

ORGANIC ION EXCHANGERS WITH ENHANCED CATALYTIC ACTIVITY

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Several methods aimed at increasing the catalytic activity of the sulphonated styrene-divinylbenzene macroporous ion exchanger Wofatit OK 80 have been tested. The activity of the prepared ion exchanger catalysts has been examined in three reactions of different type which allowed to examine the effect of the methods used in the broader range of conditions. The results obtained show that the catalytic activity of ion exchangers can be increased substantially either by increasing the total number of acid functional groups or, particularly, by such treatment which makes the maximal number of the present functional groups accessible to reaction components. However, by the chemical procedures used to enhance the activity, the ion exchangers acquire frequently also some properties which affect negatively their application as catalysts.

One of the ways by which the activity of organic polymer catalysts (*e.g.* ion exchangers) can be enhanced, is to increase the number of functional groups of the polymer or to increase the catalytic efficiency of these groups. Of the organic catalysts, sulphonated styrene-divinylbenzene copolymers have found the widest application and have been, therefore, also intensively studied in this respect. The increase in the number of sulphonic acid groups per mass unit of the ion exchanger can be achieved by the more extensive sulphonation of the starting copolymer, *e.g.* by using suitable solvent, sulphonation catalyst, elevated temperatures, longer sulphonation time¹⁻³ or the more efficient sulphonation method⁴. Enhancement of the catalytic efficiency of sulphonic acid groups has been realized by substituting the polymer with another functional groups or atoms which increase the activity by their favourable electronic induction. This effect is demonstrated in studies on sulphonated styrene-divinylbenzene copolymers containing besides sulphonic acid groups also other functional groups which do not exhibit acidity but affect the catalytic and exchange activity of the ion exchangers. Such substituents are especially nitrogroups, amino groups and halogen atoms⁵⁻⁷. The sulphonated resins containing perfluorinated chains, developed and produced by Du Pont (Nafion resins) are of special interest. The presence of fluorine in these resins increases markedly not only their thermal stability compared to the standard styrene-divinylbenzene copolymers but also the acidity of sulphonic acid groups^{8,9}.

The present work is concerned with the possibility of synthesis of the more efficient ion exchanger catalysts by using the more extensive sulphonation or substitution of the polymer with the other than sulphonic acid groups. The catalytic activity of the so prepared catalysts has been tested in the reesterification of ethyl acetate by 1-propanol carried out in gas phase at 120°C and in liquid phase at 52°C, the gas phase

dehydration of 1-propanol at 130°C and in the liquid phase hydrolysis of ethyl acetate at 52°C.

EXPERIMENTAL

Preparation of Catalysts with Enhanced Exchange Capacity

Resulphonation by sulphur trioxide in liquid phase. Wofatit OK 80 (30 g) (for its properties see Table I) was added slowly to 250 ml of 20% oleum under vigorous stirring and the temperature of the reaction mixture was increased to 120°C. The reaction was interrupted after 5.5 h. The mixture was cooled to ambient temperature and then it was added to concentrated sulphuric acid, 50% sulphuric acid and finally to distilled water. The obtained catalyst 1 (Table I) was washed in a column until neutral reaction of the eluate and then dried at 106°C for 6 h. Catalyst 2 (Table I) was prepared in the same way, except that 1 g of mercuric sulphate was used as sulphonation catalyst and sulphonation was carried out for 15 h.

TABLE I
Properties of catalysts used

Designation	Specific surface m ² /g	Exchange capacity mequiv. H ⁺ /g			Sulphur content from —SO ₃ H %	Sulphur content (analysis) %	P ^a	Mechanical properties
		—SO ₃ H	—COOH	—OH				
0 ^b	31.4	4.45	0.21	0.42	14.2	14.5	0.82	elastic
1	24.2	5.56	0.29	1.00	17.7	18.6	1.03	brittle
2	24.3	5.80	0.30	1.00	18.5	18.6	1.08	brittle
3	9.0	4.55	0.94	1.78	14.5	16.3	0.84	brittle
4	16.2	5.30	0.35	1.25	16.9	17.7	0.98	brittle
5 ^c	2.1	4.81	0.32	0.81	15.4	15.9	0.89	brittle
6 ^d	23.9	2.10	0.19	0.86	6.7	7.0	0.39	elastic
7 ^e	30.9	2.82	0.18	0.72	9.0	9.4	0.53	elastic
8 ^f	30.6	3.98	0.15	0.55	12.7	12.5	0.74	elastic
9 ^g	31.8	3.17	0.06	0.67	10.1	—	0.54	elastic
10 ^h	30.9	2.92	0.14	0.78	9.3	—	0.54	elastic

^a Number of SO₃H groups per one phenyl group of the polymer. ^b Wofatit OK 80 as the starting ion exchanger. ^c Prepared from porous styrene (90%)–divinylbenzene (10%) copolymer, specific surface = 8 m²/g. ^d Nitrogen content (analytically) = 6.43% (by mass) = 4.59 mmol/g. ^e Nitrogen content (analytically) = 5.07% (by mass) = 3.62 mmol/g. ^f Nitrogen content (analytically) = 2.79% (by mass) = 1.99 mmol/g. ^g Cl content (analytically) = 16.1% (by mass) = 4.60 mmol/g. ^h Cl content (analytically) = 15.5% (by mass) = 4.43 mmol/g.

