

## THE CATALYTIC ACTIVITY OF DIFFERENTLY CROSS-LINKED STANDARD SULPHONATED STYRENE-DIVINYLBENZENE COPOLYMERS

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The catalytic activity of differently cross-linked standard sulphonated styrene-divinylbenzene copolymers has been examined. The copolymers sulphonated both in gas phase by sulphur trioxide and in liquid phase by sulphuric acid in 1,2-dichloroethane were used as catalysts for gas phase dehydrations of methanol, 1-propanol and tert-butanol at 100°C. The results showed that the catalytic activity and selectivity of the standard ion exchangers sulphonated in polymer mass is greatly influenced by the permeation of reactants into polymer particles and of reaction products from the inside of the particles to their surface. In some special cases this permeation could be however utilized to affect the selectivity of catalytic reactions.

Our previous work<sup>1</sup> concerned with the catalytic activity of sulphonated styrene-divinylbenzene copolymers of both macroporous and standard (gel) types. The decisive factor proved to be the accessibility of acidic functional groups within the polymer mass. In continuing this study, in the present work we have been interested only in the catalytic properties of sulphonated standard styrene-divinylbenzene copolymers. This approach simplifies the situation in the sense that the accessibility of the functional groups within catalyst particles on account of porosity has not to be considered. The geometrical surface of standard ion exchangers is very small and therefore the catalytic contribution of surface functional groups can be neglected. One can assume that all the catalytically active groups are located within the polymer mass. The total catalytic activity of the ion exchangers of this type is then controlled by the accessibility of sulphonic acid groups by the permeation of reactants into the polymer mass, *i.e.* by the swelling of polymer particles.

In the present work we have used a series of standard styrene-divinylbenzene copolymers which varied greatly in the content of divinylbenzene. The ion exchangers studied were prepared by their sulphonation. The catalytic activity of these exchangers was tested in dehydrations of methanol, 1-propanol and tert-butanol. The catalysts and reactions were used also in our previous works<sup>1-6</sup>. This rendered it possible to utilize our earlier findings in discussing the results of this study. The aim of the present work was to get information about the accessibility of the functional groups of standard ion exchangers and about the effect of the degree of cross-linking of the copolymers in their application as catalysts for gas phase reactions.

## EXPERIMENTAL

*Chemicals.* The alcohols were purified by rectification and dried by a molecular sieve. Their physical constants agreed with reported data.

*Catalysts.* Standard styrene-divinylbenzene copolymers differing in the degree of cross-linking were sulphonated by two procedures: by concentrated sulphuric acid at 80°C in the presence of 1,2-dichloroethane as a swelling agent or by gaseous sulphur trioxide at 65°C. As proved in our previous work<sup>4</sup>, the former sulphonation leads to a uniform distribution of sulphonic acid groups in the whole copolymer mass, while by the latter method only a relatively thin surface layer of the copolymer particles is sulphonated. The exchange capacity and further properties of the catalysts used are given in Table I. The size of catalyst particles was 0.5–0.63 mm. Prior to using, the catalysts were dried *in vacuo* (14 Torr) at 105°C for 6 h. They were stored in a desiccator over phosphorus pentoxide.

*Apparatus and procedure.* Reactions were carried out in a glass stationary microreactor connected directly to a mass spectrometer (Finnigan, Model 3000). This enabled us to follow quantitatively the composition of the gaseous reaction mixture. The amount of gaseous reactants was determined by the measurement of their volume and pressure before their admission to the evacuated catalyst which was heated to the reaction temperature 100°C. The moment at which the space containing the known amount of the reactant was connected with the catalyst in the reactor was taken as the beginning of the reaction. The composition of the gas phase was analysed at

