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# Parahydrogen Conversion and Magnetocatalytic Effects Over Yttria and Lutetia

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Yttria ($Y_2O_3$) and lutetia ($Lu_2O_3$) pretreated in hydrogen above 550°C become effective catalysts for the ortho-parahydrogen conversion by the magnetic mechanism. The source of activity in each case appears to be the paramagnetic 2+ ion, $Y^{2+}$ or $Lu^{2+}$. This view is supported by electron spin resonance measurements.

The rate of conversion is strongly influenced by a magnetic field of a few oersteds. Over lutetia a field of 40 Oe applied to the catalyst decreases the rate by 42%, and the presence of the Earth's field may readily be demonstrated. Some recent theoretical work is consistent with these magnetocatalytic results.

It has previously been reported (*1*) that the catalyzed parahydrogen conversion rate may, in some cases, be changed by application of a weak magnetic field to the catalyst. A field of 40 Oe decreases, by as much as 10%, the conversion rate at room temperature over the paramagnetic rare earths $Pr_2O_3$, $Nd_2O_3$, $Sm_2O_3$, and $Yb_2O_3$, but not over the paramagnetic rare earths $Eu_2O_3$, $Gd_2O_3$, $Tb_2O_3$, $Dy_2O_3$, $Ho_2O_3$, $Er_2O_3$, and $Tm_2O_3$. When the rare earths are supported at low surface concentration on $La_2O_3$ all, except $Gd_2O_3$, show the magnetocatalytic effect. In these experiments the conversion mechanism is magnetic—any dissociative mechanism contributing less than 1% to the observed rates under the experimental conditions.

The self-supported rare earths exhibiting a weak-field magnetocatalytic effect are those of lower magnetic susceptibility. The use of a diamagnetic support ($La_2O_3$) makes all but $Gd_2O_3$ capable of showing the effect, the exception being related, possibly, to the unique electronic configuration of the $Gd^{3+}$ ion. It appears, therefore, that a catalyst of high susceptibility generates an intrinsic field of intensity sufficient to obscure any change produced by an extrinsic field of a few oersteds. From this it follows that the magnetocatalytic effect in a weak extrinsic field would best be observed by inducing, by appropriate chemical pretreatment, a low concentration of active sites on the surface of an otherwise relatively inert diamagnetic solid. Such a procedure would be preferable to the preparation of a supported catalyst by impregnation from solution, or other standard procedure, because such methods inevitably yield degrees of surface aggregation rather than true dispersion.

It has been known for many years that properly pretreated alumina may catalyze the parahydrogen conversion. But any magnetic mechanism over $Al_2O_3$ is generally obscured at room temperature by the strong dissociative activity simultaneously generated. At low temperatures the dissociative activity becomes less but the magnetic conversion rate also becomes small. Another possibility is lanthana, but various pretreatments have failed to produce more than a slight conversion activity over this oxide. Still other possibilities include yttria and lutetia. The purpose of the present paper is to describe the development of high magnetic conversion activity, and of very large weak-field mag-

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netocatalytic effects over these two oxides. These oxides do not show the strong-field magnetocatalytic effect that may be observed over many paramagnetic substances (*2*,*3*).

## Experimental Methods

The rare earths were obtained from American Potash and Chemical Corp. and stated to be 99.9% pure with respect to other rare earths. To minimize carbonate impurity the samples were dissolved in nitric acid, then dried and ignited in air at 850°C overnight. Transfer of samples to the reactor was done with care to avoid needless exposure to the atmosphere. Pretreatments in the reactor are abbreviated as follows: ($H_2650q25$) means that the sample was heated for 1 hr in purified hydrogen at 650°C, then cooled rapidly to 25°C.

Catalytic conversion rates from the 1:1 toward the 3:1 o-$pH_2$ ratio were measured in apparatus previously described (1), (with the use of a 5000-turn solenoid for generating the field around the reactor up to 40 Oe, and a 12 in. electromagnet for fields to 18 kOe). Unless otherwise indicated all measurements were made in the ambient Earth's field of 0.64 Oe ($10^3 A\ m^{-1} = 4\pi$ Oe) which, alone, does not measurably affect the conversion rate. Hydrogen flow rates were in the neighborhood of 50 $cm^3\ min^{-1}$ at 1 atm (1 atm = 101 325 N $m^{-2}$).