Resulphonation by sulphur trioxide in gas phase. Wofatit OK 80 (7 g) was placed in a column thermostated at 100°C and sulphur trioxide was then introduced (the oxide was generated from 20% oleum heated to 120°C by a stream of argon). Catalyst 3 (Table I) was prepared by sulphonation carried out for 3 h and catalyst 4 (Table I) was obtained after 8 hours sulphonation. After completion of the reaction, the polymer was added to 50% sulphuric acid, then transferred into ice water and washed finally with water until neutral reaction of the eluate. The catalysts were then dried at 105°C for 6 h.

Introduction of sulphonic acid groups by means of disulphur dichloride⁴. Styrene-divinylbenzene copolymer containing 10% of divinylbenzene (30 g) was allowed to stand for 24 h in a closed flask at ambient temperature in the presence of 53.6 ml (90 g) of S₂Cl₂. Then the mixture was cooled to 0°C and transferred slowly to a mixture of 65 ml of 96% sulphuric acid and 10 ml of 10% oleum. The mixture was allowed to stir without cooling for another one hour, during which period its temperature increased to 30°C with simultaneous evolution of hydrogen chloride. The mixture was then heated slowly to 85°C and maintained at that temperature for 6 h. After cooling the polymer was filtered-off, washed with sulphuric acid solutions of gradually decreasing concentration and finally it was washed with water until negative test on the presence of chloride and sulphate ions in the eluate. The polymer showed the exchange capacity of 0.56 mequiv. H⁺/g and the sulphur content determined analytically was 35.8% (by mass). The so prepared and dried polymer was added to 150 ml of 65% nitric acid, temperature was raised to 95°C and maintained for 4 h. After cooling, the polymer was transferred into a column and washed there with distilled water until neutral reaction of the eluate. The so prepared catalyst 5 (Table I) was dried at 105°C for 6 h.

Modification of Ion Exchangers by Other Functional Groups

Nitration of the ion exchanger. Wofatit OK 80 (10 g) was added to the nitration mixture containing 58 ml of 67% nitric acid and 40 ml of 96% sulphuric acid^{5,6}. In the case of catalyst 6 (Table I) the nitration was carried out at 80°C for 4 h, in the case of catalyst 7 and 8 (Table I) the reaction conditions were 65°C, 1 h and 15°C, 2 h, respectively. All the catalysts were then washed with distilled water until neutral reaction of the eluate and dried at 80°C for 6 h.

Nitration of basic polymer. The attempt was made to prepare these catalysts by nitration of styrene-divinylbenzene copolymer, followed by its sulphonation. After nitration of the copolymer containing 10% of divinylbenzene, the content of nitrogen in the polymer was 10.4% (by mass). After sulphonation of the nitrated product by 96% sulphuric acid at 90°C for 6 h, the product did not exhibit any exchange capacity.

Chlorination of the ion exchanger. A mixture of Wofatit OK 80 (20 g) and 80 ml of water was chlorinated in dark for 5 h by gaseous chlorine which was introduced into the mixture by a flow rate of 20 ml/min. Catalyst 9 (Table I) was obtained by chlorination at 80°C and catalyst 10 (Table I) by the reaction at 50°C. After chlorination, both catalysts were washed with distilled water until negative test on the presence of chlorine in the eluate (by iodometric titration).

Potentiometric Determination of Dissociable Groups

Catalyst (0.2 g) was added to 10 ml of 1 M-NaCl and the mixture was allowed to stand for 24 h to attain exchange equilibrium. Then the mixture was titrated potentiometrically with 0.1 M-NaOH. From potentiometric curves, the sulphonic acid groups were evaluated in pH region 0–3, carboxylic groups in pH region 3–6.5 and other groups (mainly hydroxyls) in pH region 6.5–10.5 (ref.¹⁰).

Determination of Catalytic Activity of Ion Exchangers

Gas phase reactions were carried out in a flow integral glass reactor with fixed catalyst bed, liquid phase reactions were made in a flow stirred glass reactor. Reaction conditions are given in Table II. Products were analysed by gas chromatography under following conditions: reesterification — 3 500 × 4 mm column filled with 15% dinonyl sebacate on Celite, 76°C oven temperature; dehydration — 1 400 × 4 mm column packed with 6% diglycerol + 6% poly(ethylene glycol) on Chromosorb, 110°C oven temperature; hydration — 3 000 × 3 mm column packed with Porapak Q, 225°C oven temperature.

