THE EFFECT OF THE CONTENT OF SULPHONIC ACID GROUPS OF AN ION EXCHANGER UPON ITS CATALYTIC ACTIVITY

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Received April 4th, 1978

Measurements of the initial reaction rates of the gas and liquid phase reesterification of ethyl acetate by 1-propanol catalysed by an acid ion exchanger showed that the gradual neutralization of the acid groups by alkali metal ions in aqueous medium decreases uniformly their concentration within the whole mass of the catalyst, which reflects in the gradual decrease in the catalytic activity. On varying the content of sulphonic acid groups by sulphonation of the starting copolymer to a different degree, the ion exchangers possessing fully sulphonated surface layer of different thickness are formed which exhibit the same catalytic activity. The decrease in the activity has been observed only after the sulphonation degree was less than 50 per cent.

Organic ion exchangers are heterogenized acids or bases for which it was already proved that the catalytic behaviour of their functional groups is identical with the action of soluble acids and bases[1-3]. The difference lies in the fact that in the case of the homogeneous catalyst all the molecules present in the system participate in the catalytic reaction while in the case of the ion exchanger only part of the functional groups is available for reactants[3].

The present work was stimulated by the study by Jeřábek[4] who investigated the effect of the partial neutralization of an ion exchanger upon kinetics of the gas phase dehydration of tert-butanol. The dependence of logarithm of the rate constant upon logarithm of the relative concentration of sulphonic acid groups of the ion exchanger was linear. These results were interpreted under the assumption that sodium ions are uniformly distributed on sulphonic acid groups within the whole mass of the ion exchanger and that sulphonic acid group concentration decreases uniformly with the degree of neutralization. The linear dependence obtained was directly related to the mechanism of the reaction. Its slope equaling to about three was in accordance with the possibility of participation of three active sites in the rate determining step. The relationship between the catalytic activity of ion exchangers for the gas phase dehydration of methanol at 100°C which were gradually neutralized by ammonia from the gas phase and by inorganic ions in aqueous media, examined by Setínek and Prokop[5], confirmed the effect of distribution of the acid functional groups in ion exchanger particles upon its catalytic activity.

In the present work we have investigated the catalytic activity of the ion exchangers prepared by partial sulphonation of the starting copolymers for the gas phase reesterification of ethyl acetate by 1-propanol and the dependence of the catalytic activity of partially neutralized ion exchangers and partially sulphonated copolymers for the reesterification carried out in the liquid phase.

EXPERIMENTAL

Catalysts. These were prepared from a styrene–divinylbenzene macroporous copolymer containing 25% of divinylbenzene and having specific surface over 100 m^2/g. Sulphonation of this copolymer by concentrated sulphuric acid in the presence of a swelling agent (1,2-dichloroethane) at 80°C yielded an ion exchanger with the exchange capacity of 3·8 mequiv H^+/g, specific surface of 44 m^2/g and medium pore diameter of 44·5 nm. Partially sulphonated copolymers were prepared by the same procedure, using the lower temperature and shorter sulphonation time. Except the exchange capacity, other properties of the ion exchangers prepared were not determined. One can, however, expect that their specific surface will lie between the values found for the copolymer and the fully sulphonated ion exchanger. Partially neutralized ion exchangers were obtained from the fully sulphonated ion exchanger by neutralization with aqueous sodium hydroxide solution. The neutralization was carried out for 48 h, to ensure the uniform distribution of sodium ions on sulphonic acid groups of the ion exchanger. After that time the ion exchanger was washed carefully with distilled water and dried. For catalytic experiments the fraction containing 0·2—0·3 mm particles was used. Before using, the ion exchangers were dried at 100°C for 6 h under reduced pressure (*c.* 10 Pa).

Compound used. Ethyl acetate, propyl acetate, 1-propanol, ethanol and 1,4-dioxane were dried over anhydrous magnesium sulphate and then distilled. As found by gas chromatography they did not contain impurities and the water content determined by Fisher titration was less than 0·5%. Sulphuric acid and 1,2-dichloroethane were of technical purity grade, nitrogen contained 0·1% of oxygen.

