

Sulphonated macroporous resin catalysts : studies on the dehydration of 2-butanol

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Abstract. Sulphonated styrene-divinylbenzene resins with various cross-linking have been synthesized and the dehydration of 2-butanol has been studied on these acid catalysts. The pore structure of the resin controls the rate of dehydration. The *cis* to *trans* ratio of the 2-butene formed indicate that the resin catalysts behave like aqueous solution of acids, *i.e.* dissociated protons are responsible for catalysis.

Keywords. dehydration of butanol; macroporous resin catalysts; sulphonated resin catalysts.

1. Introduction

Many industrial reactions are carried out using acid catalysts in solution. The drawback is that often the separation of the catalyst from the product poses difficulties; besides, the disposal of the spent catalyst (sulphuric acid, for example) sometime poses serious environmental problems. The solid acid catalysts like alumina or silica, on the other hand, are difficult to prepare with reproducible surface acidity. Sulphonic acid ion exchange resins have the advantage of strong acidity, insolubility and near homogeneity of the acid strength of the acid groups. The main disadvantage of resins is their low thermal stability and low surface area (gel type resins). In recent years, however, it has been possible to prepare macroporous resins with moderate thermal stability and large surface area and some of them (sulphonated form) have been used as matrix-bound acid catalysts. Most of the studies were conducted in liquid phase and only a few have been devoted to vapour phase reactions. Thus, Gottifredi *et al* (1968) studied the dehydration of 2-propanol using ion-exchange resin catalysts. Prokop and Setinek (1974) investigated chemisorption and catalytic properties of macroporous sulphonated styrene-divinylbenzene resins. The dehydration of 2-propanol was studied by Martinec *et al* (1978). Interesting mechanistic studies have been carried out by Cooper *et al* (1980) and Thornton and Gates (1974) on ion-exchange membranes. The steps involved in the reaction may be different in the case of membrane catalysts as compared to those in the bead form.

In view of the importance of such material as future acid catalysts, a systematic study of the preparation, characterization and catalytic activity of sulphonated styrene-divinylbenzene resins is undertaken. The results on the de-

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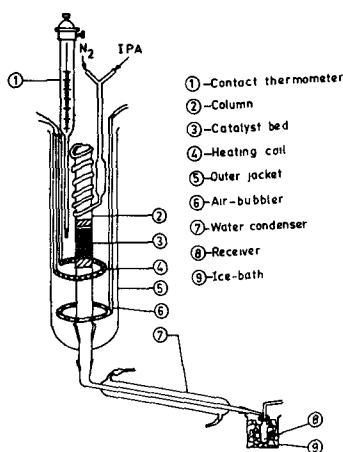


Figure 1. Schematic view of the catalytic reactor.

hydration of 2-propanol has been reported in a recent communication (Sivanand *et al* 1981). The results of 2-butanol dehydration is reported in this paper.

2. Experimental

Preparation of the sulphonated styrene-divinylbenzene copolymer catalysts has been described elsewhere (Sivanand *et al* 1981). All chemicals used were of CP grade, except divinylbenzene which was obtained from Polychem Ltd. had the following composition: divinylbenzene 54.58% (w/w); ethyl vinylbenzene 42.44% (w/w); diethyl benzene 1.51% (w/w); heaviers 1.47% (w/w). The ethyl vinylbenzene content in the divinylbenzene had been considered as styrene and appropriate corrections were made while calculating crosslinking of resins. This is a standard procedure used in the preparation of commercial ion exchangers.

Styrene and divinylbenzene were polymerized at $80 \pm 1^\circ\text{C}$ for 24 hr using heptane as diluent, benzoyl peroxide as initiator and polyvinyl alcohol as the

Table 1. Some physical properties of the resin catalysts.

Designation	Degree of cross-linking	Exchange capacity (meqH ⁺ /g)	Surface area m ² g ⁻¹	Porosity cm ³ g ⁻¹	Average pore radius (Å)
A	20	4.30	54.2	0.12	44.3
B	25	3.67	34.9	0.14	80.1
C	30	3.61	69.7	0.24	68.8
D	35	3.50	121.9	0.30	49.2
E	40	3.00	145.5	0.31	42.6
F	8	5.00	~0.1	-	-

(gel type)

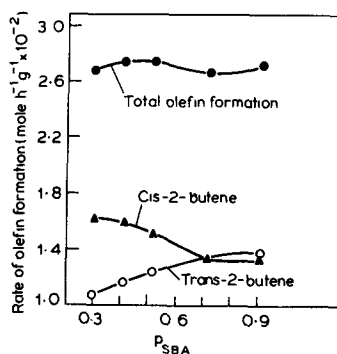


Figure 2. The variation of *cis* and *trans* 2-butene in the products of 2-butanol dehydration; the variation of the rate of total olefin formation is also shown.

suspension stabilizer. 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 hr. The volume fraction (F_M) was kept constant (at 0.6) and the crosslinking (the weight fraction of divinylbenzene) was varied from 0.2 to 0.4.