TABLE I  
Some Data on Standard Ion Exchangers Used

Ion exchanger <sup>a</sup>	Sulphonation procedure	Exchange capacity mequiv/g	Average No of particles in 1 g <sup>b</sup>
SS-2	H <sub>2</sub> SO <sub>4</sub> (1)	5.03	11.706
	SO <sub>3</sub> (g)	0.52	9.644
SS-8	H <sub>2</sub> SO <sub>4</sub> (1)	4.80	8.762
	SO <sub>3</sub> (g)	0.29	12.458
SS-15	H <sub>2</sub> SO <sub>4</sub> (1)	4.19	9.645
	SO <sub>3</sub> (g)	0.13	11.132
SS-25	H <sub>2</sub> SO <sub>4</sub> (1)	3.89	8.593
	SO <sub>3</sub> (g)	0.09	9.808
SS-50	H <sub>2</sub> SO <sub>4</sub> (1)	1.97	10.753
	SO <sub>3</sub> (g)	0.23	10.419

<sup>a</sup> Numerical data relate to the content of divinylbenzene in the copolymer (in per cent). <sup>b</sup> The average number of particles in 1 g was determined by direct counting. <sup>c</sup> The mean diameter of particles was obtained by measuring the sufficient number of the particles in a microscope.

<sup>d</sup> The specific surface of ion exchangers was determined from other data given in this Table.

fixed time intervals. In all measurements the following initial pressures of gaseous alcohols were used: methanol 93.2 Torr; 1-propanol 20.05 Torr, and tert-butanol 42.5 Torr.

## RESULTS AND DISCUSSION

To get data which would allow to discuss changes in the catalytic activity with the degree of cross-linking, some properties of the ion exchangers were measured and calculated (Table I). As it is seen from the results obtained the specific surface of standard ion exchangers is very small. As found by low-pressure thermal desorption from the macroporous ion exchangers substituted with ammonium ion, 6.8% of ammonia is desorbed from the samples having a specific surface of  $35 \text{ m}^2/\text{g}$  and 22% of the total amount of ammonia is released from the samples with a specific surface of  $227 \text{ m}^2/\text{g}$  (ref.<sup>9</sup>). Provided that the desorption takes place only from sulphonic acid groups located in surface layers the amount of desorbed ammonia represents the ratio of surface sulphonic acid groups to the total amount of the groups. A simple extrapolation of these values leads to conclusion that the standard ion exchangers used in this study have on their small specific surface located only 0.001% of sulphonic acid groups.

Mean diameter of particles <sup>c</sup> mm	Mean surface of particles $\text{mm}^2$	Specific surface of ion exchanger <sup>d</sup> $\text{m}^2/\text{g} \cdot 10^3$	Depth of sulphonated layer on particle surface <sup>e</sup> mm
0.50	0.79	9.2	—
0.53	0.78	8.7	0.02
0.59	1.09	9.6	—
0.54	0.91	11.4	0.01
0.43	0.58	5.6	—
0.38	0.45	5.0	0.005
0.57	1.02	8.8	—
0.52	0.85	8.3	0.005
0.51	0.82	8.8	—
0.45	0.64	6.6	0.015

<sup>e</sup> The depth of the sulphonated layer was calculated under the assumption that sulphonic acid groups are located only on the surface of the particle sulphonated by gaseous sulphur trioxide, their concentration being identical with the concentration in the samples sulphonated by sulphuric acid in the presence of a swelling agent.

Jeřábek<sup>10</sup> has found by electron microprobe that sulphonic acid groups of the standard ion exchangers prepared by liquid phase sulphonation with sulphuric acid in the presence of a swelling agent are very uniformly distributed within the mass of copolymer particles. This was established, however, only for the polymers containing less than 25% of divinylbenzene. At the higher cross-linking the sulphonation is not so efficient as to attack the center of particles. Also the decreasing exchange capacity of ion exchangers with the increasing content of divinylbenzene speaks against the completely uniform distribution of sulphonic acid groups. This decrease is at first slow, the difference in the exchange capacity of ion exchangers SS-25 and SS-50 is, however, considerable. One can therefore conclude that the sulphonation of the copolymers with divinylbenzene content up to 25% takes place in the whole mass of particles. However, the number of places in the mass in which sulphonation is not complete increases with increasing content of the cross-linking agent. Starting from the divinylbenzene content 25% the centers of copolymer particles are no more accessible to sulphonation.

