JOURNAL OF CATALYSIS 34, 35–40 (1974)

Parahydrogen Conversion on Neodymium and Dysprosium Oxides

D. D. ELEY, H. FORREST AND R. RUDHAM

Chemistry Department, University of Nottingham, Nottingham NG7 2RD, England

Received December 4, 1973

Parahydrogen conversion has been investigated on Nd_2O_3 and Dy_2O_3 between 77 K and the outgassing temperature. The activity at all temperatures increases with sample outgassing temperature due to improved surface cleanliness.

At temperatures above 400 K a chemical mechanism for conversion predominates, whereas below 400 K conversion proceeds by a paramagnetic physical mechanism. Comparative measurements of parahydrogen and orthodeuterium conversion on Nd_2O_3 between 77 and 273 K assist in the interpretation of low temperature activity, and suggest that orthodeuterium conversion is augmented by nuclear quadrupole–electrostatic field interaction.

INTRODUCTION

Parahydrogen conversion and hydrogen–deuterium equilibration on neodymium, gadolinium, dysprosium and erbium oxides have been investigated over the temperature range 77–657 K (*1*, *2*). At low temperatures (<140 K), where the equilibration reaction was absent, conversion proceeds by a paramagnetic physical mechanism. At high temperatures (>400 K), where rates of conversion and equilibration were similar, both reactions proceed by the same chemical mechanism. At intermediate temperatures the activity for conversion passed through a maximum at ~260 K. Since the activity for conversion was many times greater than that for equilibration the mechanism was taken as being of the physical type. Dysprosium oxide was an exception, showing no maximum for conversion at intermediate temperatures. In these investigations the oxide samples had been vacuum outgassed for 150 hr at 673 K. This pretreatment was selected since it gave reproducible activity for parahydrogen conversion on neodymium oxide at 77 K (*1*), and since further outgassing, or treatment with hydrogen, at higher temperatures had no significant effect upon this activity (*2*).

In contrast to the apparent insensitivity of catalytic activity to outgassing pretreatment, an extrinsic magnetic field effect on parahydrogen conversion at 273 K was only observed for neodymium oxide following vacuum outgassing at 673 K (*3*). Since the concentration of surface hydroxyl groups on neodymium oxide fell progressively with increasing outgassing temperature (*3*), it was concluded that the extrinsic field effect depended upon the extent of surface dehydration. Presently we report an investigation of the effects of varying outgassing temperature, and hence surface dehydration, on the activity of neodymium and dysprosium oxides for parahydrogen conversion between 77 and 823 K.

EXPERIMENTAL METHODS

The apparatus has been described (*1*), but the incorporation of an ion gauge permitted more accurate monitoring of the vacua during sample outgassing than was previously possible. Absolute reaction rates (molecules m^{-2} s^{-1}), k_m, and values of the kinetic order with respect to hydrogen pressure, n, were determined by methods previously described (*1*, *2*). The oxides used were of Specpure grade supplied by Johnson, Matthey and Co. The Nd_2O_3 (4.74 m^2 g^{-1}) was identical to that used in experiments on the extrinsic magnetic field effect (*3*), and the Dy_2O_3 (2.96 $m^2\ g^{-1}$) was identical to that used in earlier kinetic measurements (*2*). X-Ray powder diffraction of samples outgassed at 673 K showed that both oxides possessed the type-C structure.

RESULTS AND DISCUSSION

Neodymium Oxide

Three 150 mg samples of Nd_2O_3 were outgassed at 573, 673 and 823 K, respectively, for 150 hr at a pressure of 10^{-4} N m^{-2}. The activity of each sample for parahydrogen conversion at 10^3 N m^{-2} was then determined between 77 K and the outgassing temperature, first for increasing and then for decreasing temperature sequences. Good agreement was obtained between these two series of measurements, and the results obtained over increasing temperatures are shown in Fig. 1 as Arrhenius plots of the absolute rate k_m. It is evident that the activity at all temperatures increases with outgassing temperature, which is in agreement with the observation that the concentration of surface hydroxyl groups also fell with outgassing temperature (*3*). The results obtained for the sample outgassed at 673 K are in reasonable agreement with those previously obtained for a sample of higher specific surface area outgassed at the same temperature (*1*).

