

Extrinsic Field Effect and Absolute *para*-Hydrogen Conversion Rate on Lutetia

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Absolute nondissociative *para*-hydrogen conversion rates have been measured on activated lutetia. A rate change averaging -50% was found when the catalyst was placed in a magnetic field of 40 Oe. In the temperature region of 300 K and at pressures of 2 to 8 $\text{kN}\cdot\text{m}^{-2}$, the rate data are most nearly consistent with a vibrational mechanism. No major change in mechanism, as compared with that on the paramagnetic rare earths, has been found on Lu_2O_3 .

INTRODUCTION

The nondissociative *para*-hydrogen conversion rate shows several magnetocatalytic effects involving an extrinsic field. By magnetocatalytic effect is meant a change of catalyzed reaction rate caused by a field generated externally or internally. An extrinsic field is one coming from the outside. One magnetocatalytic effect is observed on catalysts of high electron spin density (1, 2). All such solids show exchange interactions leading to magnetic phase transitions at sufficiently low temperature. In the paramagnetic phase such catalysts show large positive magnetocatalytic effects for extrinsic fields in the 10 kOe region. (A field of 1 Oe is the same as $79.6 \text{ A}\cdot\text{m}^{-1}$). An example of a catalyst showing a large positive field effect is Dy_2O_3 (2), but almost all paramagnetic rare earths supported at low surface concentration on a diamagnetic solid such as Dy_2O_3 on La_2O_3 show a weak field effect (3, 4) of negative sign in fields of a few oersteds. Some rare earths, of which Nd_2O_3 is one, show both effects.

Absolute conversion rates, k_m , over Nd_2O_3 have been measured by Eley *et al.* (5) for extrinsic fields up to 2.1 kOe, which is at

the lower end of the high field region. These authors obtained the interesting result that while, at 273 K and $10^3 \text{ N}\cdot\text{m}^{-2}$, the *para*-hydrogen conversion rate is increased 16% or more in a field of 2.1 kOe, the *ortho*-deuterium rate is decreased by about the same fraction.

The purpose of the present work was to extend absolute conversion rate measurements to the weak field effect for *para*-hydrogen. It was also hoped that this information might provide a clue toward understanding the mechanism of the effect. As the weak field effect is best observed on solids of very low electron spin density it was decided to use activated Lu_2O_3 as the catalyst. This diamagnetic oxide was chosen because it shows the largest fractional decrease, in a field of 40 Oe, of any thus far investigated (6, 7).

EXPERIMENTAL

Catalyst. Lutetia was obtained from Rare Earth Division, American Potash and Chemical Corp., and stated to be 99.9% pure with respect to other rare earths. To minimize carbonate impurity (which could be reduced to catalytically active carbon

during the activation process) the Lu₂O₃ was dissolved in redistilled nitric acid, dried, and then ignited in air at 1123 K overnight. It was then transferred to the reactor with minimum exposure to air. Activation of the Lu₂O₃ consisted of heating it in purified hydrogen at 823 K for about 1 hr, rapid cooling to room temperature, and evacuation. The specific surface of the Lu₂O₃ was 52 m²·g⁻¹ (BET, N₂).

Reactor assembly. The apparatus was essentially the static reactor system with micro-Pirani gauge as developed by Bolland and Melville (8) and adapted for the present purpose by Ashmead *et al.* (9). Hydrogen was passed through a palladium-silver purifier and then into an activated charcoal converter at 77 K to obtain 1:1 *o*:*p*-H₂. The catalyst was placed on a Vycor fritted disc in a Vycor reactor of 170 cm³ capacity. A 5000-turn solenoid generated a field around the reactor up to 40 Oe. Details of the field control have been described (4). The reactor was held at the required temperature within ±0.1 K.

