Extrinsic Magnetic Field Effect on Parahydrogen and Orthodeuterium Conversion Catalysed by Neodymium Oxide

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Summary A magnetic field of 2·1 kOe increases the rate of parahydrogen conversion, but decreases the rate of orthodeuterium conversion at 10^3 N m^{-2} on Nd_2O_3 at 273 and 540 K; since the effect with parahydrogen was only observed when Nd_2O_3 was outgassed at 673 K, it appears to be sensitive to the extent of surface dehydration.

THE effect of an extrinsic magnetic field on the rate of parahydrogen conversion on metal oxide surfaces has been investigated by Selwood.[1-3] The effect occurred for both para to ortho and ortho to para conversions, and the position of equilibrium was unaffected by a magnetic field. With Nd_2O_3 at 298 K, a field of 0·04 kOe decreased the activity,[3] whereas a field of 18 kOe increased the activity.[2]

We have determined the absolute rate, k_m, of parahydrogen and orthodeuterium conversion at 77, 273, and 540 K, and of H_2–D_2 equilibration at 273 and 540 K on a 150 mg sample of Nd_2O_3, 4·74 m^{2}g^{-1}, previously outgassed at 673 K for 150 h. Measurements were made at 10^3 N m^{-2} using a technique previously described.[4] The effect of a magnetic field of 2·1 kOe upon k_m was determined for all reactions except H_2–D_2 at 273 K, where the half life of *ca.* 12 h precluded the continuous use of the electromagnet. The mean of at least four determinations of k_m are given in the Table; the data for 77 K are omitted since no extrinsic field effect was detected at this temperature. The results are consistent with Selwood's findings,[2] but add the important result that the activity for orthodeuterium conversion is decreased by a magnetic field which increased the activity for parahydrogen conversion. The results for H_2–D_2 equilibration, which proceeds by a chemical mechanism insensitive to magnetic fields, show that a physical mechanism for conversion predominates at 273 K and that there is a considerable contribution from a chemical mechanism at 540 K.

TABLE. *Absolute rates of reaction at* 10^3 N m^{-2}

Temperature (K)	Reaction	$k_m \times 10^{-17}$ H = 0·0 kOe (molecules m^{-2} s^{-1})	$k_m \times 10^{17}$ H = 2·1 kOe (molecules m^{-2} s^{-1})	$[k_m(2{\cdot}1) - k_m(0)]/k_m(0)$
273	pH_2	2·92 ± 0·03	3·39 ± 0·03	+0·16 ± 0·02
	oD_2	3·47 ± 0·05	2·87 ± 0·03	−0·17 ± 0·02
	H_2–D_2	0·016[a]	—	—
540	pH_2	3·07 ± 0·02	3·17 ± 0·02	+0·03 ± 0·01
	oD_2	2·46 ± 0·02	2·09 ± 0·02	−0·15 ± 0·02
	H_2–D_2	1·54 ± 0·05	1·54 ± 0·05	0·00 ± 0·06

[a] Single determination.

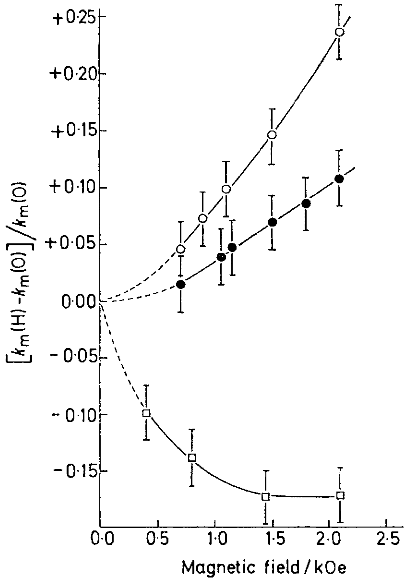

FIGURE. *Extrinsic field effect on* Nd_2O_3 *as a function of field strength:* ○ *parahydrogen conversion on oxide outgassed at* 673 K *for* 30 h, ● *parahydrogen conversion on oxide outgassed at* 673 K for 150 h, □ *orthodeuterium conversion on oxide outgassed at* 673 K *for* 150 h.

The Figure shows the fractional change in activity $\{[k_m(H) - k_m(0)]/k_m(0)\}$, determined as a function of field strength for both parahydrogen and orthodeuterium conversion at 273 K. The form of the plots differs, with the effect on orthodeuterium conversion reaching apparent saturation at *ca.* 1·5 kOe; a decrease in the rate of parahydrogen conversion at low fields[3] may also contribute to the difference. Since the magnitude of the field effect for parahydrogen conversion differed between samples outgassed for 30 and 150 h at 673 K, the influence of sample pretreatment was further investigated. For 150 mg samples of Nd_2O_3 outgassed for 150 h at 573, 673, 748, and 823 K, only oxide outgassed at 673 K exhibited a detectable field effect for parahydrogen conversion at 273 K and 2·1 kOe. Deuterium exchange showed that the concentration of surface hydroxy-groups on Nd_2O_3 falls progressively with increasing outgassing temperature, with $1{\cdot}17 \times 10^{19}$, $4{\cdot}52 \times 10^{18}$, and $1{\cdot}05 \times 10^{18}$ OH m^{-2} remaining on 1·0 g samples after outgassing for 150 h at 673, 748, and 823 K. We conclude that the extrinsic magnetic field effect depends upon the extent of surface dehydration of Nd_2O_3.

To explain our results, it is necessary to consider other factors than changes in surface paramagnetism brought about by the presence of extrinsic magnetic fields.[2,3] Electrostatic fields may govern both the direction of molecular approach to, and the efficiency of,[5] the paramagnetic centres. In this connection, it is relevant that deuterium possesses a nuclear electric quadrupole moment not present in hydrogen and the surface electrostatic field is sensitive to the extent of surface dehydration. Progress with such an explanation, where magnetic and electrostatic effects are closely linked, must await both experimental and theoretical developments.

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