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Parahydrogen Conversion on X Zeolites

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Parahydrogen conversion catalysed by X zeolites containing Na^+, H^+, and rare earth ions has been investigated over the temperature range 77–610 K. At low temperatures, conversion proceeds by a physical mechanism in which the activity is determined by rare earth ions and paramagnetic impurities. At 77 and 90 K it has been shown that the activity at 7 Torr varies with the square of the magnetic moment of the rare earth ion, demonstrating the applicability of Wigner's theory to physical conversion within zeolites. At high temperatures, conversion proceeds by a chemical mechanism which is associated with the alumino-silicate framework of the zeolite.

INTRODUCTION

Parahydrogen conversion and hydrogen–deuterium equilibration have been investigated on NaY zeolites and NaY zeolites which were decationated following exchange of sodium for ammonium ions (*1*, *2*). The same reactions have also been investigated on A zeolite and A zeolite containing neodymium ions (*3*). With NaY zeolite (*1*, *2*) it was found that the activity for hydrogen–deuterium equilibration at 298 K was similar to that for parahydrogen conversion and increased with increasing decationization. Since the concentration of active centers was considerably less than that of decationated sites, the reaction was considered to proceed chemically either at a combination of decationated sites in close proximity or at impurities located near decationated sites. The activity for parahydrogen conversion at 77 K was independent of the extent of decationization, and was considered to proceed physically at paramagnetic impurities. With A zeolites measurements of catalytic activity were made over a wide temperature range, 77–605 K, and were divisible into high and low-temperature ranges (*3*). At high temperatures, where activities for parahydrogen conversion and hydrogen–deuterium equilibration were comparable, reaction proceeds by a chemical mechanism. At low temperatures, where activities for parahydrogen conversion and orthodeuterium conversion were comparable and hydrogen–deuterium equilibration was immeasurable, reaction proceeds by a physical mechanism in which the activity is determined by paramagnetic impurities and neodymium ions. The main difference between the NaY and A zeolites lies in the effects of exposure to hydrogen. With the NaY zeolites (*2*) hydrogen treatment destroyed their activity for both parahydrogen conversion and hydrogen–deuterium equilibration at 298 K, but left the activity for parahydrogen conversion at 77 K unaffected. With A zeolites (*3*) hydrogen treatment at elevated temperatures had no effect on the activity for parahydrogen conversion at 77 K, little effect at 298 K, but caused pronounced activation for reaction at higher temperatures.

The present paper reports an investigation of parahydrogen conversion on X zeolites prepared from 13X molecular sieve by ion-exchange with protons and rare earth ions. The same amount of ion-exchange, outgassing procedure and reaction conditions used for A zeolites (*3*) were maintained, in order that the results from the two types of zeolite could be compared.

EXPERIMENTAL

All seven catalysts were prepared from Linde 13X molecular sieve in powder form, from the identical lot (No. 2898700) used to prepare sieve catalysts containing transition metal ions (*4, 5*). The catalysts were as follows:

1. 13X sieve which had been contacted with distilled water for 16 hr at 25°C, filtered, washed with distilled water and dried in an oven at 403 K for 24 hr.

2. 13X sieve in which 22% of the sodium ion content had been exchanged for protons by the progressive reduction of pH (*4*). The sieve was then washed and dried as with catalyst 1.

3-6. 13X sieve in which 22% of the sodium ion content had been exchanged for protons and ~15% of the sodium ion content exchanged for Nd^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+}, respectively. Ion exchange was brought about by contacting the sieve, after pH reduction, with an aqueous solution of the appropriate chloride (*4*) such that the final rare earth ion content after washing and drying was identical to that used in A zeolite (*3*), 2.04×10^{-4} g ion per g of sieve.

X-ray powder photographs of catalysts 1, 2, and 3, and of a sample of catalyst 3 outgassed for 48 hr at 623 K and treated with hydrogen at that temperature, were effectively identical. Calculated *d*-values for the more intense low angle lines were in close agreement with those for 13X sieve (*6*).

The same apparatus was used as in the investigation of A zeolites (*3*), and prior to measurements of either catalysis or adsorption, zeolite samples were given the same outgassing pretreatment: 14 hours at 623 K and $\sim 10^{-6}$ Torr (1 Torr = 133.3 N m^{-2}). Since it was shown with A zeolites (*3*) that the preferential adsorption of orthohydrogen had no measurable effect on the kinetics of parahydrogen conversion, measurements were restricted to those of parahydrogen depletion using hydrogen which had previously been equilibrated at 21 K. The first order rate constants k_e are given by

$$k_e = \frac{1}{t} \ln \frac{x_0 - x_e}{x_0 - x_t}, \text{ sec}^{-1},$$

where x_0, x_t and x_e are the fractions of parahydrogen present at times zero, t and equilibrium respectively. Absolute rates of reaction k_m, expressed on a mass basis, are given by

$$k_m = k_e cp/m, \text{ molecules mg}^{-1} \text{ sec}^{-1},$$

where c is the number of molecules in the reaction volume at unit pressure, p the experimental pressure and m the mass of catalyst in milligrams.