Using the assumption about the uniform distribution of sulphonic acid groups in the ion exchangers obtained by sulphonation with sulphuric acid, the number of sulphonic acid groups in the unit volume of the ion exchangers has been calculated. Provided that the so expressed local concentrations are the same for the above sulphonation and the sulphonation with sulphur trioxide, the depth of the sulphonated layer on the surface of the particles sulphonated by gaseous sulphur trioxide could be calculated. The data obtained are presented in the last column of Table I. It is seen that this layer is not too deep. For the reasons mentioned above these assumptions are not justified in the case of ion exchanger SS-50, and the calculated depth of the sulphonated layer does not have to be comparable with others.

We have attempted at determining the relative concentration of sulphonic acid groups in the surface layers of the ion exchangers by means of electron microprobe

TABLE II  
Sulphur Content (% vol.) on Ion Exchanger Surface Determined by Electron Microprobe

Ion exchanger	Sulphonation	
	H <sub>2</sub> SO <sub>4</sub>	SO <sub>3</sub>
SS-2	26.2	32.9
SS-8	27.6	23.6
SS-15	20.6	8.5
SS-25	22.9	12.1
SS-50	21.5	12.1

(Jeol, JXA-50 A). This method was standardized on an inorganic sulphide material containing the known amount of sulphur. However, this material differed significantly in its physical properties from our polymeric catalysts. The results of these measurements are presented in Table II. Each of the values is an average of several measurements made on different places on the surface of several ion exchanger particles. As we have had no information or experience concerning the depth of the polymer mass which is accessible to an electron beam, it could be only said that the sulphur content in the surface layer of the ion exchangers prepared by sulphonation with sulphuric acid decreases with increasing cross-linking at a slower rate than in the ion exchangers sulphonated by gaseous sulphur trioxide. It seems likely that this is due to the fact that the electron microprobe analyzes always the surface layers of the same depths. As in the sulphur trioxide sulphonated samples the sulphonated layer becomes thinner with increasing cross-linking, the total amount of sulphur in the examined volume is smaller. By this method it could not be confirmed, however, reliably that the local concentrations of sulphonic acid groups are identical in both sulphonations.

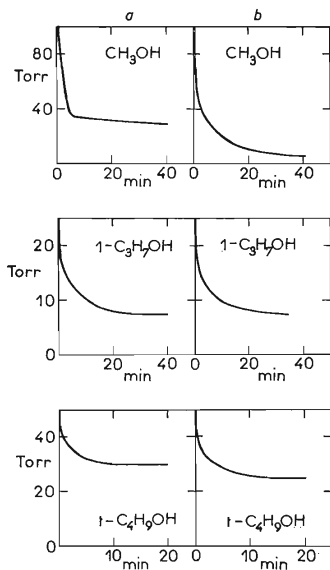


FIG. 1  
Decrease in the Pressure of the Alcohols in the System during Their Dehydration on Standard Ion Exchangers

Temperature 100°C, initial alcohol pressure: methanol 93.2 Torr; 1-propanol 20.05 Torr; tert-butanol 42.5 Torr; *a* ion exchangers sulphonated by sulphur trioxide; *b* ion exchangers sulphonated by sulphuric acid; the curves involve the whole range of the cross-linking degrees of the copolymer.

It is known that sulphonation with sulphur trioxide leads to formation of  $-\text{SO}_2-$  bridges between phenyl groups<sup>11</sup>. Similar compounds could be therefore formed also in the sulphonation of styrene-divinylbenzene copolymers. Since in our case the sulphonation was carried out under very mild conditions the presence of these bonds in our catalysts has not been presumed.

The standard ion exchangers listed in Table I were used as catalysts for the gas phase dehydration of methanol, 1-propanol and tert-butanol at 100°C. All these reactions were studied by us already earlier<sup>1,5-8</sup>, but in those studies we used mainly macroporous sulphonated copolymers as catalysts. We have found that also on standard ion exchangers these reactions proceed selectively, producing the expected products. The chosen catalytic reactions differ in their character. The dehydration of tert-butanol is by three orders of magnitude faster compared to the reaction of other alcohols<sup>6-8</sup>; tert-butanol has the bulkiest molecule, and there is also a marked difference in the stoichiometry of the reactions. We have assumed that all these differences can be utilized in discussion of obtained results.

