature parahydrogen conversion, that the conversion mechanism under the experimental conditions described is almost entirely magnetic and not dissociative, and that placing the catalyst in a magnetic field of up to 18 kOe changes the rate of conversion. For catalyst samples sufficiently pure and crystalline the change of rate is positive above the Néel temperature, and negative below. For dilute solid solutions of chromia in α-alumina, and for various other more nearly amorphous preparations, the change of rate is positive over a wide range of temperature.

In a subsequent paper (2), it was shown that all the paramagnetic rare earths (excluding promethia) give a large positive magnetocatalytic effect amounting, for ytterbia, to over 200% in a field of 18 kOe. During the course of the work on rare earths in strong fields it was noted that the residual field in a 12-in. electromagnet caused some change in the parahydrogen conversion rate, compared with that in the laboratory ambient field (~0.6 Oe) at some distance from the magnet. Further investigation of this anomaly produced the results reported below.

Two series of results are reported. The one series was on pure rare earth samples similar to those described in Ref. (2). These samples are referred to below as being "self-supported," and are in contrast to the second series that consisted of certain rare earths at relatively low surface concentration on high purity lanthana which is, of course, diamagnetic. These samples are referred to as "lanthana-supported."

A preliminary report on the weak-field studies has already been published (3).

EXPERIMENTAL METHODS

Catalysts. Self-supported rare earths (obtained from American Potash and Chemical Corporation), were stated to be

of 99.9% purity with respect to other rare earths, and 99.99% purity with respect to impurities reducible in hydrogen to catalysts capable of dissociating hydrogen at or near room temperature. All samples except praseodymia and terbia were heated in air at 800°C for 18 hr. Praseodymia was heated in hydrogen at 1100° for 12 hr, and terbia was heated in hydrogen at 800° for 12 hr. The rich green color of the praseodymia and the virtual white of the terbia indicated that the procedures used were adequate to form the sesquioxides on the surfaces, if not in the bulk of these two rare earths. Samples were all kept sealed except for momentary exposure to air for removal of small portions for X-ray, specific surface, and catalytic measurements.

Lanthana-supported rare earths were made by impregnating high purity lanthana of specific surface 2.0 m^2 (BET,N$_2$) with a dilute aqueous solution of the desired rare earth nitrate. The volume of the solution was chosen to be just sufficient to moisten the lanthana sample, and the concentration of the solution was chosen to give approximately the same rare earth surface concentration in the lanthana-supported samples as in the corresponding self-supported samples. The impregnated lanthana samples were then dried and ignited in air at 600° for 12 hr, prior to use. The catalytic properties of the pure lanthana, so far as they are related to the work on the paramagnetic rare earths, are described under Results.

All samples, both self-supported and lanthana-supported were, after being placed in the reactor, heated in hydrogen at 550° for 1 hr, then air-quenched to 25°. This procedure is abbreviated to (H,550q25). The purpose of cooling the sample rapidly to room temperature was to minimize the chemisorption of hydrogen that occurs at moderately elevated temperatures.

Apparatus. The flow system used is shown diagrammatically in Fig. 1. Hydrogen from a palladium–silver purifier was passed over a chromia/alumina catalyst converter at −196°, through a trap at −196° and into the Vycor reactor in which the catalyst
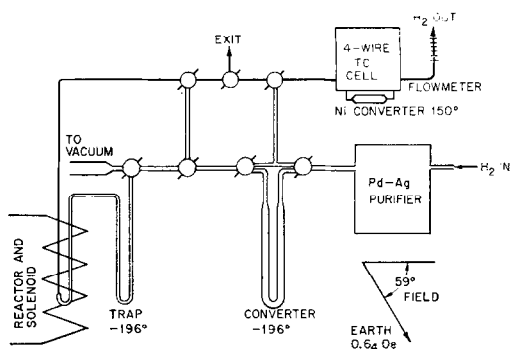

FIG. 1. Diagram of conversion rate apparatus.

sample was placed on a Vycor fritted disc. The hydrogen then flowed to a 4-wire thermal conductivity cell (Gow-Mac TR3 A, W-2), out through a nickel catalyst converter at 150°, back into the cell, and finally out through a flowmeter. Reactor temperatures were controlled from −196 to 600°. For measurements at −196° the chromia/alumina converter was bypassed, giving a 3:1 ortho–parahydrogen mixture instead of the 1:1 mixture used for measurements at room temperature.