RESULTS

The Effect of Temperature

The effect of temperature on the rate of parahydrogen conversion has been determined on catalysts, 1, 2, and 3 at numerous temperatures between 77 and 610 K, first at increasing temperatures and then at decreasing temperatures on the same sample. Arrhenius plots for k_m at a pressure of 7 Torr are shown in Figs. 1-3 for catalysts 1-3, respectively. The major difference be-

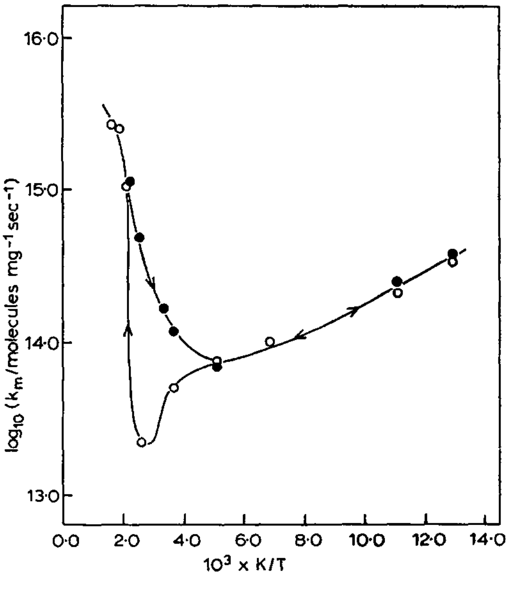

FIG. 1. Arrhenius plot for parahydrogen conversion on catalyst 1 at a pressure of 7.0 Torr: —○— increasing temperatures, —●— decreasing temperatures.

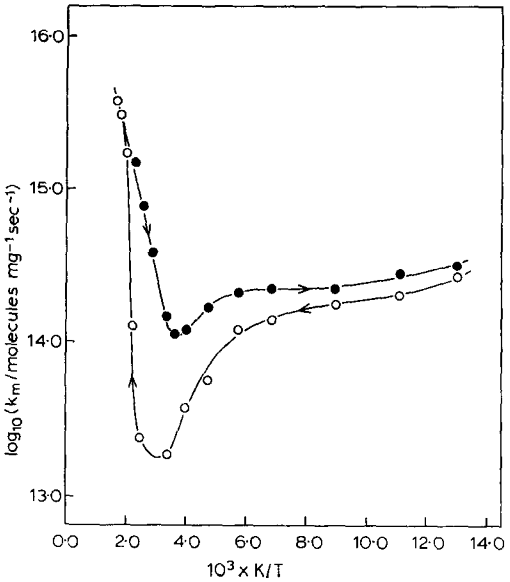

FIG. 2. Arrhenius plot for parahydrogen conversion on catalyst 2 at a pressure of 7.0 Torr: —○— increasing temperatures, —●— decreasing temperatures.

tween the catalysts is at low temperatures, where the neodymium ions in catalyst 3 greatly increase the activity over that of catalysts 1 and 2. To show this clearly the Arrhenius plots for catalysts 1 and 2 at increasing temperatures up to 435 K are shown in Fig. 3. Above this temperature the activities become closely similar and cannot be distinguished on an Arrhenius plot of the present scale. For temperatures increasing from 435 to 530 K the activity of all three catalysts can be expressed by $k_m = 3.9 \times 10^{26} \exp(-13{,}000/T)$ molecules mg^{-1} sec^{-1}, although k_m becomes less temperature dependent above 530 K.

Exposure to hydrogen during reactions at high temperatures activates all three catalysts for reaction at temperatures greater than ~270 K, and the closely similar activities at decreasing temperatures between 518 and 295 K can be expressed by $k_m = 1.5 \times 10^{17} \exp(-2{,}000/T)$ molecules mg^{-1} sec^{-1}. For reaction at temperatures below ~270 K differing effects were observed; catalyst 1 was unaffected, catalyst 2 was activated and catalyst 3 was poisoned between 233 and 90 K. The poisoning of catalyst 3 was reversible, since the activities at three decreasing temperatures (296, 195 and 146 K) after evacuation at 603 K for 36 hr were closely similar to those previously obtained at increasing temperatures following the original outgassing.