The gel-type Duolite C-20 was a gift from M/s. Diamond Shamrock (India) Ltd.

The exchange capacity of the resins was determined by the standard procedure (Kunin 1963). Surface area and average pore radius was obtained by nitrogen adsorption-desorption method on a Carlo-Erba instrument.

The catalytic reactor is shown in figure 1. The main reactor (1.5 cm diameter and 20 cm long) and the preheater is placed inside a glycerine bath through a B-19 joint. Glycerine was heated by a heating element and stirred by bubbling air. The temperature of the bath was maintained within $\pm 0.2^\circ\text{C}$

Table 2. Kinetic data for 2-butanol dehydration.

Catalyst	110°C			120°C			130°C			$E_a(o)$ kcal mole ⁻¹	$E_a(e)$ kcal mole ⁻¹
	R_o	R_e	R_o/R_e	R_o	R_e	R_o/R_e	R_o	R_e	R_o/R_e		
A	1.55	0.170	9.11	2.72	0.332	8.19	4.36	0.631	6.91	15.0	20.2
B	1.59	0.180	8.83	2.87	0.371	7.74	4.56	0.679	6.72	15.9	20.8
C	1.53	0.175	8.74	2.56	0.360	7.11	4.11	0.670	6.13	14.2	19.9
D	1.30	0.171	7.60	2.42	0.321	7.54	3.81	0.560	6.80	16.9	18.7
E	1.32	0.161	8.20	2.32	0.316	7.34	3.79	0.559	6.78	16.1	19.0
F	0.489	0.033	14.8	0.88	0.065	13.5	1.38	0.110	12.5	15.3	19.1

Rates are expressed as mol hr⁻¹ g⁻¹ × 10⁻²

$E_a(o)$ and $E_a(e)$ are the Arrhenius activation energies for olefin formation and sec-butyl ether formation respectively:

Table 3. Product distribution of olefins.

Catalyst	110°C		120°C		130°C	
	% cis-butene	% trans-butene	% cis-butene	% trans-butene	% cis-butene	% trans-butene
A	50.1	49.9	49.6	50.4	52.0	48.0
B	49.8	50.2	53.1	46.9	52.1	47.9
C	50.1	49.9	51.5	49.5	50.2	49.8
D	50.9	49.1	50.6	49.4	50.7	49.3
E	49.2	50.8	49.7	50.3	48.0	52.0
F	50.3	49.7	49.5	50.5	51.2	48.8

using a mercury contact thermometer. The products were passed through a condenser and the liquid was collected in the ice-salt bath and the gaseous products allowed to enter the sampling valve of an on-line gas chromatograph. The reactants were fed continuously using a dosing pump (sigma motor).

The liquid products were analyzed by gas liquid chromatography using carbowax 20M on chromosorb column (length 1.5 m, diameter 3.15 mm, temperature 60°C). The gaseous products were analyzed using chromosorb-P loaded with a saturated solution of silver nitrate in benzyl cyanide (length 3 m, diameter 3.15 mm, temperature 27°C). Kinetic data were collected between 110-130°C keeping the total conversion below 5%. Initial rates were calculated for total butene formation (R_0) and also for secondary butyl ether formation (R_e). Selectivity is defined as (R_0/R_e). Before every run, the catalyst was dried *in situ* at 120°C in a current of dry nitrogen for 2 hr.

3. Results

Some physical properties of the resins are given in table 1. The average pore radius attains maximum value at 25% cross-linking (catalyst B) and then falls. Exchange capacity falls and surface area and porosity increase continuously with increased cross-linking. Catalytic property of the resins is likely to be controlled by one or more of these factors.

Kinetic data for the dehydration of 2-butanol are shown in table 2. It can be seen that the catalyst B (25% crosslinked) has the maximum activity.

The product distribution of the olefins on the various catalysts at various temperatures is shown in table 3. It can be seen that the ratio of *cis*- to *trans*-2 butene remains more or less constant. No 1-butene was detected in the product. The *cis*- to *trans*- ratio, however, changes with the partial pressure of 2-butanol (figure 2). The product distribution may give some clue to the mechanism of dehydration.

4. Discussion

It is seen from table 2 that resin B with 25% cross-linking has maximum activity per gram of the catalyst. Specific surface of the catalyst increases from B to E (table 1). Hence, surface area is not the most critical factor in controlling catalytic activity. Exchange capacity of H^+ also does not show any large variation from catalyst to catalyst. Table 2 shows that catalytic activity varies regularly with the average pore radii of the resins.