Procedure and analysis. Hydrogen of 1:1 *o*:*p*-H₂ ratio was admitted to the activated catalyst at pressures and temperatures shown in Table 1. From time to time samples were removed for analysis. The gauge, containing a spiral tungsten filament, had a volume of about 70 mm³ and was operated at a pressure of 6.7 kN·m⁻². The "constant voltage-variable resistance" method was used for calibration and for analysis. It

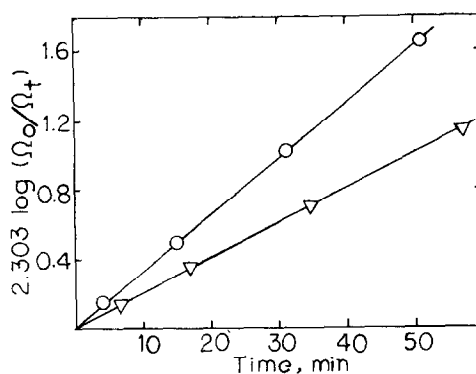


FIG. 1. Plots of $2.303 \log(\Omega_0/\Omega_t)$ against time (pressure 4.0 kN·m⁻², temperature 301.6 K) for *p*-H₂ conversion rates on Lu₂O₃. O, Zero field; Δ, 40 Oe.

was possible to estimate the *p*-H₂ concentration in the sample to ±0.2%.

RESULTS

The conversion kinetics proved, as expected from Eley's early work (10), to be first order. The rate constants were, therefore, calculated in the usual manner from the expression:

$$k_e = (2.303/t) \log (\Omega_0/\Omega_t)$$

where *t* is the time, Ω₀ the gauge resistance difference for 3:1 *o*:*p*-H₂ and 1:1 *o*:*p*-H₂, and Ω_{*t*} the resistance difference for 3:1 and that of the sample (introduced as 1:1) after *t* seconds in the reactor.

Figure 1 shows $2.303 \log(\Omega_0/\Omega_t)$ vs *t* at a temperature of 301.6 K for both zero field (except for the ambient Earth's field, ~0.6 Oe, which is without effect on the conversion rate) and for a field of 40 Oe. From these and similar data the rate constants, *k_e*, were obtained for several temperatures and pressures. Absolute rates, *k_m*, were calculated by multiplying *k_e* by the number of molecules in the reactor per unit of catalyst surface. For all runs the catalyst surface was 48 m².

Fractional changes of *k_m* caused by the extrinsic field were calculated as follows: $\Delta k_m = (k_{m(H)} - k_{m(O)})/k_{m(O)}$, where *k_m*(H)

TABLE 1

Absolute Conversion Rates, *k_m*(O), and Extrinsic Field Effects, *k_m*(H) and Δ*k_m*(H) at 40 Oe

Temperature K	Pressure (kN·m ⁻²)	<i>k_m</i> (O) × 10 ⁻¹⁴ N(H ₂)·m ⁻² ·s ⁻¹	<i>k_m</i> (H) × 10 ⁻¹⁴ N(H ₂)·m ⁻² ·s ⁻¹	Δ <i>k_m</i> (H)
343	2.4	1.48	0.72	-0.5
323	2.4	3.26	1.11	-0.7
301.6	2.4	5.14	2.20	-0.6
301.6	4.0	12.6	7.73	-0.4
301.6	5.9	13.1	8.60	-0.3
301.6	8.6	18.1	11.2	-0.4

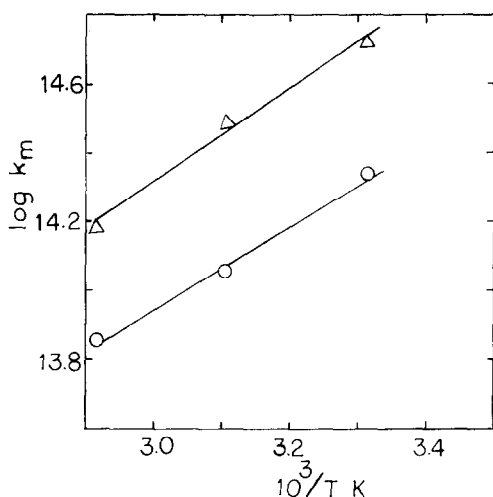


FIG. 2. Arrhenius plots of $\log k_m$ against reciprocal temperature (pressure $2.4 \text{ kN} \cdot \text{m}^{-2}$). Δ , Zero field; O , 40 Oe.

and $k_{m(0)}$ are the absolute rates in fields of 40 Oe and zero, respectively. All results are given in Table 1. Absolute rates are given in molecules per unit surface per second.