RESULTS AND DISCUSSION

Properties of studied polymer catalysts are summarised in Table I. Catalysts 1–4 are those which were prepared with the aim to increase the content of sulphuric acid groups as much as possible by further sulphonation of the starting ion exchanger Wofatit OK 80. Catalyst 5 is the polymer into which the sulphonic acid groups were

TABLE II
Initial reaction rates of model reactions ($\text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$) for catalysts studies

Designation of catalyst ^a	Reesterification ^b		Dehydration ^c			<i>S</i> ^e	Hydrolysis ^d
	liquid phase	gas phase	olefin	ether	total conversion		
0	4.4	10.4	4.3	2.3	6.6	0.53	4.7
1	7.4	16.6	8.8	7.2	16.0	0.82	7.2
2	8.5	17.1	12.7	9.0	21.7	0.71	8.4
3	13.9	10.1	7.1	4.1	11.2	0.58	8.7
4	11.6	11.1	13.5	6.1	19.6	0.45	8.8
5	10.4	9.7	6.4	5.5	11.9	0.86	6.4
6	3.9	12.6	4.1	2.5	6.6	0.61	6.8
7	3.9	11.8	4.2	2.7	6.9	0.64	6.2
8	3.9	12.7	5.7	2.5	8.2	0.44	6.6
9	3.3	10.1	7.5	2.8	10.3	0.37	6.6
10	2.9	8.4	8.0	3.9	11.9	0.49	6.6

^a For designation of catalysts see Table I. ^b Reesterification of ethyl acetate by 1-propanol was carried out at the molar ratio of reactants equaling to 1, in the liquid phase at 52°C without solvent, in the gas phase at 120°C and partial pressure of inert diluent (argon) = 33 kPa. ^c Dehydration of 1-propanol was carried out in the gas phase at 130°C and partial pressure of the reactant = 50 kPa (nitrogen as the inert gas). ^d Hydrolysis of ethyl acetate was carried out at 52°C, using a mixture of the reactant (6 mol.%) and water. ^e The selectivity (*S*) is expressed by the ratio of initial rate of ether formation to olefin formation.

introduced by the action of disulphur dichloride, which—according to literature⁴—would lead to the ion exchanger with the exchange capacity of 6 mequiv. H⁺/g. Catalysts 6–10 are those in which the catalytic activity of sulphonic acid groups of the ion exchanger was influenced by the presence of other functional groups on the organic polymer.

In the first group of the catalysts, the number of sulphonic acid groups has been increased by nearly 30 per cent, and that by sulphonation with oleum at elevated temperatures or by sulphonation with gaseous sulphur trioxide at elevated temperatures. The sulphonation with disulphur dichloride did not yield the results reported in literature. However, it was found that all the methods used to increase the content of sulphonic acid groups in organic polymer lead also to the considerable distortion of polymer skeleton, which reflects in the dark colour of polymer particles, the reduced specific surface and especially in the brittleness of the polymer. The greater distortion of styrene–divinylbenzene copolymer during extensive sulphonation is indicated also by the content of carboxylic and hydroxyl groups formed during sulphonation. These groups are present already in the starting polymer but in smaller amounts, since sulphonation used to prepare the starting polymer was carried out under milder conditions.

The introduction of nitro groups and chlorine atoms into the polymer is accompanied by the cleavage-off of sulphonic acid groups. The number of the groups so incorporated was always greater than that of sulphonic acid groups cleaved off. This allows to assume that in a certain part of the polymer both functional groups are bonded to the same benzene ring. The chemical procedures used to introduce nitro groups and chlorine atoms did not affect unfavourably the organic polymer of the catalyst, since its colour remained light, particles were elastic and their specific surface did not decrease.

The results of testing the catalytic activity of prepared polymer catalysts are presented in Table II. The reesterification of ethyl acetate by 1-propanol catalysed by the ion exchangers in gas and liquid phase was already subject of our interest earlier and that with respect to its kinetics¹¹, the number and distribution of sulphonic acid groups in the catalyst¹² and the dependence of the reaction rate on the crosslinking of the ion exchanger copolymer^{13,10}, similarly as was the gas phase dehydration of 1-propanol^{15,16}. The reesterification was chosen as bimolecular reaction taking place on several active centres, the dehydration is the set of three reactions taking place according to the triangle scheme¹⁵ and the hydrolysis is the reaction which is characterized by the presence of the greater amount of water in the reaction medium in which the ion exchanger swells. We have expected, therefore, that these differences in the character of these reactions would manifest themselves in the activity of the catalysts prepared by different methods.