Specific o-$H_2$ formation rates, $k_0$ (in zero field) and $k_H$ (in an extrinsic field H), 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, $S$ the total catalyst surface, $C_{eq}$ the equilibrium fractional concentration of o-$H_2$, $C_0$ the initial concentration, and $C_X$ the emerging concentration.

Specific surfaces were determined by the BET($N_2$) method.

Electron spin resonance measurements were made on a Varian V-4502 X-band instrument operating at 9.175 GHz, with 100 Hz field modulation. The quartz sample tube was designed for *in situ* flow-through pretreatment.

## Results

**Yttria.** Figure 1 shows typical specific rates of orthohydrogen formation (mol $s^{-1}$ $cm^{-2}$) at 25°C over a 500 mg sample of $Y_2O_3$ of specific surface 38 $m^2$, as a function of maximum pretreatment temperature $T$, in flowing hydrogen ($H_2Tq25$). As expected, the sample showed no dissociative catalytic activity (as measured by $H_2$–$D_2$ equilibration) below about 250°C. During the first heating the sample released water above 150°C and again above 500°C. In contrast to the case of chromia, similarly pretreated, there was no appreciable poisoning in hydrogen at any temperature. Alternate pretreatment, namely ($H_2550evac25H_2$) gave results almost identical with those shown in Fig. 1. A sample pretreated ($O_2550q25H_2$) was inert at room temperature but ($O_2550evac25H_2$) was moderately active as was ($O_2550He25H_2$).

Application of a magnetic field of up to 10 kOe to the yttria catalyst pretreated ($H_2700q25$) changed the conversion rate as shown in Fig. 2. There was no significant change in the fraction (%) rate change, $\Delta k = [(k_H - k_0)/k_0] \times 100$, with changing zero-field activity produced by raising the maximum pretreatment temperature.

A more detailed study of the field effect

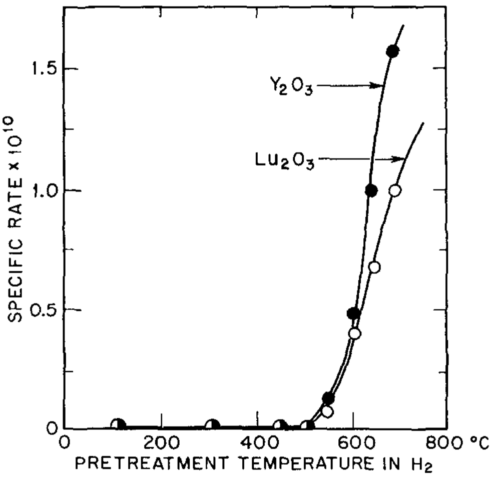

Fig. 1. Specific orthohydrogen formation rates at 25°C over yttria and lutetia, as a function of maximum pretreatment temperature in hydrogen.

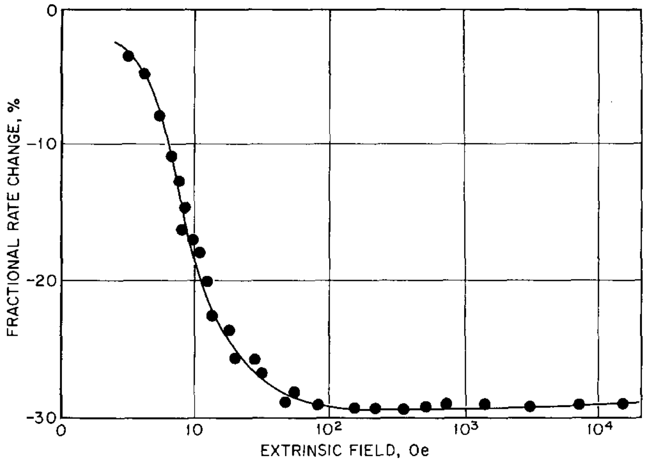

FIG. 2. Fractional (%) rate decrease, as a function of applied extrinsic field up to 10 kOe over yttria pretreated ($H_2650q25$). Measurements at 25°C.

from 0 to 40 Oe gave results much like those shown for lutetia in Fig. 5.

Measurements of catalytic activity and of field effect at 0° and at 65° gave results almost identical with those on the same sample and same pretreatment but measured at 25°. At −197° the activity (for the 3:1 to 1:1 conversion) was negligible.