It is known that organic ion exchangers act as solid solutions and are able to absorb substances from gaseous or liquid phase. This results in the concentration difference between the gas or liquid phase and the mass of the ion exchanger. Since for the reaction catalysed by an ion exchanger the concentration of reactants in the polymer mass is decisive factor, we have also followed the amounts of alcohols absorbed in the catalyst during the reaction. The results are graphically represented in Fig. 1 and show that the ion exchangers dissolve a great amount of the alcohols. In no case depended the course of the pressure decrease of the alcohol significantly upon the degree of cross-linking of the ion exchanger. In approx. 10 min after the beginning of the reaction the equilibrium state of dissolution is established and the alcohol is

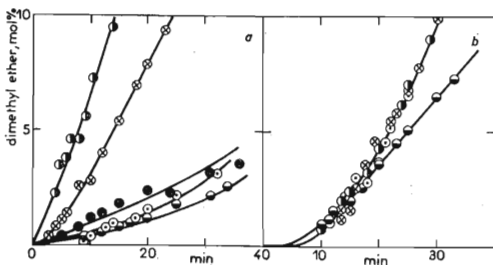


FIG. 2

Kinetic Curves for Dehydration of Methanol on Standard Ion Exchangers

For conditions and denotation see Fig. 1. ● SS-2, ○ SS-8, □ SS-15, ■ SS-25, ● SS-50.

consumed slowly by its transformation to the dehydration product. It should be noted that the alcohols are soluble only in the polar, sulphonated part of the copolymer. The solubility of the alcohols in unsulphonated styrene-divinylbenzene copolymers is very poor. On taking into account this fact, the concentration of a given alcohol in the sulphonated surface layer of the ion exchangers sulphonated by gaseous sulphur trioxide is higher than that in the fully sulphonated particles, since the difference in the amount of the absorbed alcohol is not great (0 to 25%). However, the gas phase sulphonated ion exchangers have more than ten times lower exchange capacity.

In Figs 2–4 are shown kinetic curves for all the reactions on the ion exchangers listed in Table I. Comparison of the shape of these curves reveals differences between the behaviour of the ion exchangers sulphonated by gaseous sulphur trioxide and by sulphuric acid and also the differences between the course of the kinetic curves for the dehydration of tert-butanol and of other alcohols. With the gas phase sulphonated ion exchangers, the degree of their cross-linking affects markedly the reaction rate

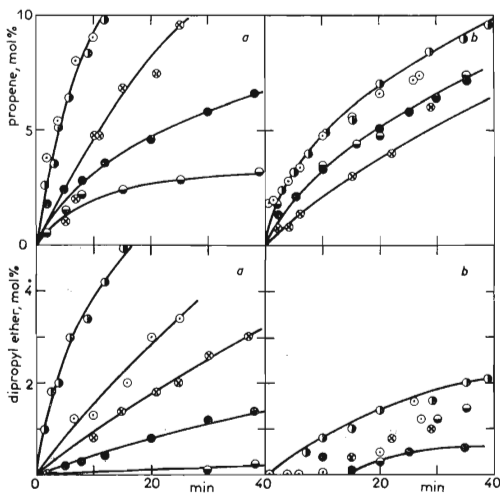


FIG. 3

Kinetic Curves for Dehydration of 1-Propanol on Standard Ion Exchangers

For conditions and denotation see Figs 1 and 2.

of the dehydration of methanol and 1-propanol. The less cross-linked ion exchangers exhibit high activity which decreases with increasing cross-linking. In the case of the ion exchangers sulphonated in liquid phase the effect of cross-linking is not too pronounced in the dehydration of 1-propanol, and in the dehydration of methanol it is practically none.

When using a flow reactor and standard ion exchangers as catalysts we have observed in general the higher activity for the less cross-linked samples<sup>2,5</sup> which decreased with cross-linking.