The increased content of sulphonic acid groups per mass unit of the ion exchanger was achieved by both methods of resulphonation used. Although the increase in the

exchange capacity is greater for catalysts 1 and 2, their catalytic activity is not always enhanced. The difference in the activities of the catalysts resulphonated by both methods mentioned above is seen especially in gas and liquid phase reesterifications. These differences in the catalytic activity cannot be explained only by the total number of active acid groups but also their distribution and state of polymer skeleton of the ion exchanger play here an important role. From the results presented in Table II it follows that for the liquid phase reesterification, the resulphonation with gaseous sulphur trioxide is more advantageous, while for the gas phase reaction it is resulphonation with liquid oleum. Similarly, ion exchangers 1 and 2 show the higher selectivity in the gas phase dehydration of 1-propanol than do ion exchangers 3 and 4. As found by Martinec¹⁵, the higher selectivity is observed with the ion exchangers in which the smaller portion of reaction components penetrates into the mass of polymer particles. Therefore, it seems likely that ion exchangers 1 and 2 have the majority of functional groups participating in the reaction located on the surface of macromolecular gel and the remaining functional groups are not utilized. In the case of ion exchangers 3 and 4 one can expect the more extensive swelling and thus the catalytic utilization of functional groups within the gel. These assumptions are corroborated by the differences between the activity of these ion exchangers in the gas and liquid phase reesterifications. The surface sulphonation of catalysts 1 and 2 is fully exploited in the gas phase reaction, which results in the strong enhancement of catalytic activity, while in the case of catalysts 3 and 4 the determining factor in the liquid phase is swelling of the ion exchanger in the reaction mixture and thus the accessibility of the greater number of acid functional groups. In hydrolysis in aqueous medium, all the exchangers 1–4 exhibit enhanced catalytic activity compared to the starting Wofatit OK 80 resin and ion exchangers 3 and 4 increase somewhat also the reaction rate, which relates most likely to their greater swelling ability.

Ion exchanger 5 did not show the expected exchange capacity. However, its catalytic activity was higher than the activity of Wofatit. The most distinct difference has been found for the liquid phase reesterification, which would speak for good swelling ability of the ion exchanger. On the other hand, dehydration of 1-propanol showed the highest selectivity, and the increase in the activity of catalyst in hydrolysis reaction was relatively small. With regard to the fact that in dehydration the parameter of selectivity seems to be conclusive (according to the study by Martinec), it is reasonable to assume that in catalyst 5 mainly the surface functional groups participate in the reaction.

Ion exchangers 6–10 which besides sulphonic acid groups contain also other functional groups, have turned out to be as active as the starting Wofatit resin. The distinct increase in the activity was found only for hydrolysis and with chlorinated ion exchangers also for dehydration, but the selectivity of the latter reaction was somewhat lower than that observed for Wofatit. If, however, in the case of these ion exchangers containing additional functional groups one takes into account the activity related

to the concentration of sulphonic acid groups present in the polymer, which are assumed to be active centres of all the reactions studied in this work, then these ion exchangers exhibit higher activity than Wofatit. This indicates that the added functional groups show positive effect on the catalytic activity of sulphonic acid groups. However, with regard to the fact that their introduction is accompanied by the cleavage of some of the already present sulphonic acid groups, the resulting activity of the so prepared catalysts is only comparable to that of Wofatit. As the incorporation of other functional groups into Wofatit OK 80 ion exchanger does not result in the distortion of polymer skeleton structure (as follows from the specific surfaces of ion exchangers 6–10, their appearance and mechanical properties) and the incorporated functional groups cannot be expected to show any catalytic activity, the enhanced activity of the remaining sulphonic acid groups on the polymer should be ascribed to the favourable inductive effect of the introduced functional groups.

The results of this work prove again that there exist methods by which the catalytic activity of organic ion exchangers can be markedly increased. This enhancement does not depend only on the total number of acid (or base) functional groups in the mass unit of the polymer, but also, and that to the greater extent, on their distribution on polymer skeleton and on the character of polymer as far as its structure and chemical origin is concerned, since the just mentioned factor can affect strongly the activity of functional groups. Furthermore, one should have in mind that these parameters differ for different types of catalytic chemical reactions and differ even for gas phase and liquid phase reactions.

The serious problem from the standpoint of practical application is the fact that it is not easy to find the way how to ensure optimal properties from all the above mentioned aspects, without creating some undesired properties (such as the brittleness of particles, the cleavage of the already bonded functional groups, *etc*) which result from chemical procedures used to prepare such polymers. For economic reasons, styrene–divinylbenzene copolymer is usually used as the starting resin and any substitution of its hydrogens for functional groups requires rather drastic chemical conditions and forcing reaction conditions. If the greater number of procedures is needed to realize this goal, the greater problems arise, prevailing over the success achieved in enhancing the catalytic activity of ion exchangers.

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