Apparatus and procedure. The liquid phase reactions were carried out in a glass, ideally mixed, flow reactor described earlier[3]. The samples were withdrawn with the use of a capillary after the steady state conditions had been established in the reactor. The gas phase reactions were measured in a glass flow reactor. The catalyst was heated first for 2 h in a stream of nitrogen (dried over molecular sieve). The liquid reactants were fed to the evaporator, evaporated, mixed with nitrogen (carrier gas) and preheated to the reaction temperature and then introduced into the reactor. Reaction products were separated from nitrogen by condensation at −78°C.

Analytical methods. Reaction products were analysed gas chromatographically at 80°C using 0·4 × 250 cm column packed with 20% dinonyl sebaccate on Cellite (nitrogen as carrier gas). The injection port was heated to 150°C.

RESULTS

Gas phase. Reaction rates of the reesterification of ethyl acetate by 1-propanol in the gase phase at 120°C were measured for a series of ion exchangers which were prepared by sulphonation of the starting copolymer (which was identical with the polymer used by Jeřábek[4]) to a different degree. The catalytic activity of these ion exchangers was characterized by initial reaction rates of the reesterification which were determined for varying ratios of the concentrations of the reactants and nitrogen (Table I). It was found that the initial reaction rate of reesterification does not change with the degree of sulphonation over the whole series of partially sulphonated ion exchangers, regardless of concentration conditions. Only with the least sulphonated sample (47%) the initial reaction rate was somewhat lower.

Liquid phase. Initial reaction rates of the reesterification on partially sulphonated ion exchangers (prepared from the same copolymer as in the case of the gas phase reesterification) were determined at 52°C for a broad range of mole fractions of the reactants and solvents (dioxane and cyclohexane). As it is seen from Tables II and III the values of initial reaction rates are essentially identical under given concentra-

TABLE I

Initial Reaction Rates of Reesterification of Ethyl Acetate by 1-Propanol (mol/h kg_{cat}) in Gas Phase at 120°C and at Total Partial Pressure of 0·1 MPa on Partially Sulphonated Ion Exchangers

Sulphonation degree, %	Initial reaction rate for the mixture[a]		
	A	B	C
100	30·2	26·2	19·7
88	29·9	26·8	18·8
82	28·1	—	—
68	31·5	26·8	20·1
63	26·9	—	—
58	29·5	—	—
47	26·2	23·7	14·8

[a] Reaction mixtures had the following composition (in mole fractions): A ester 0·4, alcohol 0·4; B ester 0·6, alcohol 0·2; C ester 0·2, alcohol 0·6.

TABLE II

Initial Rates of Reesterification of Ethyl Acetate by 1-Propanol (mol/h kg_{cat}) in Dioxane at 52°C on Partially Sulphonated Ion Exchangers

Mole fractions of reaction components			Initial reaction rates on ion exchanger with sulphonation degree, %				
Ester	alcohol	dioxane	100	89	63	47	30
0·24	0·56	0·20	1·78	1·83	1·83	1·67	—
0·40	0·40	0·20	2·41	2·49	2·08	2·35	1·80
0·55	0·25	0·20	2·72	2·63	2·86	2·59	1·77
0·72	0·08	0·20	1·88	2·00	1·51	1·53	1·21
0·30	0·30	0·40	1·38	1·41	1·28	1·30	—
0·42	0·18	0·40	1·72	1·66	1·41	1·68	—
0·54	0·06	0·40	0·98	1·05	0·89	0·74	—
0·20	0·20	0·60	0·56	0·55	0·64	0·68	—
0·36	0·04	0·60	0·55	0·30	0·54	0·36	—

tion conditions for all the catalysts sulphonated to a different degree. Variations in the values are only due to experimental error and to the nonhomogeneity of the ion exchangers used.

Another situation has been encountered in the case of partially neutralized ion exchangers which were prepared from the fully sulphonated copolymer. Here, the values of initial reaction rates found in a series of experiments decreased with decreasing degree of neutralization. A typical form of this dependence is shown in Fig. 1; for other concentration values it was analogous.

