DEHYDRATION OF PROPAN-2-OL ON Y ZEOLITES

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Studies of propan-2-ol dehydration made in a flow system operating at a total pressure of one atmosphere, show that propene and di-isopropyl ether are readily produced by parallel reactions occurring at BRØNSTED acid centres within Y zeolites. In addition to HY; MgY, CaY, NiY, CuY, AgY and LaY were found to be active catalysts. Treatment with H_2S greatly increased the activities of NiY and CuY, had smaller effects on AgY and LaY, and none on MgY and CaY. A reaction mechanism involving carbonium and oxonium ion intermediates is discussed.

Introduction

Variations in alcohol structure, the nature and extent of cation exchange, and the susceptibility to base poisons show that carbonium ion intermediates are involved in alcohol dehydration on faujasitic zeolites [1—3]. Dehydration of propan-2-ol on X and Y zeolites in microreactors [4] and recirculatory-flow reactors [5] yields propene and water, whereas di-*iso*propyl ether is also produced in continuous-flow reactors [6, 7]. From a study of propan-2-ol dehydration on a series of HX zeolites, GENTRY and RUDHAM [6] proposed an ionic mechanism involving one O1H group for propene formation and two O1H groups for di-*iso*propyl ether formation. JACOBS *et al.* [7] investigated alkali cation exchanged X and Y zeolites, and showed that propene and di-*iso*propyl ether were formed by parallel reactions catalysed by weakly acidic OH groups. The OH groups were formed either by interaction of water with cations and the zeolite lattice, or by hydrolysis of polyvalent cation impurities. The generation of acidic OH groups through cation hydrolysis is also considered to be the source of activity for propan-2-ol dehydration on a number of di- and trivalent cation exchanged X and Y zeolites [4, 8—10].

Experimental

Propan-2-ol dehydration was studied in a continuous-flow system in which the total pressure of alcohol and nitrogen diluent was one atmosphere [6]. A small number of infra-red measurements were made using a cell which could take the place of the reaction vessel, and had provisions for dehydrating samples at elevated temperatures.

The catalysts were prepared from binder-free NaX (B. D. H./Linde 13X, lot 0003940) or NaY (Linde SK—40, lot 3606-150) by cation exchange with aqueous solutions of analytical grade salts. Catalysts are designated MX-*n* or MY-*n*, where *n* represents the extent of exchange in terms of the number of exchange cations M per unit cell.

Results and Discussion

Catalysis on HX *and* HY *Zeolites*

Catalysts were prepared by calcination of either 10 mg or 100 mg samples of NH_4X and NH_4Y for 16 hr at 623 K in a 1.67 $cm^3\ s^{-1}$ flow of cylinder N_2. Infra-red examination of ~50 mg, 2.5 cm pressed disc of NH_4Y-14.0 subjected to identical calcination showed deammoniation to be complete. A band at 3640 cm^{-1} superimposed on a broad band between 3700—3250 cm^{-1} and a band at 1642 cm^{-1} indicated the presence of molecular water in addition to OH groups. Under these circumstances it is unlikely that any dehydroxylation occurs during calcination.

A series of comparative experiments between X and Y zeolites were made with samples of HX-8.6 and HY-8.4. It was found that the rate of formation of both di-*iso*propyl ether (r_e, molecules $g^{-1}\ s^{-1}$) and propene (r_p, molecules $g^{-1}\ s^{-1}$) on HY-8.4 between 372 and 400 K obeyed zero-order kinetics with respect to propan-2-ol pressure between $2.8 \cdot 10^2$ and $4.2 \cdot 10^3$ Pa. Similar experiments with HX-8.6 confirmed the small pressure dependencies previously observed [6]. Negligible error is introduced in assuming zero-order kinetics for both catalysts at low extents of reaction, when r_e and r_p become the zero-order rate constants k_e and k_p. The effect of temperature on k_e and k_p was investigated with both catalysts under conditions where extent of dehydration was <10% of $1.11 \cdot 10^3$ Pa of alcohol in a total flow of 0.5 $cm^3\ s^{-1}$. Measurements covering ~35 degrees gave excellent Arrhenius plots, and values of the activation energies E_e, E_p, pre-exponential factors k_e^0, k_p^0, and k_e and k_p at 377 K are given in Table 1. The data clearly indicate that differences in activity between HX-8.6 and HY-8.4 are controlled by energetic considerations rather than by differences in the concentration of active sites. The concentration of active Brönsted acid sites was thus determined by titrating working catalysts by the progressive adsorption of pyridine or piperidine. Figure 1 shows plots obtained with HY-8.4,

