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The Activation of Yttria, Lutetia, and Ytterbia for the *ortho–para*hydrogen Conversion

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The diamagnetic oxides Y_2O_3 and Lu_2O_3 may be activated for the p-H_2 conversion by heating them in H_2 between 823 and 973 K. This pretreatment appears to generate the ions Y^{2+} and Lu^{2+}, respectively. From the quantity of water formed during the activation it is possible to estimate the surface concentration of paramagnetic sites. By combining this information with the specific conversion rates it is possible to obtain the net conversion rate per active site. The results are in agreement, to about one order, with recent theoretical calculations of the absolute rates.

From conversion rate studies over Lu_2O_3 and Yb_2O_3 and from extrinsic field studies, it is concluded that heating Yb_2O_3 in H_2, and possibly other rare earths in the *C* crystallographic form, causes surface reactions resulting in a $4f^n5d^0 \rightarrow 4f^n5d^1$ electronic change rather than $4f^n5d^0 \rightarrow 4f^{n+1}5d^0$.

INTRODUCTION

In a previous paper (*1*) from this laboratory it was shown that yttria and lutetia, heated in hydrogen to 973 K become good catalysts for the *ortho-para*hydrogen conversion at room temperature. It was also shown that the conversion rate is diminished by applying to the catalyst a magnetic field not much stronger than that of the Earth. The conversion reaction in these cases occurs by the magnetic mechanism and not by the dissociative. This was shown by the negative temperature coefficient and the absence of measurable H_2–D_2 equilibration (below about 523 K). It was surmised that the active species was a paramagnetic ion, Y^{2+} or Lu^{2+}, produced by reduction of surface ions from the diamagnetic 3+ state with elimination of water. The possibility of paramagnetic atomic hydrogen in any form seemed unlikely because such a species would have caused H_2–D_2 equilibration. The paramagnetic O^- ion was eliminated by the method of pretreatment.

The purpose of the present work was to characterize the active sites more accurately and to measure the surface concentration of these sites. The method used was to obtain the quantity of water evolved per unit of catalyst surface during the activation process. In the course of the work it was found useful to extend the measurements to several rare earths other than lutetia, but all in the *C* crystallographic form. This in turn led to some hitherto unsuspected conclusions concerning the surface electronic structure of ytterbia subject to hydrogen pretreatment.

EXPERIMENTAL

Yttria and all rare earths used were obtained from Rare Earth Division American Potash and Chemical Corp., or from Kerr-McGee Chemical Corp. All samples were stated to be 99.9% pure with respect to other rare earths, with the exception of one yttria sample stated to be 99.9999% pure. To minimize carbonate impurity all samples were dissolved in redistilled nitric acid, then dried and ignited in air at 1123 K overnight. One sample of 99.9% yttria was

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ignited at 1373 K for the purpose of diminishing the specific surface. Work was not extended to rare earths unobtainable in the *C* crystallographic form or to neodymia for which the composition of the *C* form is uncertain (*2*).

Because surface migration of hydrogen occurs readily over alumina and certain other solids one sample of yttria was dissolved, prior to ignition, in HNO_3 to which $PdCl_2$ had been added to give a final palladium concentration of 0.1%. The purpose of this was to determine if catalyzed surface reduction of the Y_2O_3 could be observed. The result of this test was negative and no further consideration was given to the sample so prepared.

Water evolved during surface activation of the two diamagnetic oxides and identical pretreatment of the several paramagnetic rare earths was measured by thermal conductivity as the water was carried in hydrogen from the sample while the temperature was raised through the range, 823–973 K, necessary for activation. The apparatus was calibrated with pure CuO. The sample, weighing several grams, was placed in a Vycor tube fitted with a Vycor fritted disc and was heated in pure dry O_2 to 973 K for 1 hr. The sample was then cooled to 673 K at which temperature the O_2 was replaced by pure dry He. The temperature was further lowered to 298 K, the He was replaced by pure dry H_2, and the temperature was raised as shown in Fig. 1. The temperature was held at 973 K until water evolution became negligible. The H_2 STP flow rate throughout the experiment was 850 mm^3 s^{-1}. During the heat treatment in H_2, as shown in Fig. 1, a small quantity of water was evolved in the 623–773 K region but as this evolution was not associated with any development of catalytic activity it was ignored. During activation in the 823–973 K region the water evolution for a typical sample was about 1 mg and always corresponded to less than 0.1% of the total oxide ion content of the sample. Reproducibility for a given sample was better than ±1% and for different samples it was about ±5%. It is believed that this method for determining active site surface concentration for these samples is considerably more reliable than EPR measurement of the electron spin concentration. An example of the results obtained for Y_2O_3 is shown in Fig. 1.