TABLE III

Initial Rates of Reesterification of Ethyl Acetate by 1-Propanol (mol/h kg_{cat}) in Cyclohexane at 52°C on Partially Sulphonated Ion Exchangers

Mole fractions of reaction components			Initial reaction rates on ion exchanger with sulphonation degree, %		
Ester	alcohol	cyclohexane	100	86	47
0·30	0·50	0·20	2·69	2·73	2·35
0·55	0·25	0·20	3·93	3·12	3·12
0·64	0·16	0·20	3·67	3·23	2·92
0·24	0·36	0·40	1·46	2·10	2·09
0·36	0·24	0·40	2·29	2·65	3·56
0·12	0·28	0·60	0·60	0·89	1·08
0·28	0·12	0·60	1·23	2·25	1·68

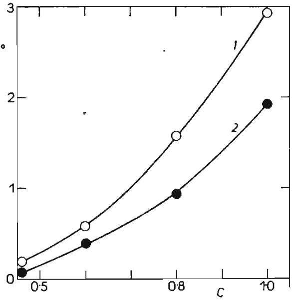

FIG. 1

Dependence of the Initial Reaction Rate of Reesterification in Dioxane Upon the Relative Concentration of Sulphonic Acid Groups of Ion Exchanger

Reaction temperature 120°C, r^0 initial reaction rate (mol/h kg_{cat}), C relative concentration of sulphonic acid groups related to the fully sulphonated copolymer; *1* the ester concentration 5·67 mol/l, the alcohol concentration 3·39 mol/l, dioxane concentration 2·26 mol; *2* similarly 4·72 mol/l, 2·09 mol/l and 4·48 mol/l.

DISCUSSION

From the results obtained in the present work and in a study by Jeřábek[4] it follows that there exists basic difference between the ion exchangers prepared by partial neutralization with alkali metal ions in aqueous medium and by partial sulphonation of the starting copolymer to a different degree as to the effect upon their catalytic activity is concerned.

This difference stems likely from the fact that in the case of partial neutralization of ion exchangers the concentration of acidic active sites decreases uniformly within the whole polymer mass. As the catalytic activity is proportional to the concentration of active groups, it is quite understandable that the activity decreases with decreasing concentration. In the case of the gas phase reaction Jeřábek[4] suceeded in isolating a kinetic parameter of the reaction in the form of its direct correlation with the relative concentration of the active sites of the catalyst and the character of the mechanism of the catalytic reaction.

Independence of the activity of the ion exchangers upon the degree of their sulphonation follows from the fact that also on using the swelling agent in which sulphonic acid dissolves, the sulphonation proceeds from the surface of the polymeric mass. Therefore, the lower the degree of sulphonation, the thinner is the layer of the polymer mass containing surface sulphonic acid groups. In the sulphonated layer, however, the concentration of sulphonic acid groups is uniform and is given essentially by the number of benzene rings. As it is known that in the reaction catalysed by ion exchangers only part of the active sites is operating in the reaction, *i.e.* those which are accessible to reactants and hence nearer to surface, the reaction should proceed at the same rate. Only in those cases in which the degree of sulphonation is so low that the sulphonated layer is thinner than that to which the reactants penetrate in the case of the fully sulphonated copolymer, the decrease in the activity takes place. In our case this was observed in the gas phase reactions on the catalyst sulphonated to 47%. This effect is not so important in the liquid phase reactions.

The initial reaction rates of the reesterification studied are higher in cyclohexane than in dioxane (Tables II and III). This results obviously from the fact that dioxane adsorbs on acidic functional groups and decreases thus the catalytic activity. This agrees with the study by Rodriguez[5] who examined the kinetics of reesterification of ethyl acetate by 1-propanol in dioxane and cyclohexane catalysed by the fully sulphonated ion exchanger of the same type as was that used in the present work. He found that in both solvents the reaction proceeds differently from the kinetic point of view. Dioxane exhibited rate-retarding effect due to its adsorption on acidic functional groups of the ion exchanger, while cyclohexane did not affect the reaction rate.

REFERENCES

1. Thornton R., Gates B. C.: J. Catal. *34*, 275 (1974).
2. Gates B. C., Wisnouskas J. S., Heath H. W. jr: J. Catal. 24, 320 (1972).
3. Rodriguez O., Setínek K.: J. Catal. *39*, 449 (1975).
4. Jeřábek K., Bažant V., Beránek L., Setínek K.: Proc. V. Int. Congr. Catal., West Palm Beach 1972, p. 1193. North Holland Publ. Co., Amsterdam 1973.
5. Setínek K., Rodriguez O.: All-Union Conference on Mechanism of Catalytic Reactions, Moscow 1974.

Translated by J. Hetflejš.