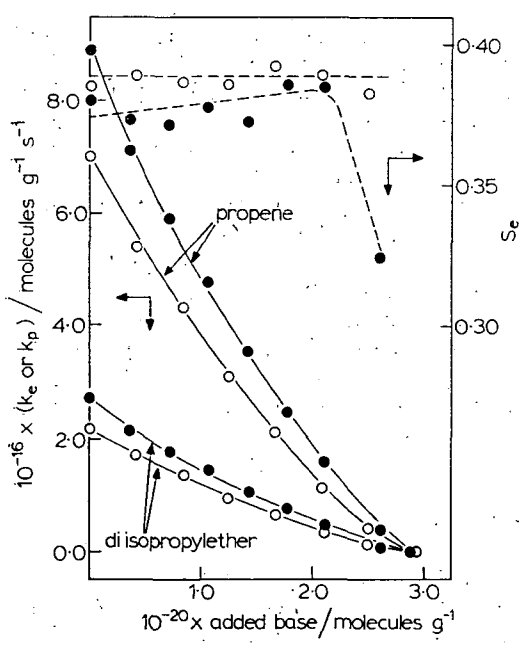

Fig. 1. Progressive poisoning of HY-8.4 with: ● — pyridine at 381 K, ○ — piperidine at 379 K.

where, for each base, the curves for k_e and k_p intersect on the zero activity axis. Similar results were obtained for HX-8.6, and values for the concentration of active sites, taken to be the amount of base necessary for complete poisoning, are given

Table I

Comparison of HX *and* HY *catalysts*

		HX-8.6	HY-8.4
Di-isopropyl ether formation	k_e at 377 K/molecules g^{-1} s^{-1}	$3.98 \cdot 10^{14}$	$2.24 \cdot 10^{16}$
	k_e^0/molecules g^{-1} s^{-1}	$1.8 \cdot 10^{30}$	$1.6 \cdot 10^{30}$
	E_e/kJ mol^{-1}	113	100
Propene formation	k_p at 377 K/molecules g^{-1} s^{-1}	$2.82 \cdot 10^{15}$	$6.17 \cdot 10^{16}$
	k_p^0/molecules g^{-1} s^{-1}	$1.6 \cdot 10^{32}$	$1.5 \cdot 10^{32}$
	E_p/kJ mol^{-1}	121	111
Brönsted acid site concentration/ $10^{-20} \cdot x$ sites g^{-1}	from NH_4^+ exchange	2.91	2.89
	from pyridine poisoning	2.61	2.88
	from piperidine poisoning	2.97	2.93

in Table I. The values obtained from the bases of different strength, and that calculated from the NH_4^+ content of the catalyst precursors, are closely similar. We conclude that all the hydroxyl groups produced by deammoniation are available, and are of sufficient acid strength, to catalyse the dehydration of propan-2-ol to di-*iso*propyl ether and propene. The selectivities for ether formation on HY-8.4, shown in Fig. 1 and defined as $S_e = 2k_e/(2k_e + k_p)$ remain effectively constant with increasing base adsorption until very high coverages are achieved. This, together with the observation that wide variations in reactant space velocity could not achieve a condition where $k_e > k_p$, show that propene and di-*iso*propyl ether are formed by parallel reaction paths.

The effects of varying the extent of ion exchange have been investigated with a series of HY catalysts using $1.11 \cdot 10^3$ Pa of propan-2-ol in a total flow of 0.5 cm^3 s^{-1} (a reactant mixture and flow rate used in all further experiments). Since values of E_e and E_p were all within 4 kJ mol^{-1} of the respective mean values of 99 and 111 kJ mol^{-1}, catalytic activities can be directly compared. Values of k_e and k_p at 377 K, an experimental temperature common to all catalysts, are plotted against the extent of exchange in Fig. 2. Linear plots are obtained for both products on catalysts containing more than 4 OH groups per unit cell, with values of S_e showing a monotonic increase from 0.36 for HY-4.3 to 0.47 for HY-16.6. This indicates that both propene and di-*iso*propyl ether formation involve a single OH group.