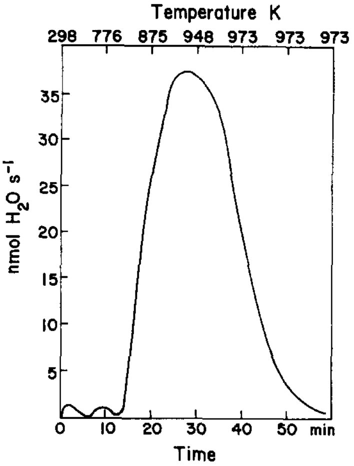

FIG. 1. Typical example of water evolution obtained by heating pretreated Y_2O_3 in H_2 to 973 K. Sample weight 2.3 g.

Other measurements including catalytic activity, extrinsic field effect, and (BET, N_2) specific surface measurements were done as previously described (*1*, *3*).

RESULTS

Results on water evolved from all samples are shown in Table 1. Except for the (6–9's)Y_2O_3 conversion rates for all samples have previously been published (*1*, *3*). The *o*-H_2 formation rate over the (6–9's)Y_2O_3 of surface 11.8 m^2g^{-1} and pretreated in H_2 at 973 K was found to be 17

TABLE 1

WATER EVOLVED DURING H_2 TREATMENT BETWEEN 823 AND 973 K

Sample	Purity	Specific surface (m^2 g^{-1})	Water (μmol m^{-2})
Y_2O_3	3–9's	13.0	1.5
Y_2O_3	3–9's	4.0	1.4
Y_2O_3	6–9's	11.8	~1.6
Lu_2O_3	3–9's	7.1	2.4
Yb_2O_3	3–9's	8.2	3.1
Gd_2O_3	3–9's	6.1	1.8
Eu_2O_3	3–9's	5.3	2.8

TABLE 2

p-H_2 CONVERSION RATES, k, AND FIELD EFFECT, Δk, AT 3.2 kA m^{-1}, OVER Yb_2O_3 AT 298 K

H_2 pretreatment (K)	k μmol s^{-1} m^{-2}	$\Delta k \times 10^2$
823	2.2	−10
873	5.1	−10
923	8.2	−7
973	14.2	−1

μmol s^{-1} m^{-2} at atmospheric pressure and 298 K. This is only somewhat larger than the value 1.6 μmol s^{-1} m^{-2} previously reported for (3–9's)Y_2O_3 of comparable specific surface. The extrinsic field effect on the (6–9's) sample gave a fractional rate change of −0.30 at 3.2 kA m^{-1} (or 40 Oe). This is the same as previously reported for the (3–9's) sample.

Conversion rates and extrinsic field effects as a function of pretreatment temperature in H_2 for ytterbia are given in Table 2. All rates were measured at 298 K, field effects at 3.2 kA m^{-1}. The specific surface of this Yb_2O_3 sample was 5.6 m^2 g^{-1}.

DISCUSSION

The discussion consists of two parts. These are, first, the nature and surface concentration of the active conversion sites generated by heating Y_2O_3 and Lu_2O_3 in H_2 above 823 K and, second, the electronic configuration of the sites generated on the surface of Yb_2O_3, and possibly of other rare earths, by similar pretreatment.

From the method by which they are prepared and from the nature of the catalytic activity generated it appears that paramagnetic sites must be formed on the surfaces and that these are Y^{2+} and Lu^{2+} from Y_2O_3 and Lu_2O_3, respectively. The underlying electronic levels being filled for both Y^{3+} and Lu^{3+} it seems most probable that a $4d$ electron and a $5d$ electron are, respectively, inserted in the two diamagnetic ions. This could occur by one or both of the following reactions:

$$2Y^{3+} + O^{2-} + H_2 \rightarrow 2Y^{2+} + H_2O$$

$$2Y^{3+} + 2OH^- + H_2 \rightarrow 2Y^{2+} + 2H_2O.$$

A third reaction that may occur:

$$Y^{3+} + 2OH^- \rightarrow Y^{3+} + O^{2-} + H_2O$$

would not generate a paramagnetic site. Eley *et al.* (*4*) have shown that Nd_2O_3 outgassed at 823 K still contains 1.05×10^{18} OH^- m^{-2} on the surface. Nevertheless, the fact that the Y_2O_3 and Lu_2O_3 were heated to 1123 K in air, and then again to 973 K in the reactor in O_2, suggests that the first reaction written above is the most probable. In this case two paramagnetic sites are generated for every molecule of water evolved in the 823–973 K temperature range.