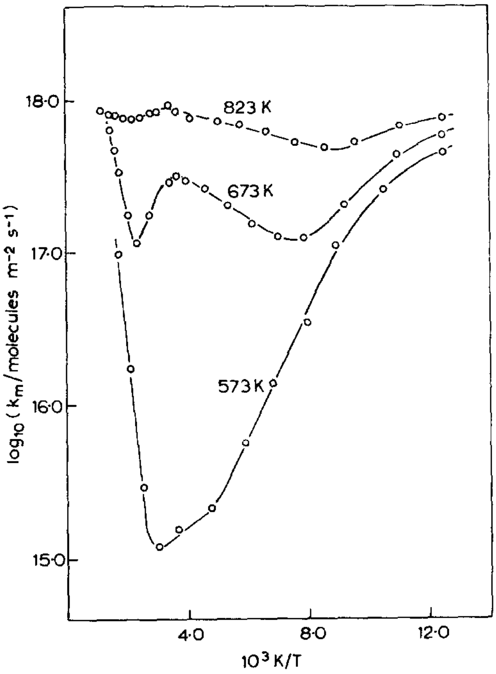

FIG. 1. Arrhenius plots for parahydrogen conversion at 10^3 N m^{-2} on Nd_2O_3 outgassed at 573, 673 and 823 K.

The dependence of activity upon outgassing is least pronounced at low reaction temperatures, and this offers an explanation for the previous failure to observe an effect upon the activity at 77 K (*2*). Such a suggestion is reinforced by the possibility of sintering occurring in the earlier work due to the higher outgassing temperatures used. The peak in activity previously found at intermediate temperatures (*1*) is sensitive to outgassing temperature, with a well-defined peak only being observed for the sample outgassed at 673 K. With the sample outgassed at 823 K the peak exists, but is partially masked by the increased and extended activity from the low and high temperature ranges. A much greater contribution to the overall activity from the mechanisms associated with these temperature ranges provides an explanation for the failure to observe an extrinsic magnetic field effect at 273 K for Nd_2O_3 outgassed at temperatures above 673 K (*3*). Only at high temperatures (>400 K) are the Arrhenius plots linear over an extended range of temperature. Where this is so the temperature dependence of k_m can be represented by $k_m = k_m{}^0 \exp(-E_a/RT)$, and values of the preexponential factor $k_m{}^0$ and the apparent activation energy E_a are given in Table 1. For Nd_2O_3 outgassed at 673 K an extrinsic magnetic field effect has been observed for parahydrogen conversion at 540 K, but not for hydrogen–deuterium equilibration at the same temperature (*3*). In addition, the rates of parahydrogen conversion, orthodeuterium conversion and hydrogen–deuterium equilibration at 540 K have been found to decrease in the sequence $pH_2 > oD_2 > H_2 + D_2$. For any chemical mechanism the effect of zero-point energy on the activation energy

TABLE 1

Parahydrogen Conversion at High Temperatures on Nd_2O_3 and Dy_2O_3

Oxide	Outgassing temp (K)	$\log_{10} k_m^0$ (molecules m^{-2} s^{-1})	E_a (kJ mol^{-1})	Temp range (K)
Nd_2O_3	573	20.3	37	398–568
	673	19.3	19	427–667
	823	18.0	1.6	525–823
Dy_2O_3	573	20.2	36	435–566
	623	20.2	36	473–621
	673	19.8	28	540–671
	748	19.9	19	563–748
	823	19.0	3.8	558–823

(*4, 5*) results in the rate sequence $pH_2 > H_2 + D_2 > oD_2$, whereas for a physical mechanism the rate sequence is $pH_2 > oD_2 \gg H_2 + D_2 = 0$. It follows that the high temperature activity contains an appreciable contribution from a physical mechanism in addition to conversion by a chemical mechanism. The decrease in both k_m^0 and E_a with increasing outgassing temperature suggests that this contribution increases with the increasing cleanliness of the Nd_2O_3 surface.