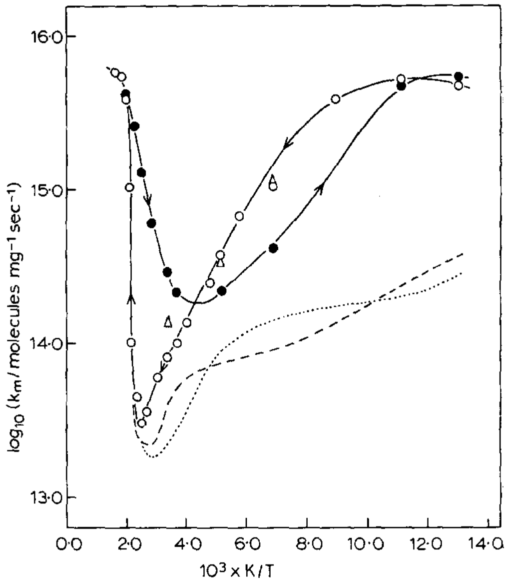

FIG. 3. Arrhenius plot for parahydrogen conversion on catalyst 3 at a pressure of 7.0 Torr: —○— increasing temperatures, —●— decreasing temperatures, —△— decreasing temperatures after outgassing at 603 K for 36 hr, - - - catalyst 1 increasing temperatures, ... catalyst 2 increasing temperatures.

With catalysts 4, 5, and 6, activities for parahydrogen conversion were only determined at 77 and 90 K, and the values of k_m obtained, together with those for catalysts 1, 2, and 3 and A zeolites (*3*), are given in Table 1.

The Effect of Pressure

The pressure dependence of the rate of parahydrogen conversion was measured over the range 2–30 Torr at a number of temperatures for catalysts 1–3. In all cases the effect was described by

$$k_m = k_1 p^n,$$

where n is the kinetic order with respect to pressure p and k_1 is a constant. Values of n, obtained from the slope of plots of $\log_{10} k_m$ against $\log_{10} p$, are plotted as a

TABLE 1
ACTIVITIES AND KINETIC ORDERS FOR PARAHYDROGEN CONVERSION AT 77 AND 90 K

	77 K		90 K	
Catalyst	k_m at 7 Torr (molecules mg^{-1} sec^{-1})	n	k_m at 7 Torr (molecules mg^{-1} sec^{-1})	n
1	3.4×10^{14}	0.36	2.2×10^{14}	0.38
2	2.7×10^{14}	0.29	2.1×10^{14}	0.30
3	4.9×10^{15}	0.00	5.3×10^{15}	0.00
4	1.0×10^{15}	0.21	7.7×10^{14}	0.21
5	2.1×10^{16}	0.00	2.1×10^{16}	0.00
6	3.9×10^{16}	0.00	3.8×10^{16}	0.00
No. 1 of Ref. 3[a]	4.0×10^{14}	0.28	2.3×10^{14}	0.30
No. 2 of Ref. 3[b]	4.2×10^{15}	0.00	3.8×10^{15}	0.07

[a] Water washed 5A molecular sieve.

[b] 2.04×10^{-4} g ion of Nd^{3+} exchanged into 1 g of 5A molecular sieve.

function of reaction temperature in Fig. 4. The two curves which enclose the values of n both possess a broad maximum at ~290 K, which is close to the average temperature for minimum activity, 297 K, taken from the Arrhenius plots at both increasing and decreasing temperatures. It follows that a negative apparent activation energy for conversion is associated with a kinetic order which increases with increasing temperature, where a positive apparent activation energy is associated with a kinetic order which decreases with increasing temperature.

For catalysts 4–6, kinetic orders were determined at 77 and 90 K and the values obtained are given in Table 1, together with the values for catalysts 1–3 at the same temperatures.

Adsorption Isotherms

Adsorption isotherms were determined for hydrogen on catalyst 3 at 77, 90, and 112 K for pressures up to 20 Torr. Adsorption was rapid and fully reversible, and the time between the admission of gas and the measurement of the equilibrium pressure ensured that the hydrogen was equilibrated with respect to ortho-para composition. The adsorption isotherms, together with the isosteric heat of adsorption as a function of coverage, are shown in Fig. 5. Corresponding data obtained for A zeolite containing the same concentration of neodymium ions (*3*) are also shown in the figure, and it is evident that both the extent and heat of adsorption are greater for this catalyst 3. The uptakes at 77 and 90 K can be expressed in terms of the Freundlich isotherm, $V_{ads} = k_2 p^m$, where V_{ads} is the volume adsorbed, expressed in milliliters at STP, at pressure p and k_2 and m are constants for any one isotherm. The value of m was 0.56 at 77 K and 0.88 at 90 K.