For Y_2O_3 in samples of different specific surfaces and different purities the experimental results for water evolution are in excellent agreement, averaging 1.5 μmol m^{-2} or 9.0×10^{17} molecules m^{-2}. For Gd_2O_3 the results are essentially the same, and for Lu_2O_3 only slightly larger. Somewhat larger results for Eu_2O_3 and Yb_2O_3 have an explanation that will be discussed later. These results, and especially those for Y_2O_3, show that the effect described is a true surface effect and that it is not influenced by impurities in the maximum range present on the surface or in the bulk.

There have been few comparable studies on the rare earths and apparently none on yttria and lutetia. Barrett and Barry (*5*) have measured the sorption of hydrogen and of oxygen on Eu_2O_3 (and on Nd_2O_3). From their data it is possible to estimate the quantity of water generated by a procedure involving heating in O_2 at 1073 K, evacuating, and measuring the H_2 taken up at 823 K. For a sample of Eu_2O_3 of specific surface 4.3 m^2 g^{-1} this gives 9.4 μmol m^{-2} of H_2O formed. More recently Ross and Delgass (*6*) have obtained a value of 3.2 μmol m^{-2} from Eu_2O_3 supported on η-Al_2O_3 and by somewhat lower H_2 reduction temperature. It cannot be said with certainty that the differences between these results are significant.

There is another method, based on crystal structure, by which the number of active sites may be estimated. For the C crystallographic form (Fig. 2) there are eight R^{3+} ions at the corners of a cube and

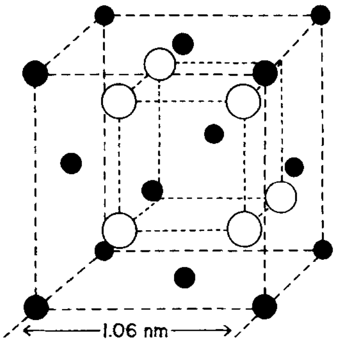

FIG. 2. Rare earth C structure subcell.

six more at the face centers. The O^{2-} ions are also arranged at the corners of a cube smaller than, and inside, the R^{3+} cube. But as only 6 O^{2-} ions are needed for every 4 R^{3+} ions two of the O^{2-} ion positions are vacant. These vacancies lie alternately on a face diagonal or on a body diagonal and are thus not the same vacancies for all cells defined in this way. The unit length of the cell face $a = 1.06$ nm for Y_2O_3 and 1.04 nm for Lu_2O_3. (Most authorities point out that the true unit cell actually contains 16 R_2O_3 groups, rather than the 2 such groups implied here.)

If 2 R^{3+} ions must be reduced to R^{2+} for each O^{2-} ion removed and if, as seems probable, no more than 1 O^{2-} may be removed from the 6 O^{2-} normally coordinated to any 1 R^{3+}, then it seems unlikely that more than one surface O^{2-} could be removed from any one unit cell face such as the 010 defined as above. For Y_2O_3, therefore, the number of O^{2-} ions removable is $1/(1.06 \times 10^{-9}\ \mathrm{m})^2 = 9 \times 10^{17}\ \mathrm{m}^{-2}$. This is equivalent to a maximum of 1.5 μmol m^{-2} of water that could be generated. For Lu_2O_3 the result is essentially the same. Some further evidence that these estimates of active site concentration are of the proper order has already been found *(1)* by comparing the specific conversion activity of pretreated Lu_2O_3 with that of Yb_2O_3. Corrected for the probable difference in atomic magnetic moments of the respective sites, these two oxides give specific activities equal within a factor of two.

The specific conversion rate previously reported *(1)* for Y_2O_3 preheated in H_2 at 973 K and measured at 298 K was 1.6 μmol $\mathrm{s}^{-1}\ \mathrm{m}^{-2}$. For Lu_2O_3 similarly pretreated the rate was 1.0 μmol $\mathrm{s}^{-1}\ \mathrm{m}^{-2}$. These values correspond to 9.6×10^{17} molecules $\mathrm{s}^{-1}\ \mathrm{m}^{-2}$ for Y_2O_3 and 6.0×10^{17} for Lu_2O_3. If the number of active sites generated is twice the number of water molecules evolved, then the net conversion is $(9.6 \times 10^{17}$ molecules $\mathrm{s}^{-1}\ \mathrm{m}^{-2})/(2 \times 9 \times 10^{17}) = 0.5$ molecules s^{-1} per site for Y_2O_3 and 0.13 for Lu_2O_3.