Kinetic data were obtained by varying the resin bead size. Bead with size 18-25 and 52-60 mesh (BS) were chosen for this purpose. This change did not affect the rates and hence external diffusion control can be excluded. Since the beads are spherical, packing leaves about 30% void and channeling of the reactants in a catalyst bed containing 1-2 g of the catalyst is not expected. Thus, the rates may be considered free of external mass transfer effects.

In the case of a macroporous resin bead, catalytic reaction need not be restricted at the outer surface of the bead. The reaction will definitely occur inside the bead as long as the reactant molecule can penetrate. This is borne by the fact that catalytic activity increases with average pore radius. There will be, however, a limit up to which the reactant can penetrate, beyond which the macro-structure of the polymer is more dense. Thus, a bead may be divided into a reactive zone and a nonreactive zone. Such a model has been used by Martinec *et al* (1978). This is quite justified in view of the fact that crosslinking will be greater when the formation of the bead had started than in the outer part of the bead.

The poisoning effect of replacing the protons of the sulphonic acid groups by Na^+ ions on the rate of 2-propanol dehydration was reported earlier (Sivand *et al* 1981). It was shown that the rate of dehydration falls to less than half by substituting only about 20% of the hydrogen ions. Thus, poisoning of the outer sphere of the beads, where most of the reaction occur was sufficient to cause a drastic fall in the reaction rate. Thus, it seems that the reaction is limited by the permeation of the reactant molecules into the bulk of the porous bead and it may be possible to maximize the reaction rate by increasing the average pore radius of the resins.

The product distribution of the olefins show the formation of *cis* and *trans* 2-butene; no 1-butene was detected in the product. This is in contrast to reports by other authors (Thornton and Gates 1974) who found all the three straight-chain butenes to be formed. However, as in previous studies, a distinct *cis*-preference is shown as compared to the equilibrium *cis* to *trans* ratio of .045. Thornton and Gates (1974) who studied the dehydration of 2-butanol on ion-exchange membranes observed that *cis*- to *trans* ratio increases with the concentration of polar molecules (alcohol or water) in the catalyst bead. This may be compared with results of Manassen and Klein (1960) who studied the dehydration of 2-butanol in an aqueous solution of perchloric acid at 100°C and observed a *cis* to *trans* ratio between 1 and 2, close to our

results. From this, it appears that at higher alcohol partial pressure (our results are obtained at alcohol partial pressure from 0.3 to 1 atm.), the mechanism is similar to that in aqueous solution of protonic acids.

The mechanism of 2-butanol dehydration by aqueous protonic acid has been discussed by Manassen and Klein (1960) involving a carbonium ion. The *cis* preference was explained as due to greater stability of the *cis* π -complex between the olefin and proton. Pines and Haag (1961) similarly explained the *cis* preference in the reaction over alumina. One may conclude that at higher alcohol partial pressure, the protons of the sulphonic acid groups are ionized and the mechanism involves dissociated protons as in the case of the reaction by aqueous acids. This seems reasonable as the alcohol molecules are polar. At low alcohol partial pressure and in the absence of polar molecules like water, the mechanism may involve an alcohol molecule hydrogen bonded with several $-\text{SO}_3\text{H}$ groups as suggested by Thornton and Gates (1974).

Another interesting aspect is the change in the isomer ratio with the partial pressure of 2-butanol; *cis* to *trans* ratio decreases through 1.51 to 0.98 as p_{SBA} is increased from 0.3 to 0.91, showing a decrease in *cis* preference.

It is possible that the *cis* isomer formed undergoes an isomerization to *trans* form and increase in the rate of this reaction with p_{SBA} is responsible for the lowering of *cis* to *trans* ratio. But there is evidence that isomerization of butenes and dehydration of 2-butanol proceeds on the same acid site (Pines and Haag 1961). This will reduce the rate of isomerization with increase of p_{SBA} as more of the active sites will be blocked by the 2-butanol molecules.

The other alternative is that the rate of 2-butanol dehydration falls appreciably with p_{SBA} so that the isomerization reaction becomes competitive with it. The experimental results, however, show that the rate of 2-butanol dehydration is independent of p_{SBA} in the range of our study. Thornton and Gates (1974) observed that the rate of 2-butanol dehydration increases up to 0.1 atmosphere of p_{SBA} and then falls. Similar results were observed for 2-propanol dehydration (Cooper *et al* 1980). These authors also noted that there is no appreciable change in the dehydration rate at higher values of alcohol partial pressure. Thus, the cause for the variation of *cis* to *trans* 2-butene ratio is not clear at present.

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