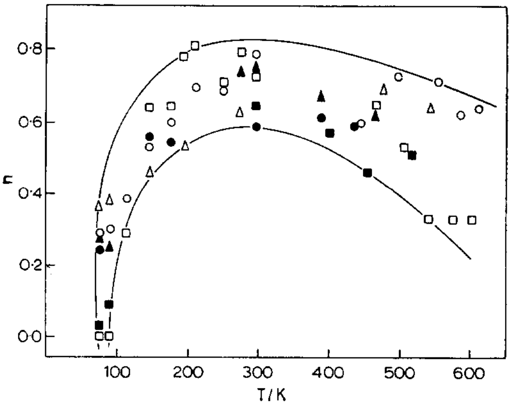

FIG. 4. Kinetic orders with respect to hydrogen pressure: △ catalyst 1 increasing temperatures, ▲ catalyst 1 decreasing temperatures, ○ catalyst 2 increasing temperatures, ● catalyst 2 decreasing temperatures, □ catalyst 3 increasing temperatures, ■ catalyst 3 decreasing temperatures.

DISCUSSION

Low Temperatures

Restricting discussion to reaction at temperatures below those at which the minima in the Arrhenius plots occur, parahydrogen conversion is characterised by a negative apparent activation energy and a kinetic order which increases with increasing temperature. This behavior indicates that conversion proceeds by a paramagnetic physical mechanism involving adsorbed hydrogen, in which the true activation energy is less than the heat of adsorption of the hydrogen. The closely similar activities of catalysts 1 and 2, and the higher activity

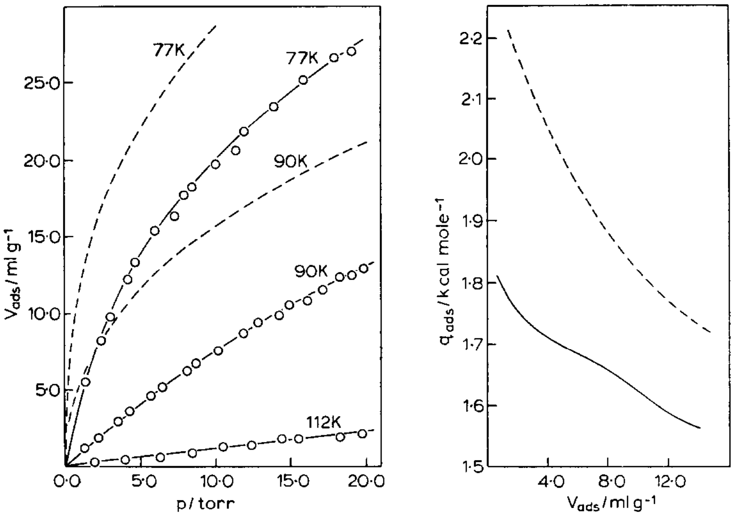

FIG. 5. Adsorption isotherms and isosteric heats of adsorption for hydrogen on catalyst 3. Corresponding data for A zeolite containing the same concentration of Nd^{3+} - - -.

of catalyst 3 containing the paramagnetic Nd^{3+} ions supports this view. Detailed mechanisms for paramagnetic conversion of parahydrogen in the adsorbed state (*7–9*) have been developed from Wigner's original theory (*10*), and in each of these the rate of conversion is proportional to μ^2, the square of the magnetic moment of the paramagnetic centers. The linear plots of k_m against μ^2 for catalysts 2–6 at both 77 and 90 K (Fig. 6) show the applicability of Wigner's theory to parahydrogen conversion by rare earth ions in zeolites. The kinetic orders for conversion, n, for catalyst 3 at 77 and 90 K indicate saturation of the catalytically active sites, whereas the pressure exponents of the corresponding Freundlich isotherms, m, indicate that hydrogen adsorption had not reached saturation. We conclude that low-temperature conversion proceeds by the vibrational mechanism on strongly adsorbing sites (*9*). This mechanism, which most probably holds for the other X zeolites studied, also holds for conversion on A zeolites (*3*).