For all samples it was considered necessary to maintain the degree of catalytic conversion at between 30 and 50% of complete conversion from 1:1 to the room temperature equilibrium 3:1 mixture. This was achieved for the self-supported samples by varying the hydrogen flow rate between 30 and 120 ml STP/min and also varying the mass of catalyst between 20 and 100 mg. For the lanthana-supported samples there was the additional necessity of minimizing the small but not negligible activity of the pure lanthana (4, 5). This was done by using a fixed mass of sample (1 g) but of varying the concentration of rare earth present between 0.1 and 0.5 wt % R$_2$O$_3$. These procedures were necessary because of both the wide variation in magnetic moment, effective as μ^2, in the several rare earths, but also because of the surprising variation in specific surface (from 2 to 5 m^2) in samples prepared by what seemed to be identical methods.

The magnetic field used for most of the measurements was produced by a 5000-turn solenoid, previously described (6).

This was mounted with the axis vertical which had the advantage of convenience although it was 31° from the angle at which the earth's field is a maximum. The solenoid was operated at up to 200 mA dc and produced, at its center, almost exactly 0.20 Oe/mA. The field was calibrated with an axial-probe Empire Scientific Co. Gaussmeter, itself calibrated at 92 Oe. The implications of the earth's field, which was not shielded, and of the use of ac instead of dc is described under Results. The few measurements reported for higher fields were made on similar apparatus but with the reactor mounted in the gap of a 12-in. electromagnet giving fields up to 18 kOe.

RESULTS

Specific rates, k, of conversion were calculated in the usual manner from the relation $k = (F/s) \ln[(C_{eq} - C_0)/(C_{eq} - C_x)]$ where F is the hydrogen flow rate (moles sec^{-1}); s, the total catalyst surface (cm^2) for self-supported samples. For the lanthana-supported samples, the effective surface of the paramagnetic oxide was estimated by assuming that for Dy_2O_3/La_2O_3 the specific rate was the same as for Dy_2O_3. This gave the not unreasonable results that in Dy_2O_3/La_2O_3 about 2% of the lanthana surface had been covered by Dy_2O_3 for the case in which the sample contained 0.1 wt % Dy_2O_3. C_{eq} is the equilibrium fractional concentration of O-H$_2$, C_0 the initial concentration, and C_x the emerging concentrations[2].

The values for k_0, the specific rates in the ambient laboratory magnetic field of about 0.6 Oe, were reproducible on different catalysts within a factor of five for the self-supported samples, part of this variation being due to uncertainties in the specific surfaces. For the lanthana-supported samples this problem was aggravated and it is doubtful if k_0 may be considered accurate to better than one order of magnitude. However, the purpose of this work was not to determine k_0, but rather to determine $\Delta k_H = (k_H - k_0)/k_0$ where k_H is the specific rate in a field H kOe. Determination of this fractional change depends on a differential measurement (field on and field off)

that can be completed in a few seconds with high reproducibility. Consequently Δk_H is believed to be accurate to ±5%. In some cases it was possible to detect a change in percentage conversion of from, say, 30.0% to 29.8%. The fields used were measured to ±0.5%. There was no detectable rate change for any sample in a field of 0.6 Oe as compared with zero field although, as described below, this does not mean that the earth's field is without influence.

Self-supported catalysts. Table 1 shows rate data for zero field conversion k_0, and for the fractional percentage change, $\Delta k_{0.04} \times 10^2$, observed at 40 Oe, all at 25°.

Figure 2, for self-supported Pr_2O_3, shows percentage conversion as a function of extrinsic field from 0 to 40 Oe. This plot is typical of all samples giving any rate change in a weak field although, as shown in Table 1, the magnitude of the change was not the same for all samples.

As described previously (2) all self-supported paramagnetic rare earths exhibit a large positive conversion rate change in strong extrinsic fields up to 18 kOe.