DISCUSSION

There appear to be no previous absolute conversion rate measurements on Lu_2O_3 . Rossington and Capozzi (11) have reported that the chemically similar oxide Y_2O_3 gives a rate of $2.9 \times 10^{16} \text{ N}(\text{H}_2) \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in the 298–418 K temperature region. This is considerably larger than the rate over Lu_2O_3 reported in the present paper, but the catalyst and pretreatment conditions are not strictly comparable.

Figure 2 shows Arrhenius plots of $\log k_m$ vs reciprocal temperature from which apparent activation energies may be calculated. These are $-26 \text{ kJ} \cdot \text{mol}^{-1}$ for the conversion in zero extrinsic field and $-24 \text{ kJ} \cdot \text{mol}^{-1}$ for that in a field of 40 Oe. The value in zero field may be compared with $-8.0 \text{ kJ} \cdot \text{mol}^{-1}$ found by Rossington and Capozzi on Y_2O_3 . It is doubtful if any significance may be attached to the small difference in negative activation energy for

the conversion with and without the extrinsic field. An estimate of the surface fraction active for conversion, made as described by Rossington and Capozzi for Y_2O_3 , yielded a fraction of 0.01 for Lu_2O_3 . This is consistent with approximations made by other methods (7). An attempt to compare theoretical and experimental mechanisms gave the following results: collisional $k_m = 2.0 \times 10^{10} \text{ N}(\text{H}_2) \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, vibrational 3.5×10^{13} , and experimental 5.1×10^{14} . The Bohr magneton number used for Lu_2O_3 in these calculations was 1.7. (Some justification for this choice is given in Ref. 7.) The present results favor the vibrational mechanism as was the case for Y_2O_3 (11).

An understanding of the several extrinsic field effects is hampered by our failure to identify, thus far, the sites of activity in Lu_2O_3 and Y_2O_3 . Nevertheless some potentially useful conclusions may be drawn from the work described. First, the mechanism of the zero field conversion cannot be very different, on Lu_2O_3 and Y_2O_3 , from that on the paramagnetic rare earths in which the catalytic site is easily identified. Second, there is no indication that the conversion mechanism changes appreciably on application of the magnetic field. There is considerable evidence to show that the active sites associated with a decrease of conversion rate at low extrinsic field are different from those associated with an increase at higher field. This latter behavior is found on the paramagnetic rare earths and on numerous other catalysts. Some of the evidence mentioned will be summarized. Some catalysts show large positive field effects but no trace of negative effect (in the paramagnetic phase). Some catalysts show fairly large negative field effects but no trace of positive effect. Some catalysts show both positive and negative effects. The positive effect is generally saturated at about 10 kOe, but the negative effect is saturated below 0.1 kOe.

If there is indeed a kind of catalytic site present in activated Lu₂O₃ (and Y₂O₃) that is different from those found in the paramagnetic rare earths then it is appropriate to speculate concerning the nature of such sites. There is ESR evidence (6) that a paramagnetic site is generated during activation. Nuclear magnetism might conceivably be responsible for the activity in Lu₂O₃ but it is much less probable in Y₂O₃. The various species that have been suggested for conversion activity on Al₂O₃, such as H₂⁺ and O⁻, would themselves react chemically with H₂ at room temperature. In view of this the most probable species on Lu₂O₃ appears to be the ion Lu²⁺ generated through addition of an electron to the 5*d*, or to the 6*s*, level during the activation process. But the manner in which the conversion rate may be changed by application of a magnetic field not much larger than that of the Earth remains obscure.

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