Petzinger and Scalapino *(7)* have derived, from theory, expressions for the parahydrogen conversion rate over dilute, random surface sites and also for surfaces with the regular, dense lattice of sites. Yttria and lutetia, activated as described, appear to fit the concept of providing a surface containing paramagnetic sites sufficiently diluted so that each site separately affects molecules of hydrogen in its vicinity, although we cannot definitely exclude the possibility that the paramagnetic sites occur in pairs. It is by no means clear that this requirement can be met by any other catalyst system.

The basis for comparison of theory and experiment is found in Petzinger and Scalapino's Eq. (74) from which the net number of molecular conversions per surface site per second may, in principle, be found. It is necessary to make estimates concerning relative fractional surface coverages and some details of mechanism but, using the widest reasonable values, we reach the conclusion that the theoretical net number of conversions lies within one or at most two orders of the experimental.

We turn now to consideration of the electronic structure of the surface atoms present in paramagnetic rare earths isostructural with lutetia and subject to the same pretreatment at elevated temperature in hydrogen. If H_2 at 973 K produces the change $Lu^{3+}4f^{14}5d^0 \rightarrow Lu^{2+}4f^{14}5d^1$ it might be supposed that the isostructural Yb_2O_3 would undergo a similar change, namely, $Yb^{3+}4f^{13}5d^0 \rightarrow Yb^{2+}4f^{13}5d^1$. It is, however, established beyond question *(8)* that the Yb^{2+} ion in $YbSO_4$ and $YbCl_2$ is diamagnetic, or that it has possibly a temperature-independent paramagnetic susceptibility less than 2% that of the Yb^{3+} ion at room temperature. Schieber (9) lists Yb^{2+} in the monoxide, YbO, as having the S_0 ground state.

Various rare earth sesquioxides strongly heated show some increase in specific o-pH_2 conversion activity (*3, 4*) . This is generally thought to be due to progressive elimination of water formed by condensation of surface OH^- groups. But ytterbia is unique among the rare earths in that the usual product of reduction has zero moment. If normal Yb^{2+} is formed on the surface of Yb_2O_3 then H_2 treatment at 973 K should render it substantially less active catalytically. But Table 2 shows that a large increase of activity actually occurs. It may be concluded, therefore, that either the Yb^{3+} ion is not reduced to Yb^{2+} ion under these conditions or that the Yb^{2+} ion so formed has an electronic configuration different from that of the normal Yb^{2+} ion. The first alternative is improbable in view of the strong activity generated in Lu_2O_3 by identical pretreatment. We conclude, therefore, that the electronic configuration of surface-active Yb^{2+} is probably $4f^{13}5d^1$ and not $4f^{14}5d^0$.

The idea in the preceding paragraph has been discussed by Moeller (*10*). The ground state $4f^{n-1}5d^16s^2$ differs so little in energy from $4f^n6s^2$, compared with terms significant in any chemical reaction, that they are normally of little importance. But this is not necessarily the case for the *ortho-para*hydrogen conversion proceeding by the magnetic mechanism.

Some further support for the view that there may actually be some increase in the total magnetic moment of Yb_2O_3 strongly heated in hydrogen is found in the decrease of the extrinsic field effect at 3.2 kA m^{-1} as the pretreatment temperature is raised, as shown in Table 2. It has already been established (*1, 3*) that the negative extrinsic field effect observed at weak fields is found only at relatively low paramagnetic site densities such as occur over solids of moderate to low susceptibility, over most paramagnetic solids supported at low concentration on diamagnetic solids, and, most impressively, on sites generated by pretreatment of diamagnetic solids such as Y_2O_3 and Lu_2O_3.

The occurrence of this unique electron distribution in the surface ytterbium atoms may not be restricted to this rare earth. There is no obvious reason why it should not occur for all the rare earths or, at least, for all that form the *C* crystallographic structure. But the relatively small fractional change in moment between 3+ and 2+ ions for all except Yb_2O_3 would make it difficult to detect any such effect.

It will be noticed that the water evolution in the 823–973 K region is about the same for all rare earths studied except that it is moderately larger for Yb_2O_3 and for Eu_2O_3. These are the only two rare earths containing ions that are fairly readily reducible. It may be concluded that for these two oxides superficial reduction to the 2+ state proceeds to a moderate degree below the true surface.

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