To investigate further the low temperature activity, measurements of the rates of both parahydrogen and orthodeuterium conversion have been made at 10^3 N m^{-2} between 77 and 273 K on a single 150 mg sample of Nd_2O_3 outgassed for 150 hr at 673 K. The Arrhenius plots in Fig. 2 show that the activity for the two reactions is closely similar, the greatest divergence in rates being at 135 K where $k_m(pH_2)/k_m(oD_2)$ equals 1.6. The kinetic order with respect to pressure, n, was measured for both reactions at 77, 96 and 273 K, and the values at 10^3 N m^{-2} are given in Fig. 2. These values are indicative of reaction taking place under conditions approaching catalyst saturation, whereas the hydrogen uptake only constitutes $\sim 1\%$ of a physically adsorbed monolayer at these temperatures and pressures (*1, 2*). As in earlier work (*1, 2, 6*), we conclude that the majority of conversion proceeds by the vibrational mechanism on strongly adsorbing paramagnetic sites. If both reactions proceed by this mechanism, the theoretically predicted value of the ratio $k_m(pH_2)/k_m(oD_2)$ is $2.8\theta_{H_2}/\theta_{D_2}$ at 77 K, increasing to $5.1\theta_{H_2}/\theta_{D_2}$ at 273 K (*7*). Since $n = (1 - \theta)$ over a limited pressure range (*8*) we can use values of n to determine θ_{H_2} and θ_{D_2}, and hence values for the ratio of 3.3 at 77 K and 4.4 at 273 K. Experimental values of the ratio of absolute rates are generally less than those predicted from theory (*5, 7, 9*), and the present values of 1.28 at 77 K and 0.81 at 273 K are no exception. Such discrepancies can be accounted for if orthodeuterium conversion is augmented by the effect of an inhomogeneous electric field at the solid sur-

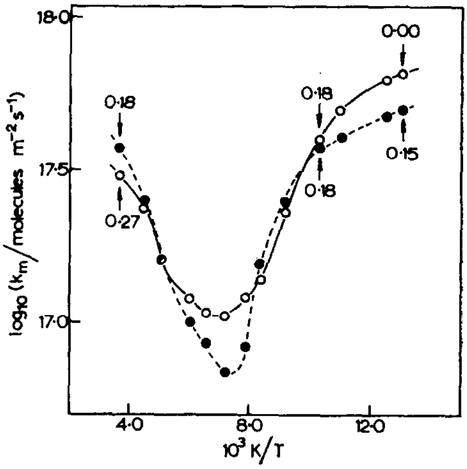

Fig. 2. Arrhenius plots for parahydrogen (○—) and orthodeuterium (●- -) conversion at 10^3 N m^{-2} on Nd_2O_3 outgassed at 673 K.

face operating on the electric quadrupole moment of the deuteron, which cannot occur with the proton which has no quadrupole moment (*9*, *10*).

An alternative to increasing the outgassing temperature as a means of increasing the activity of Nd_2O_3 would be to increase the pumping speed and ultimate vacuum achieved in the system. Since this was impracticable, experiments using smaller samples were made in order that the interparticulate pore volume and thus the ambient pressure over the sample during outgassing were reduced. Four samples of Nd_2O_3 were outgassed for 150 hr at 673 K, and their activity for parahydrogen conversion at 77 K was subsequently measured as a function of pressure. From the data given in Table 2 it is evident that both k_m and n at 10^3 N m^{-2} increase as the sample weight decreases, confirming that increased activity is associated with increased surface cleanliness. The results also indicate the error that would be introduced in attempting to relate the activities presently observed for 150 mg samples with surface hydroxyl concentrations previously obtained (*3*) with 1 g samples outgassed at the same temperatures. In addition to exposing more Nd^{3+} ions active in paramagnetic conversion, the further removal of hydroxyl groups will increase the electrostatic field at the oxide surface. In this connection it is relevant that for an 8 mg sample of Nd_2O_3 outgassed for 150 hr at 673 K the value of $k_m(pH_2)/k_m(oD_2)$ at 5×10^2 N m^{-2} was less than unity at both 77 and 273 K; values of k_m and the ratio are given in Table 3. The proportionately greater increase in the activity for orthodeuterium conversion following the reduction in sample weight may be taken as evidence for the operation of an electrostatic field–nuclear quadrupole mechanism. However, to account for the low temperature activity of alumina for conversion reactions, Van Cauwelaert and Hall (*11*) have suggested that the influence of the electrostatic fields at exposed cations is such that both parahydrogen and orthodeuterium conversion are affected. This could occur either by the field ionization of H_2 to H_2^+ and D_2 to D_2^+ such that they

TABLE 2
THE EFFECT OF SAMPLE WEIGHT ON THE ACTIVITY OF Nd_2O_3 FOR PARAHYDROGEN CONVERSION AT 77 K AND 10^3 N m^{-2}

Sample (mg)	k_m (molecules m^{-2} s^{-1})	n
12	5.4×10^{18}	0.29
35	9.6×10^{17}	0.16
154	6.4×10^{17}	0.00
170	6.2×10^{17}	0.00