In the case of the dehydration of tert-butanol the more significant dependence has been observed for the liquid phase sulphonated ion exchangers. The most efficient catalyst was, however, the ion exchanger SS-25 and the others were distinctly less active. This result can be explained by assuming that the bulky molecule of tert-butanol penetrates only with difficulty to a nonporous, though lightly cross-linked, mass of the sulphonated copolymers. The ion exchanger SS-25 possesses an optimal cross-linking in the sense that the space lattice is firm enough to preserve the holes, the dimensions of which are so great that the molecule of tert-butanol can pass through them. This space structure of the copolymer collapses at the lower cross-linking, and tert-butanol is no more able to penetrate into it by swelling. On the other hand, at the higher cross-linking (more than 25% of divinylbenzene) the holes in the space lattice of the copolymer become smaller and the penetration of the bulky molecule of tert-butanol is difficult.

Comparison of the reaction rate of the dehydrations on the ion exchangers sulphonated in different ways shows that the highest activity is exhibited by the lightly cross-linked ion exchangers sulphonated in the gas phase. The high reaction rate is

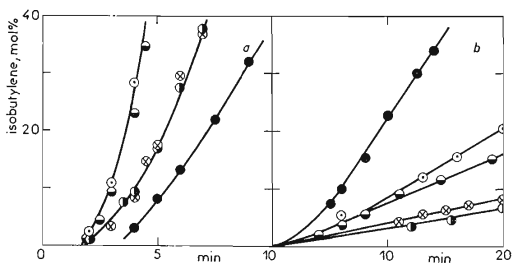


FIG. 4

Kinetic Curves for Dehydration of tert-Butanol on Standard Ion Exchangers  
For conditions and denotation see Figs 1 and 2.



achieved in spite of the fact that the ion exchangers of this type have by more than one order of magnitude lower exchange capacity than the ion exchangers sulphonated by sulphuric acid. This high activity is obviously due to the high concentration of the alcohol in the surface sulphonated layer of the ion exchangers and further also to the fact that in this type the catalytic cycle is not disturbed by diffusion processes in the particle, *i.e.* by the permeation of reactants to the inside of the particles and of the product from the inside to the surface of these particles. It is known that permeation through organic ion exchangers differs considerably for different substances and depends on a number of chemical and structural properties of both the permeating substance and the ion exchanger. Martinec<sup>8</sup> have demonstrated the effect of permeation rate upon the activity and selectivity of the dehydration of 1-propanol on macroporous ion exchangers of varying degree of cross-linking and his conclusions can be applied also to the reactions discussed in the present work. The low activity of the sulphuric acid sulphonated ion exchangers (which is demonstrated by the formation of dipropyl ether) confirms the effect of 1-propanol permeation to the inside of the catalyst particles and also the slow permeation of the reaction products to the surface of particles, during which the ether formed is dehydrated to propene. Similarly, also the dehydration of tert-butanol proceeds at a faster rate on the gas phase sulphonated ion exchangers than on those sulphonated in the liquid phase, and this rate difference is considerable. This results, at least partially, from the high specific rate of the dehydration of tert-butanol and the slow permeation of this alcohol to the inside of the mass of catalyst particles. This permeation is especially extensive in the case of the ion exchangers fully sulphonated by sulphuric acid.

In conclusion, with standard ion exchangers the permeation plays always an important role, retarding the course of the catalytic reaction. This is due to the fact that the reactants disappear in the inside of particles and the products which permeate to the surface prevent other molecules of the reactants from being adsorbed from the gas phase. For that reason the types sulphonated on the surface are more advantageous, since here permeation is practically unimportant. It would be most advantageous to ensure the surface as large as possible, with the catalytically active sulphonated layer located on this surface. This means that the macroporous, higher cross-linked copolymers sulphonated only in surface layers seem to be most promising. Other solution is the diminuation of particle size, which leads to increase in the surface. Very small particles are, however, unsuitable since they cause a high hydrodynamic resistance in the reactor and require the use of the fluidized catalyst bed, which brings about considerable technical difficulties. On the other hand, permeation processes can be sometimes utilized to control the selectivity of reactions, although this is usually achieved at the expense of the total reaction rate.

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