The electron spin resonance results for yttria are shown in Fig. 3. The relative intensity of the line at g = 2.03 as a function of pretreatment temperature is shown in Fig. 4.

**Lutetia.** Figure 1 shows the rate of orthohydrogen formation at 25°C over a 500 mg sample of $Lu_2O_3$ of specific surface 52 m², as a function of maximum pretreatment temperature in flowing hydrogen. All results were similar to those described above for yttria, including those for modified pretreatment and other experimental conditions. The effect of an applied field of up to 40 Oe on the conversion rate over lutetia is shown in Fig. 5. Higher fields gave effects similar to those over yttria.

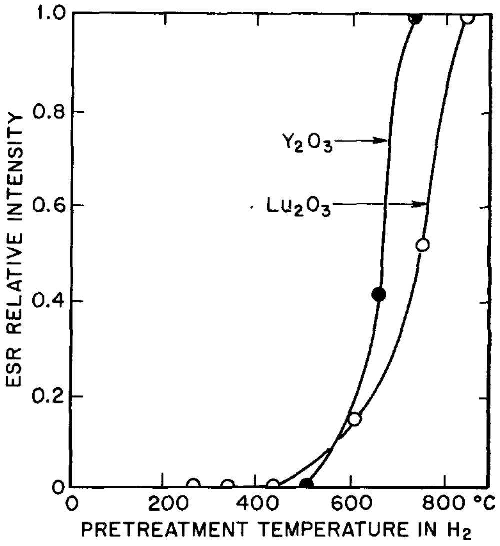

FIG. 4. ESR relative intensities for lines at $g = 2.03$ and $g = 2.04$ (est.) possibly attributable to $Y^{2+}$ and $Lu^{2+}$, respectively, as a function of maximum pretreatment temperature in hydrogen. Measurements at 25°C.

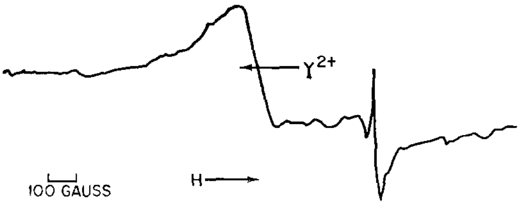

FIG. 3. ESR tracing for yttria pretreated ($H_2600q25$) showing a line at $g = 2.03$ possibly attributable to $Y^{2+}$. Measurement at 25°C.

The effect of a field of 40 Oe on the measured percent conversion rate (from 1:1 toward 3:1 $o\text{-}pH_2$) is shown in Fig. 6.

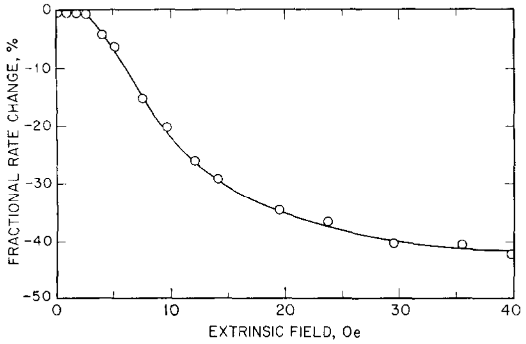

FIG. 5. Fractional (%) rate decrease, $\Delta k$, as a function of applied extrinsic field up to 40 Oe over lutetia pretreated ($H_2600q25$). Measurements at 25°C.

The slow approach to the new steady state, clearly visible in Fig. 6, was thought originally to show some kind of hysteresis. But this is now believed to be due to an artifact, namely a change in the concentration gradient profile as it moves from reactor to thermal conductivity cell. It appears, therefore, that the field effects observed are both reversible and instantaneous.

The electron spin resonance results for lutetia are shown in Figs. 4 and 7. The latter figure shows a typical spectrum in which two series of fine structure from $^{171}Lu$ (nuclear spin = 7/2) are observed. The major set (A) consists of eight lines, with separation of 87 G and an estimated *g* value of 2.04. The other set (B) consists of a continuous series of peaks, with 83 G separation.

The variation in relative intensity of the lutetia signals as a function of pretreatment in hydrogen is shown in Fig. 4.