TABLE 3
PARAHYDROGEN AND ORTHODEUTERIUM CONVERSION ON 8 mg OF Nd_2O_3 AT 5×10^2 N m^{-2}

Temp (K)	$k_m(pH_2)$ (molecules m^{-2} s^{-1})	$k_m(oD_2)$ (molecules m^{-2} s^{-1})	$k_m(pH_2)/k_m(oD_2)$
77	4.5×10^{18}	1.7×10^{19}	0.26
273	4.3×10^{17}	6.2×10^{17}	0.69

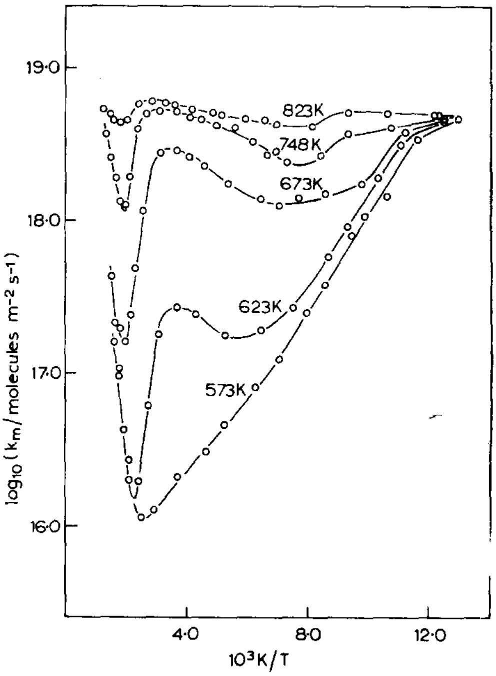

FIG. 3. Arrhenius plots for parahydrogen conversion at 10^3 N m^{-2} on Dy_2O_3 outgassed at 573, 623, 673, 748 and 823 K.

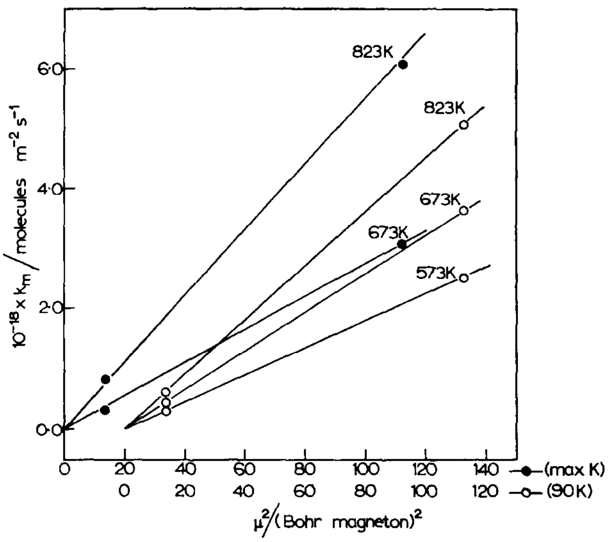

FIG. 4. Plots of k_m at 10^3 N m^{-2} against μ^2: k_m at 90 K (○—) k_m at intermediate maxima (●—).

are self converting, or by increasing the Wigner transition probability (*12*) by reducing the energy difference between nuclear spin levels. In view of the substantial evidence showing the dependence of the activity for low temperature parahydrogen conversion upon the magnetic properties of the surface sites (*2*, *6*, *13*, and references therein) the latter suggestion seems the more likely. Experiments using a well-defined paramagnetic species supported on surfaces of different polarity should assist in verifying the suggestion, but, even then, it is doubtful if electrostatic factors could be unambiguously separated from geometric factors in such measurements.

Dysprosium Oxide

Experiments with Dy_2O_3 were limited to an investigation of the effects of outgassing temperature on the activity for parahydrogen conversion at 10^3 N m^{-2}. Five 32 mg samples were outgassed for 150 hr at 573, 623, 673, 748 and 823 K, and the subsequent activity of each sample was found to be similar over increasing and decreasing temperature sequences between 77 K and the outgassing temperature. The Arrhenius plots of k_m, given in Fig. 3, show that the activity increases with outgassing temperature, and that the maximum in activity at intermediate temperatures is found for all samples except that outgassed at 573 K. No maximum was previously observed with Dy_2O_3 outgassed at 673 K (*2*), and we ascribe its appearance in the present work to improved vacuum conditions giving a cleaner surface. A maximum in activity at intermediate temperatures can now be taken as normal behavior for thoroughly outgassed rare earth oxides possessing the type-C structure.