Lanthana-supported catalysts. The choice of lanthana as a diamagnetic support was dictated by its relatively low dissociative catalytic activity as compared with the

TABLE 1
WEAK FIELD MAGNETOCATALYTIC EFFECTS FOR THE RARE EARTHS

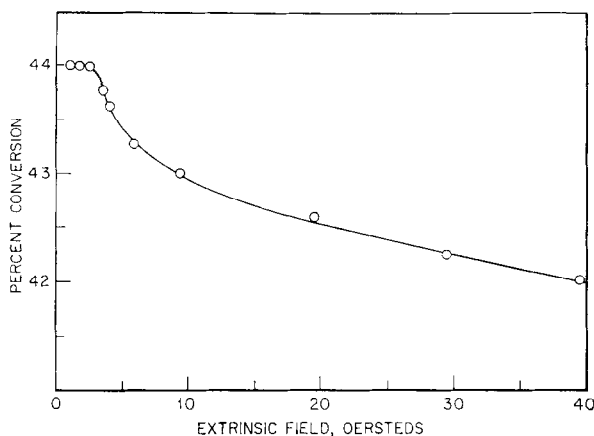|	Self-supported		Lanthana-supported	
R_2O_3	$k_0 \times 10^9$	$\Delta k_{0.04} \times 10^2$	$k_0 \times 10^9$	$\Delta k_{0.04} \times 10^2$
Pr_2O_3	3.6	−10		
Nd_2O_3	1.8	−2		
Sm_2O_3	0.25	−7		
Eu_2O_3	2.6	0	11.5	−24
Gd_2O_3	17.3	0	18.3	−3
Tb_2O_3	35.8	0	14.8	−31
Dy_2O_3	23.9	0	17.1	−23
Ho_2O_3	21.5	0		
Er_2O_3	20.5	0	13.6	−28
Tm_2O_3	11.3	0		
Yb_2O_3	2.2	−11	9.1	−26

FIG. 2. Percentage parahydrogen conversion as a function of magnetic field applied to the catalyst, Pr_2O_3, at 25°C.

more familiar alumina. But the activity of lanthana, whether due to lattice defects or to accidental impurities, is not negligible. Thus, 1 g of La_2O_3 pretreated $(H_2550q25)$ gave, at 25° and 80 ml of H_2 min^{-1} at 1 atm, 7% conversion that fell to 4.5% in a field of 40 Oe. This is less than 0.5% of the specific conversion rate produced by Gd_2O_3, but the preparation of a supported paramagnetic oxide at low surface concentration requires the use of a fairly large mass of support. An alternative would be to use a high area diamagnetic support, but this would introduce a host of complications from the dissociative activity present in such samples.

Table 1 also shows rate data for the zero field conversion, k_0, and the fractional percentage change, $\Delta k_{0.04} \times 10^2$, observed at 40 Oe for all lanthana-supported samples. These data have not been corrected for the activity shown by the lanthana support. Thus the value, -3%, shown for $\Delta k_{0.04}$ with respect to Gd_2O_3/La_2O_3 is actually less than that for pure La_2O_3. This suggests that, to a degree, the supported paramagnetic oxide had covered, and thus rendered inactive, some of the indigenous catalytic sites on the lanthana.

The results on Tb_2O_3/La_2O_3 were similar to those previously mentioned (2, 3) on a sample of 0.5 wt % Tb_2O_3/γ-Al_2O_3 9 years old (7), but considered more reliable because of the lower catalytic activity of

the lanthana as compared with high area alumina.

Figure 3 shows k_H as a function of (log) field from 1 to 1.8×10^4 Oe for Gd_2O_3/La_2O_3 for Er_2O_3/La_2O_3, and, for comparison, for self-supported Gd_2O_3. The Gd_2O_3/La_2O_3 behavior was unique among all samples studied. The Er_2O_3/La_2O_3 was typical of all lanthana-supported samples studied other than Gd_2O_3/La_2O_3. The self-supported Gd_2O_3 was typical of all self-supported samples, except Pr_3O_2, Nd_2O_3, Sm_2O_3, and Yb_2O_3.