To account for our observations we propose the reaction sequence shown in Fig. 3. Since water is present after deammoniation, OH groups are ionised (1) to form H_3O^+ ions associated with structural O^- ions in the α-cages. At high propan-2-ol concentrations, proton transfer (2) gives an oxonium ion, which yields a carbonium ion by the E_1 elimination of H_2O (3). Subsequently, proton transfer (4) yields propene and H_3O^+. Alternatively, interaction with propan-2-ol (5) results in an oxonium ion which, on proton transfer (6) yields di-*iso*propyl ether and H_3O^+. In view of the partial pressure of propan-2-ol being relatively high to that of the water produced,

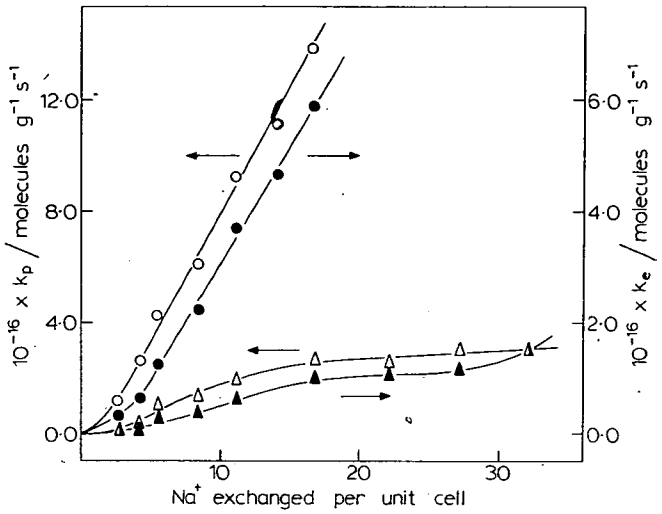

Fig. 2. Activity for di-isopropyl ether and propene formation at 377 K as a function of the extent of ion exchange: ● — k_e on HY, ○ — k_p on HY, ▲ — k_e on CuY, △ — k_p on CuY.

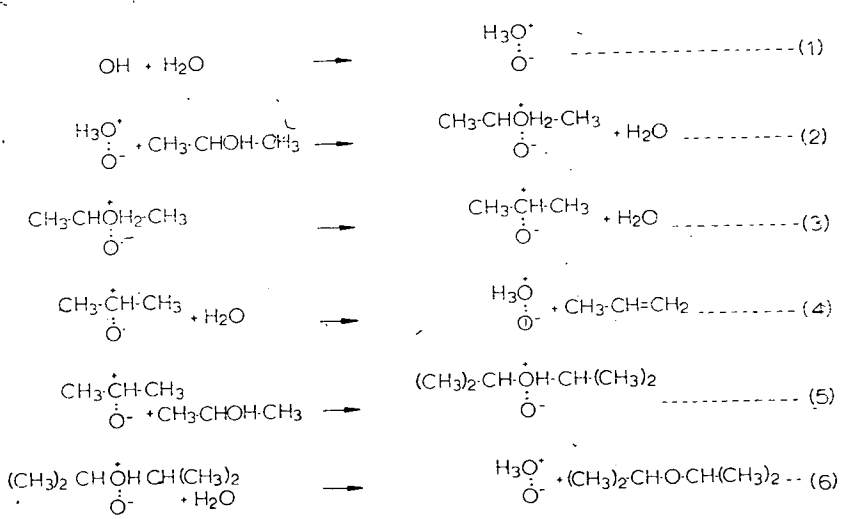

Fig. 3. Reaction sequence for di-isopropyl ether and propene formation on HY catalysts.

possible alternatives to (4) and (6) may be proton transfer to propan-2-ol to give the oxonium ion produced in (2). Presumably, the water elimination (3) makes the largest contribution to the overall activation energy, and this accounts for the similarity in E_e and E_p. This mechanism, although basically similar to those previously suggested [6, 7], differs in that only a single site is involved in ether production. Furthermore, it obviates the interaction of positively charged carbonium and oxonium ions [6].