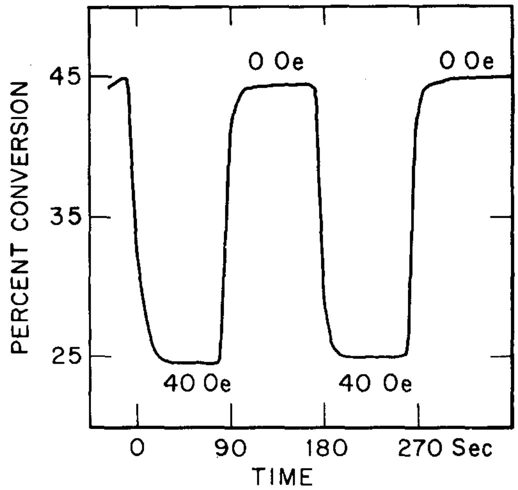

FIG. 6. Percentage conversion over lutetia pretreated ($H_2600q25$) and subject to a field of 40 Oe for 90 sec out of every 180 sec. Measurement at 25°C.

**The Earth's magnetic field.** Both yttria and, especially, lutetia pretreated as described above are suitable for showing the presence of the Earth's magnetic field as previously described (1) for lanthana-supported erbia. This is done by passing through the solenoid a current sufficient to generate a field of about 4 Oe but in the sense opposite to the Earth's field. Reversal of current through the solenoid then changes the resultant field from about 3.4 to 4.6 Oe. This change in field produces a readily measurable change of catalytic conversion rate. It is possible to measure the Earth's field by this method with an accuracy of about ±10%, with pretreated lutetia as catalyst.

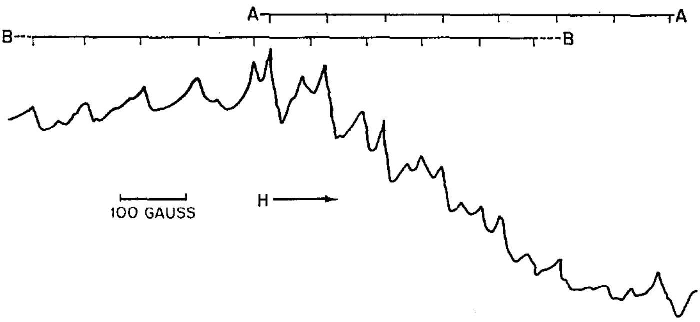

FIG. 7. ESR for lutetia pretreated ($H_2600q25$) showing two series of fine structure (A and B).

## DISCUSSION

It has been found that, by appropriate reductive pretreatment, the diamagnetic oxides yttria and lutetia may be converted to effective catalysts for the interconversion of para- and orthohydrogen. The activity so generated appears to be magnetic in mechanism and there is little or no dissociative activity in the room temperature region. Conversion rates over these oxides, thus activated, show a large depression if the reaction takes place in a magnetic field of a few oersteds. Over lutetia the loss is 42% in a field of 40 Oe.

For these effects to occur it would appear that the pretreatment must generate sites in a manner analogous to those often postulated for alumina similarly treated. These sites are restricted to the surface, and the bulk of the catalyst remains diamagnetic. According to the conventional, Wigner, theory the zero-field activity of such catalysts is proportional to the magnetic moment (squared) and to the surface concentration of a paramagnetic species. But it is clear from these results and those previously published (*1*) that the effect of an applied field on the catalytic activity is related to the magnetic susceptibility of the bulk catalyst. Thus $Dy_2O_3$ with a very high moment and a correspondingly high catalytic activity shows no weak-field effect. But $Dy_2O_3$ supported on $La_2O_3$ shows both a high zero-field activity and a large weak-field effect. The active sites generated on $Y_2O_3$ and on $Lu_2O_3$ show very large weak-field effects.

