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Vapour-Phase Dehydration of Isopropanol on Macroporous Ion Exchange Resins

Although the use of ion exchange resins as acidic catalysts is well known (*1*), the most commonly used are the gel-type resins. Macroporous resins, however, have the advantage of better mechanical, thermal, and osmotic stabilities. Prokop and Setinek (*2*) studied the chemisorption and catalytic activity of macroporous sulphonated styrene–divinylbenzene resins with varying degree of crosslinking and the dehydration of *n*-propanol on similar catalysts was reported by Martinec *et al.* (*3*). There are several factors that may influence the catalytic activity and selectivity of the macroporous resins. In this Note we report the effect on surface area, pore structure, and catalytic activity towards dehydration of isopropanol (IPA) of the degree of crosslinking of macroporous sulphonated styrene–divinylbenzene resins. The effect of temperature, space velocity, bead size, and poisoning of the acid sites on activity and selectivity of the catalysts has been studied to understand the process.

Styrene and divinylbenzene were polymerized at 80 ± 1°C for 24 h using heptane as diluent, benzoyl peroxide as initiator, and polyvinyl alcohol as the suspension stabilizer (*4, 5*). The beads were washed with water at 60°C, dried at 80°C, and then swollen in 1,2-dichloroethane and sulphonated using oleum at 100°C for 20 h. The volume fraction (F_M) was kept constant at 0.6 and the crosslinking (the weight fraction of divinylbenzene) was varied from 0.20 to 0.40. The gel-type Duolite C-20 was a gift from Ms. Diamond Sharmock (India) Ltd.

The exchange capacity of the resins was determined by standard procedure (*6*). BET nitrogen adsorption was used for determining surface area and helium density. Porosity and average pore radius were obtained using the nitrogen adsorption–desorption method on a Carlo–Erba instrument.

A flow-type catalytic reactor was used. The temperature of the catalyst bed was maintained within ±0.2°C. The liquid products were analysed by glc using a Carbowax 20M on Chromosorb column (length 1.5 m, diameter $\frac{1}{8}$ in.; temperature 100°C). The gaseous products were analysed using a molecular sieve 13X column (length 2 m, diameter $\frac{1}{8}$ in.) at room temperature. Kinetic data were collected between 100 and 120°C keeping the total conversion below 5% and the initial rates were calculated for propene formation (R_p) as well as for diisopropyl ether (DIE) formation (R_e). Selectivity has been defined as R_p/R_e. Before every run, the catalyst was dried at 120°C in a current of nitrogen for 2 h.

The various properties of the resins are summarized in Table 1. The average pore radius is a maximum at 25% crosslinking and decreases continuously thereafter. Exchange capacity and helium density fall and surface area and porosity increase with increased crosslinking. Kinetic data are presented in Table 2. Figure 1 shows the effect of the partial pressure of water on R_p and R_e. The effect of the partial pressures of propene, DIE, and IPA were found to be negligible. The last quantity was varied by diluting the reactant with nitrogen gas. Rates were also found to be independent of the resin bead size which was varied between 18–25 and 52–60 mesh. Replace-

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TABLE 1

Some Physical Properties of the Resins

Designation	Degree of crosslinking[a]	Exchange capacity (meq H^+/g)	Surface area (m^2/g)	Helium density (g/cm^3)	Porosity (cm^3/g)	Average pore radius (Å)
A	20	4.30	31.5	1.40	0.12	44.3
B	25	3.67	61.0	1.38	0.14	80.1
C	30	3.61	88.7	1.37	0.24	68.8
D	35	3.50	108	1.35	0.30	49.2
E	40	3.0	114	1.34	0.31	42.6
Gel-type Duolite F (C-20)	8	5.0	0.1	1.26	—	—

[a] The degree of crosslinking means here the content of divinylbenzene taken before the polymerization.

ment of H^+ of the resin by Na^+ reduces the catalytic activity. The results of such a study on resin B are summarized in Table 3.

Table 2 shows that catalyst B has the highest activity towards IPA dehydration. It also shows that the surface area and exchange capacity of the resins have no bearing on their catalytic activity. On the other hand, the dependence of activity on average pore radius is clearly shown. Since the activity falls with average pore radius, it may be concluded that the reaction occurs in the entire bulk of the bead and is governed by the permeation of the reactants. It is most likely that DIE is formed as an intermediate. This is supported by the finding that as inverse space velocity is increased, the fraction of IPA changed to DIE initially increases as expected, and then falls, whereas the fraction converted to propene increases continuously (Fig. 2). This suggests that DIE formed reacts further to give propene. Activity and selectiv-

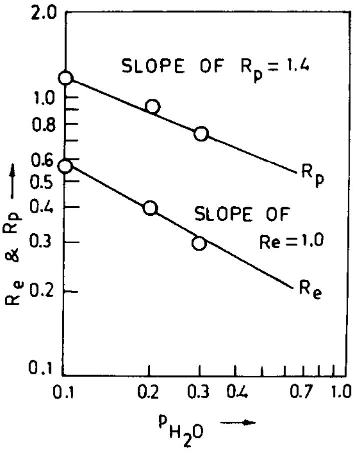

FIG. 1. Log–log plots of rate vs p_{H_2O}.