Catalysis on CuY *Zeolites*

CuY zeolites catalyse propan-2-ol dehydration, but, in contrast to HY, they took an appreciable time to achieve constant activity following changes in the reaction conditions. The activity also depended on the initial dehydration conditions, but the chosen pretreatment of 2 hr in flowing N_2 (0.67 $cm^3\ s^{-1}$) at 523 K gave the optimum activity most rapidly. Infra-red examination of CuY-8.4 given this pretreatment indicated the presence of molecular water. Values of k_e and k_p at 377 K obtained at nine Cu^{2+} contents are shown in Fig. 2, where the activity consistently falls below that suggested by the hydrolysis of *all* Cu^{2+} according to:

$$Cu^{2+}(H_2O)+O_z^- = (CuOH)^+ + O_zH, \tag{7}$$

possibly followed by

$$2\,(CuOH)^+ + 2\,O_zH = (Cu—O—Cu)^{2+} + 2\,O_zH. \tag{8}$$

Although zero-order kinetics were obeyed, E_e increased from 82 to 122 kJ mol^{-1} and E_p increased from 98 to 132 kJ mol^{-1} with increasing Cu content. The experimental findings show that the concentration of Brönsted acid centres is critically dependent on cation distribution and the extent of cation hydrolysis. In addition to concentration effects with water and other molecules on k_e and k_p, E_e and E_p vary from those on HY by contributions from the ΔH values associated with changes of cation location and hydrolysis.

Catalysis on Other Y *Zeolites and the Effects of* H_2S *Treatment*

Catalytic activities at 377 K have been determined for a number of Y zeolites in which the extents of exchange of Na^+ for other actions were approximately equivalent. In all cases the catalysts were dehydrated as with CuY, and no dehydrogenating activity to acetone was observed. Values of k_e and k_p given in Table II show

Table II

Effect of H_2S *treatment on dehydration activity at* 377 K
(values of k_e and k_p in 10^{-14}·molecules $g^{-1}\ s^{-1}$)

		HY-11.1	AgY-11.5	MgY-5.5	CaY-5.5	NiY-5.1	CuY-5.6	LaY-3.8
Before H_2S	k_e	370	330	0.68	0.076	4.5	60	230
	k_p	930	790	2.2	0.71	25	190	490
	S_e	0.44	0.46	0.38	0.18	0.27	0.39	0.48
After H_2S	k_e	—	420	0.68	0.096	220	450	200
	k_p	—	910	2.2	0.93	680	1000	450
	S_e	—	0.48	0.38	0.17	0.39	0.47	0.47

a wide spread of activities, with only that of AgY-11.5 approaching HY-11.1. This most probably occurred through a substantial reduction of $Ag^+ \rightarrow Ag^0$ accompanied by O_zH formation in the initial stages of reaction. The S_e values, apart from those of low activity catalysts which are subject to appreciable error, suggest the same mechanism as on HY zeolites.

In view of the increase in cumene cracking activity observed following H_2S treatment of certain ion-exchanged Y zeolites [11], we have determined activities following treatment of the catalysts with $\sim 20\,cm^3$ H_2S for 15 min. The data in Table II show a large increase in the activities of NiY-5.1 and CuY-5.6, a smaller effect with AgY-11.5, no effect with MgY-5.5 and Ca-5.5, and even slight poisoning with LaY-3.8. Additional experiments also showed that there was no effect with NaY and HY-14. Such observations are in accord with those of SUGIOKA *et al.* [11]. A series of experiments with H_2S treated CuY-4.2 confirmed that the activity increase was associated with Brönsted acidity, since complete poisoning with pyridine readily occurred at 377 K. In addition, the source of the additional activity possessed similar stability to that of untreated CuY zeolites, since there was no diminution in activity following heating at 523 K for 2 hr in flowing nitrogen. We believe the increases in activity arise from hydroxyl groups generated in the reaction:

$$M_e^{n+} + n\,O_z^- + 0.5n\,H_2S \rightarrow MeS_{0.5n} + n\,O_zH, \tag{9}$$

and that the neutral $MeS_{0.5n}$ entity resists hydrolysis in the cases of AgY-11.5, NiY-5.1 and CuY-5.6. With AgY-11.5 both Ag^0 and Ag^+ probably react with H_2S, but only the Ag^+ will generate additional O_zH groups, so accounting for the smaller H_2S effect with this catalyst.

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