The results for Dy_2O_3 are closely similar to those obtained for Nd_2O_3, apart from the generally higher activity which necessitated the use of lower weight samples. At high temperatures the Arrhenius plots are linear over an extended temperature range, and values of k_m^0 and E_a are given in Table 1. The decrease in E_a with increasing outgassing temperature supports the suggestion made for Nd_2O_3, that the contribution to high temperature activity from a physical mechanism increases with surface cleanliness.

Catalytic Activity and Magnetic Properties

Detailed mechanisms for the paramagnetic conversion of parahydrogen (*1*, *14*, *15*) have been developed from Wigner's original theory (*12*), and in each of these the rate of conversion is proportional to μ^2, the square of the magnetic moment of the paramagnetic center. With rare earth oxides outgassed at 673 K plots of k_m at 5.3×10^2 N m^{-2} against μ^2 were linear for data obtained at 90 K and for the maximum activities achieved at intermediate temperatures (*2*). Similar linear plots were obtained for rare earth ions in X zeolites using values of k_m obtained at 77 and 90 K at a pressure of 9.3×10^2 N m^{-2} (*13*). The plots either passed through the origin (*2*), or through the activity for zeolite free from rare earth ions (*13*). Following this earlier work, we have plotted k_m against μ^2 for 90 K and for the maximum k_m achieved at intermediate temperatures. Accepting that the plots pass through the origin, Fig. 4 shows that good straight lines are obtained and that their slopes increase with increasing outgassing temperature. The plots are further evidence for the earlier conclusion (*2*) that conversion occurs by a paramagnetic mechanism at both low and intermediate temperatures, and also show that this holds for surfaces outgassed at temperatures other than 673 K. The applicability of a paramagnetic mechanism at intermediate temperatures is also supported by the constancy of the ratio k_0/μ^2 at 298 K, where k_0 is the absolute rate in mole cm^{-2} s^{-1}, found by Selwood (*16*) for 11 rare earth oxides following activation in hydrogen at 823 K.

If the surface layers of rare earth oxides became nonstoichiometric from the loss of oxygen during outgassing, electron transfer would affect the surface paramagnetism by generating cations of valency less than three. The stability of trivalent rare earth ions, the linearity of the plots in Fig. 4, and the values of k_0/μ^2 obtained by Selwood (*16*), indicate that surface nonstoichiometry is not the source of the increase in activity with increasing outgassing temperature. We ascribe the increase to the further exposure of trivalent rare earth ions in positions of high adsorption potential by the progressive elimination of surface hydroxyl groups as molecular water under conditions of improved vacuum or higher temperature.

ACKNOWLEDGMENT

The authors thank the Science Research Council for a studentship held by H.F.

REFERENCES

1. ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *Trans. Faraday Soc.* **59,** 207 (1963).
2. ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *J. Catal.* 3, 280 (1964).
3. ELEY, D. D., FORREST, H., PEARCE, D. R., AND RUDHAM, R., *J. C. S. Chem. Commun.* 1176 (1972).
4. FAJANS, E., *Z. Phys. Chem., Abt. B* **23,** 239 (1935).
5. ELEY, D. D., AND NORTON, P. R., *Discuss. Faraday Soc.* **41,** 135 (1966).
6. PEARCE, D. R., RICHARDSON, P. C., AND RUDHAM, R., *Proc. Roy. Soc., Ser. A* **310,** 121 (1969).
7. BROWN, D. E., ELEY, D. D., AND RUDHAM, R., *J. Catal.* **16,** 292 (1970).
8. ELEY, D. D., *Nature (London)* **194,** 1076 (1962).
9. ELEY, D. D., AND NORTON, P. R., *Z. Phys. Chem. N.F.* **64,** 145 (1969).
10. KALCKAR, F., AND TELLER, E., *Proc. Roy. Soc., Ser. A* **150,** 520 (1935).
11. VAN CAUWELAERT, F. H., AND HALL, W. K., *Trans. Faraday Soc.* **66,** 454 (1970).
12. WIGNER, E., *Z. Phys. Chem., Abt. B* **23,** 28 (1933).
13. BROWN, D. E., ELEY, D. D., AND RUDHAM, R., *J. Catal.* **29,** 246 (1973).
14. HARRISON, L. G., AND MCDOWELL, C. A., *Proc. Roy. Soc., Ser. A* **220,** 77 (1953).
15. SANDLER, Y. L., *Can. J. Chem.* **32,** 249 (1954).
16. SELWOOD, P. W., *J. Catal.* **19,** 353 (1970).