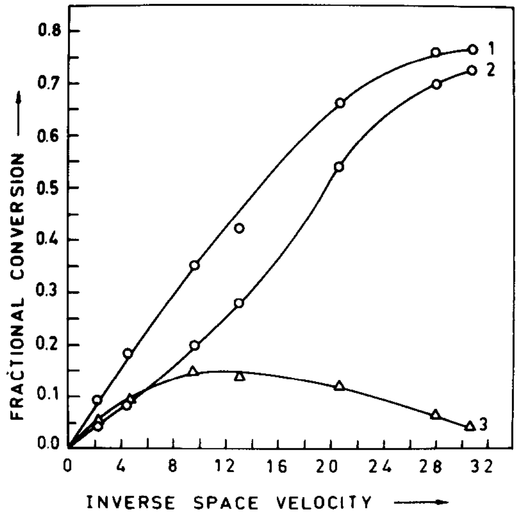

FIG. 2. Conversion vs reciprocal space velocity plots (catalyst: resin B; temperature 120°C). 1—Fraction of total IPA converted; 2—fraction converted to propene; 3—fraction converted to diisopropyl ether.

TABLE 2

Kinetic Data for Isopropanol Dehydration

Catalyst	100°C			110°C			120°C			E_a(p) (kcal · mole^{-1})	E_a(e) (kcal · mole^{-1})
	R_p	R_e	R_p/R_e	R_p	R_e	R_p/R_e	R_p	R_e	R_p/R_e		
A	0.506	0.134	3.78	0.97	0.279	3.47	1.70	0.672	2.53	17.2	22.9
B	0.670	0.150	4.47	1.10	0.40	2.75	1.94	1.00	1.76	15.5	27.0
C	0.485	0.150	3.23	0.780	0.377	2.07	1.43	0.905	1.58	15.4	25.5
D	0.442	0.146	3.02	0.676	0.366	1.83	1.33	0.90	1.47	15.6	25.8
E	0.390	0.141	2.76	0.660	0.360	1.83	1.16	0.878	1.32	15.5	26.0
F	0.252	0.046	5.52	0.427	0.100	4.27	0.735	0.212	3.47	15.2	21.8

Note. Rates are expressed as mole h^{-1} g^{-1} × 10^{-2}. E_a(p) and E_a(e) are the Arrhenius activation energies for propene formation and diisopropyl ether formation, respectively.

TABLE 3

The Effect of Na$^+$ Substitution on Rates; Catalyst—Resin B, Temperature 120°C

$\frac{\text{Na}^+ \text{ sites}}{(\text{Na}^+ + \text{H}^+) \text{ sites}}$	$R_p \times 100$ (mole h^{-1} g^{-1})	$R_e \times 100$ (mole h^{-1} g^{-1})
0	1.94	1.0
0.22	0.97	0.41
0.40	0.61	0.20
0.75	0.39	0.035
1.0	0	0

ity towards propene should then decrease if the permeation of the bulkier DIE towards the interior of the bead is restricted by smaller pores. This is in agreement with the experimental results. Selectivity also falls at higher temperature because the rate of DIE desorption increases with temperature to a greater extent than its permeation.

Table 3 shows that replacement of H$^+$ by Na$^+$ reduces the catalytic activity, but the decrease in rate is much more rapid than the fall in proton concentration. Normally, one would expect this effect to be much less pronounced because Na$^+$ ions will penetrate easily and replace even those H$^+$ ions that are not accessible to reactants. It is possible that there is more than one type of acid site in the resin and sodium preferentially poisons the more active ones. Alternatively, the reaction might use simultaneously more than one acid site. The dependence of rates on p_{H_2O} suggests that water molecules block the sites and make them inaccessible to the reactants.

REFERENCES

1. Helfferich, F., "Ion Exchange." McGraw-Hill, New York, 1962.
2. Prokop, Z., and Setinek, K., *Collect. Czech. Chem. Commun.* **39,** 1253 (1974).
3. Martinec, A., Setinek, K., and Beranek, L., *J. Catal.* **51,** 86 (1978).

4. Mikes, J. A., *in* "Ion Exchange in the Process Industry Conference, London, 1969," p. 16. Soc. Chem. Ind., London, 1970.

5. Kunin, R., *in* "Ion Exchange in the Process Industry Conference, London, 1969," p. 10. Soc. Chem. Ind., London, 1970.

6. Kunin, R., "Ion Exchange Resins." Wiley, London, 1963.

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