Related results. The following several pieces of information were obtained incidentally to the main purposes of the work, described above.
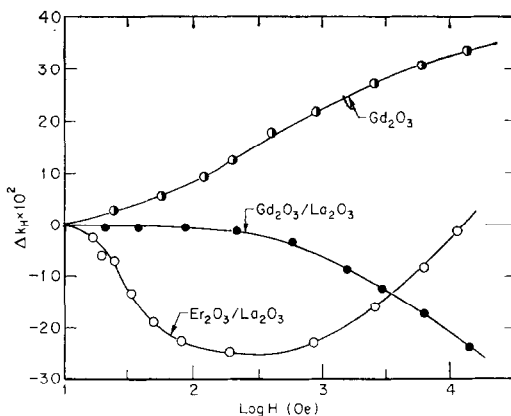

FIG. 3. Field dependences of conversion rates.

It has already been reported (2) that application to the catalyst of an extrinsic field up to 18 kOe causes no shift in the ortho–parahydrogen equilibrium at either 25 or −196°, that the high field effects observed for the para to ortho conversion also occur for ortho to para, and that the field causes no measurable change in the hydrogen flow rate (no "nuclear magnetic wind"). The same results were found for the catalysts and fields described in the present paper.

Decay of catalytic activity from surface transitions, or poisoning, rarely exceeded a few percent per hour at room temperature. In general, the rare earths proved to be less susceptible to decay of activity than had previously been observed for chromia similarly pretreated (8).

Alternating current at 60 Hz applied to the solenoid gave results similar to those reported for dc except that it required about 500 mA rms ac to produce the same change in catalytic activity as 200 mA dc. It might be thought that this implied some failure of the catalyst to utilize both halves of the ac cycle, but Fig. 2 shows that, as the current is rising, no effect may be expected until the magnetic field builds up to over 2 Oe, and field changes above 10 Oe have a diminishing effect. Consequently for each cycle an appreciable fraction of the time is wasted. The possibility of exploring the effect of increasing frequency appears to be hampered by the rapidly increasing impedance of the solenoid.

Changing the reactor temperature was briefly investigated for Pr_2O_3, Tb_2O_3, and Yb_2O_3. At −196° all three samples showed considerable loss of zero field activity (measured by the ortho to para reaction), and all three showed no change of activity in a field of 40 Oe. At temperatures moderately above 25°, all three samples showed a slow loss of activity followed by an increasingly sharp rise, owing to onset of the dissociative mechanism, above 250°. The loss in activity in a field of 40 Oe remained substantially the same until an appreciable fraction of the total activity became dissociative. It appears from these results that the low field effect, where

applicable, could be used for a simple test as to whether parahydrogen conversion is proceeding primarily by the magnetic or the dissociative mechanisms.

The possibility that the pretreatment (H₂550q25) might result in reduction of Eu^{3+} to Eu^{2+} and of Yb^{3+} to Yb^{2+} has been discussed (2). This question becomes more important when it is found (Table 1) that there is a large difference in the magnetocatalytic effects shown by Eu_2O_3 and Gd_2O_3, in the lanthana-supported form. Both self-supported rare earths show a large increase of activity in a field of 18 kOe, but Gd_2O_3/La_2O_3 does not show the loss of activity in 40 Oe that is found in Eu_2O_3/La_2O_3. Two considerations are important here: the maximum pretreatment temperature, and the gas to which the sample is exposed during pretreatment. There is little doubt that pretreatment (H₂650q25) yields a more active Eu_2O_3 than does (H₂550q25). This might be attributed to formation of Eu^{2+}, isoelectronic with Gd^{3+} and, of course, of higher effective magnetic moment. Substitution of evacuation for quenching in hydrogen, thus (H₂550ev25H₂) or (H₂650ev25H₂), also raised the activity somewhat over (H₂-550q25). The self-supported oxides Pr_2O_3, Gd_2O_3, Er_2O_3 and Tm_2O_3 showed little increase of zero field activity after the above special pretreatments. On the other hand, Yb_2O_3 showed increased activity which could not possibly be related to formation of the diamagnetic Yb^{2+}. For Eu_2O_3/La_2O_3 the more severe pretreatment conditions raised the zero field activity but did not change the loss of activity observed in 40 Oe, as, presumably, would have been the case if the europium ion had become isoelectronic with Gd^{3+}. The conclusion from this series of experiments is, therefore, that partial reduction of Eu_2O_3 on the surface *may* have occurred but it appears less probable for Eu_2O_3 supported on La_2O_3, the latter acting perhaps, by the valence-inductivity effect. The results give no evidence for surface reduction of Yb_2O_3 in any form.