It has also been found that the surface concentration of active sites on $Y_2O_3$ and $Lu_2O_3$ may be changed at will by changing the maximum temperature of pretreatment. Below 550°C few such sites are generated, at 700°C the surface approaches saturation. It is also almost certain that the active sites are distributed at random over the surface and are not aggregated in the manner generally found for supported catalysts. It is possible to compare the surface concentration of catalyst sites in $Lu_2O_3$ with that in the isostructural but paramagnetic $Yb_2O_3$ by comparing the specific conversion rates in these two oxides and assuming that each active site in $Lu_2O_3$ contains only one unpaired electron. This comparison is done as follows: Let $k_{Lu}$ and $k_{Yb}$ be the specific conversion rates, respectively, for $Lu_2O_3$ and $Yb_2O_3$ pretreated in identical manner. The magnetic moment for the active surface sites in $Lu_2O_3$ is assumed to be 1.7 $\mu_B$ and that for $Yb^{3+}$ is known to be 4.5 $\mu_B$. ($Yb^{2+}$ is diamagnetic but there is no evidence that it is formed by the pretreatment used.) Let the surface concentration of active sites be $C_{Lu}$ and $C_{Yb}$. Then as the specific rates are proportional to surface concentration times magnetic moment squared, we have: $k_{Lu}/k_{Yb} = (1.7^2/4.5^2) \times C_{Lu}/C_{Yb}$. From earlier work (*2*) $k_{Yb} = 9.4 \times 10^{-10}$ mol s$^{-1}$cm$^{-2}$ and from the present work $k_{Lu}$ for a sample pretreated ($H_2650q25$) is $1.0 \times 10^{-10}$. Hence $C_{Lu} = 0.75C_{Yb}$. It appears, therefore, that the assumption of a lutetia site involving one unpaired electron (spin only) is not unrealistic.

It has often been suggested that the adsorptive and catalytic properties of $Al_2O_3$ in several forms may be related to the formation of $Al^{2+}$ ions during pretreatment with hydrogen at elevated temperatures (*4*), this suggestion being based on the certainty that the energetics on the surface of a solid are quite different from those in the bulk. A similar suggestion seems appropriate for $Y_2O_3$ and for $Lu_2O_3$ which are electronically similar outside the core. It is, therefore, suggested that the results described in this paper are related to the generation of $Y^{2+}$ and $Lu^{2+}$ ions and that these may be formed until virtually all $Y^{3+}$ and $Lu^{3+}$ ions normally present on the surfaces of the respective oxides have been so reduced. Such 2+ ions would have one unpaired electron. Whether there would be an orbital contribution to the magnetic moment cannot be answered with certainty, but analogy with $Ti^{3+}$ suggests that there would not. The ESR results confirm that paramagnetic species are formed on $Y_2O_3$ and on $Lu_2O_3$ by heat treatment in hydrogen above 500°C and that the species so formed are approximately linear in surface concentration with the observed catalytic specific conversion rates.

The only theoretical treatment of the magnetocatalytic effect to appear thus far is a very brief report from Petzinger and Scalapino (*5*). The effect is explained as being due to a field-induced decoupling of the nuclear spin states from the molecular rotation on the catalytic surface. This leads to the conclusion that an effect would be observed for an applied (extrinsic) field greater than the internuclear dipole field and that the catalytic conversion rate would be depressed. Both theoretical predictions are in qualitative agreement with experimental data presented here.

It must be pointed out that the assumption of a paramagnetic species such as $Al^{2+}$ on the surface of $Al_2O_3$ properly pretreated, has been challenged by Van Cauwelaert and Hall (*6*) who conclude that the rapid ortho–para conversion found over pure alumina dehydroxylated above 300°C is related to the strong electric fields emanating from the surface. If such is the case it is not inconceivable that an extrinsic magnetic field would alter the rotation of an adsorbed hydrogen molecule and thus affect the transition probability. (*7*). There is no obvious reason why such an explanation could not be extended to yttria and lutetia, but whether it would be applicable to both the positive strong-field magnetocatalytic effect shown by all paramagnetic solids (*2,3*) and to the negative weak-field effect, described in the present paper, remains obscure.

Both yttria and lutetia are thus seen to have hitherto unsuspected useful properties in surface studies, the latter having some advantages but being the more expensive. These properties are:

1. Value as diamagnetic diluents or solvents that are surprisingly inert unless heated in a reducing atmosphere above 500°C.
2. Formation, on simple pretreatment, of a surface layer of presumably paramagnetic sites in excellent dispersion and in readily controllable surface concentration.
3. Virtual freedom from dissociative catalytic activity near room temperature.
4. A weak-field catalytic effect (especially for lutetia) of such magnitude as to make possible precise measurements of the effect and its theoretical implications, including the influence of the Earth's magnetic field on the parahydrogen conversion rate.

## ACKNOWLEDGMENTS

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