Table 1 shows that the exchange of 2.04×10^{-4} g ion of Nd^{3+} into 1 g of either 13X or 5A molecular sieve yields catalysts of closely similar activity at 77 and 90 K, although hydrogen is more strongly ad-

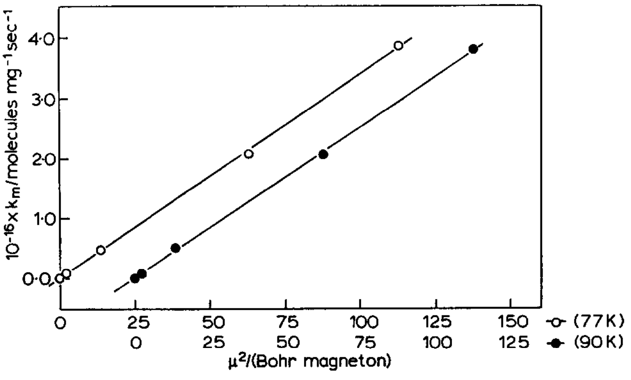

FIG. 6. Plots of k_m at 7.0 Torr against μ^2 for catalysts 3–6 at 77 and 90 K. Each line passes through the point for catalyst 2, for which $\mu = 0$.

sorbed on the A zeolite at these temperatures. Assuming all the Nd^{3+} ions contribute to reaction, their specific activity lies between 0.029 and 0.041 molecules ion^{-1} sec^{-1}, which is low compared with the experimental value of 0.33 molecules ion^{-1} sec^{-1} for Nd^{3+} supported on rutile (*11*) and 0.3 molecules ion^{-1} sec^{-1} calculated using accepted values for the parameters in the theoretical rate equation (*12*). Inaccessibility of the majority of the Nd^{3+} ions cannot account for their low specific activity, since all ions apart from those at site I should be accessible to hydrogen in X zeolite, and all ions should be accessible in A zeolite. It is also unlikely that the low activity arises from the Nd^{3+} ions being hydrated, since further outgassing at temperatures in excess of 623 K did not lead to higher activities for Nd^{3+} in A zeolite (*3*). The most probable explanation for the low-specific activity lies in different frequencies of vibration and distances of interaction between hydrogen molecules and Nd^{3+} ions on oxide surfaces and within zeolites.

To account for the activity of alumina in low-temperature parahydrogen conversion, Hall (*13*) has suggested that the electrostatic fields at exposed aluminum ions play an important role. This could be either in the field ionization of H_2 to H_2^+, such that it is self converting, or in increasing the Wigner transition probability by reducing the energy difference between nuclear spin levels. Since high electrostatic fields exist within the supercages of X zeolites (*14*) it is desirable to consider the probability of such effects with the present catalysts. The surface area of catalysts 1 and 2 may be expected to lie between 10^2 and 10^3 m^2 g^{-1}, so that the mean activity at 77 and 90 K lies between 2.6×10^{10} and 2.6×10^{11} molecules cm^{-2} sec^{-1} when expressed on an area basis. Since this is appreciably less than the general level of activity found for alumina at these temperatures (*13*, *15*, *16*), we conclude that the electrostatic fields in zeolites have little effect. Such a view is reinforced by the observation that exchange of sodium for protons has little influence upon activity, and by the need to explain a low specific activity for Nd^{3+} in catalyst 3. As with A zeolite, we believe the activity of catalysts 1 and 2 to arise from paramagnetic impurities, and it has been shown (*3*) that a ferric iron concentration of 7×10^{-6} g ion per g is sufficient to account for our results.

High Temperatures

In the high-temperature region above 297 K catalysts 1, 2, and 3 exhibit closely similar behavior, indicating that Nd^{3+} ions or protons, most probably present as acidic hydroxyl groups, are unimportant in determining activity. It follows that parahydrogen conversion proceeds by a chemical mechanism which is associated with the alumino-silicate framework of the zeolite itself, rather than with the charge balancing cations. The kinetic orders shown in Fig. 4 indicate coverages for the active surface or sites (*17*) which are less than unity, but which tend to increase with temperature. Discounting the possibility of endothermic adsorption, this suggests that true adsorption equilibrium is not achieved during catalytic measurements and that activated adsorption occurs to give a surface hydrogen active in reaction.

Activation by prolonged exposure to hydrogen occurs with all three catalysts, and in this way they parallel A zeolites (*3*) rather than NaY zeolite (*2*). We conclude that decationated sites, either in association with other decationated sites or in association with impurities, are not responsible for the activity of our A and X zeolites. Since activation is accompanied by the reversible poisoning of the low-temperature activity of catalyst 3, further dehydration, by either direct desorption or interaction of hydrogen with hydroxyl groups (*3*), does not offer an explanation for the effect. The most probable explanation is that the coverages of active hydrogen, resulting from activated adsorption, are greater over a decreasing temperature sequence than over an increasing temperature sequence. Unfortunately, however, the kinetic orders are insufficiently sensitive to lend support to this.

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