All activity changes in the extrinsic field appeared to be reversible. Any change of

extrinsic field produced an abrupt change of catalytic activity (observed as soon as the hydrogen flow reached the thermal conductivity cell, in about 20 sec). But in every case the approach to a steady state was gradual, as if some form of hysteresis were operative. This was observed both with rising and falling extrinsic field. An indication of the slow approach to the steady state may be seen in Fig. 4. The peculiar effect was not so obvious at high fields because of the considerable time lag in rise or fall of the field in a large iron-cored electromagnet.

The catalytic response to the applied field appeared to be isotropic, as expected over a powder sample. The change in conversion rate for a given field was the same whether the field was applied transversely to the hydrogen flow direction, as for the 12-in. magnet, or parallel, as for the solenoid.
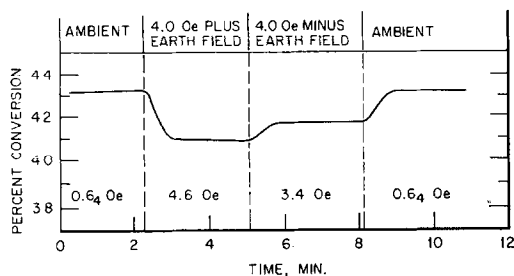

FIG. 4. Influence of the earth's magnetic field on conversion rate for Er_2O_3/La_2O_3.

Figure 2 shows a surprisingly abrupt dependence of conversion rate on field in the region of 3 to about 10 Oe, but not below 3 Oe and sharply decreasing above 10 Oe. Because of this behavior, it was possible to observe a change of conversion rate over several catalysts including Pr_2O_3, Eu_2O_3/La_2O_3, Tb_2O_3/La_2O_3, $Tb_2O_3/\gamma\text{-}Al_2O_3$, and Yb_2O_3 for a change in the extrinsic field of less than 0.2 Oe. Thus the presence of the earth's magnetic field ($\sim$0.6 Oe) was demonstrated by applying a fixed current sufficient to develop about 4.0 Oe approximately parallel to the earth's field (inclination angle 59°), then reversing the current in the solenoid. By this reversal the resultant field in which the catalyst was placed underwent a change of slightly over 1.0 Oe. The effect is shown, with Er_2O_3/La_2O_3 as the catalyst, in Fig. 4.

DISCUSSION

In summary of the results, reported here and previously (2), it may be said that all self-supported rare earths show a large positive change of catalytic conversion activity in strong magnetic fields, and that Pr_2O_3, Sm_2O_3, Yb_2O_3, and (to a lesser degree) Nd_2O_3, show a moderate negative change in weak fields. It may also be said that of six rare earths supported at low surface concentration on the diamagnetic lanthana, all but Gd_2O_3 show a negative change in a weak field, and little or no change in a strong field. This is true whether like Er_2O_3 they show no weak-field effect in the self-supported form or, like Yb_2O_3, they do. The system Gd_2O_3/La_2O_3 shows a large negative change in a strong field.

Whatever may be the reason(s) for these magnetocatalytic effects, it appears that the suggestion previously made (2), namely that the effects could be related to the field gradients established at the surfaces of paramagnetic particles in a field, is consistent with the changes observed when the active oxide is shifted from a paramagnetic support, as for Er_2O_3 on Er_2O_3, to a diamagnetic support, as for Er_2O_3 on La_2O_3. It appears from the peculiar behavior of Gd_2O_3 in the two forms, and in relation to the unique electronic configuration of of Gd^{3+}, that the weak-field magnetocatalytic effect may be the more fundamental of the two.

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