THE EFFECT OF PARTIAL EXCHANGE
OF SULPHONATED MACROPOROUS STYRENE–DIVINYLBENZENE
COPOLYMERS FOR DIFFERENT IONS
ON THEIR CATALYTIC ACTIVITY

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The catalytic activity of sulphonated macroporous styrene–divinylbenzene copolymers, the exchange capacity of which was neutralized from 30, 50 and 80% by Fe(III) ions and from 30% by Na ions and that of Wofatit Y-37 ion exchanger neutralized from 10% of its total exchange capacity by several transition metal ions and by sodium has been studied in isomerisation of cyclohexene and dehydration of 1-propanol in the gas phase at 130°C. It was demonstrated that in both reactions transition metal ions exhibit additional effect to the expected neutralization of the polymer acid groups. In the case of cyclohexene isomerization, this effect depends on the degree of crosslinking of polymer mass of the catalyst. Such dependence has not been, however, observed in dehydration of 1-propanol. The type of transition metal ions did not exhibit any significant effect on the catalytic activity of the polymer catalysts studied.

Organic polymer ion exchangers are frequently used as catalysts for acid–base reactions. The exchange by inorganic ions on acid centres of the polymer leads to a decrease in its activity. This decrease is not, however, proportional in all cases to the number of neutralized acid groups and depends on the type of the ion used for the exchange. In the gas phase isomerization of 1-butene on Amberlyst 15 exchanger at temperatures $40-70°C$ it has been *e.g.* demonstrated that the catalysts with exchanged transition metal ions exhibited higher activity than the catalysts with exchanged alkali metal ions[1]. The authors ascribe the enhanced activity of the ion exchangers containing higher valent transition metal ions to the participation of their Lewis acidity in formation of the activated complex. In the liquid phase addition of methanol to isobutene at 85°C on the ion exchangers of similar type, the partial exchange for transition metals resulted in increased catalytic activity compared to the solely acidic ion exchanger[2]. The addition of transition metal ions leads also to the activation of inorganic oxide catalysts (MgO, ZnO), the degree of activation being dependent on the kind of the incorporated ion and on its vicinity[3].

In the case of partial exchange for alkali metal ions on ion exchangers there exists a linear relation between logarithmic values of rate constants of the surface reaction of gas phase dehydration of tert-butanol and logarithms of relative con-

centrations of residual acid functional groups[4]. Under the assumption of the uniform distribution of alkali metal ions in polymer mass of the ion exchanger, it was possible to calculate the order of the reaction in the catalyst, *i.e.* the number of active centers participating in the catalytic process, from the slope of obtained straight line. As the so obtained reaction order corresponded to the value derived from kinetic analysis of the studied reaction, it was also possible to conclude that alkali metal ions fully neutralize the acid functional groups.

The catalytic activity and selectivity of ion exchangers depend strongly also on the structure and chemical properties of polymer mass and thus on the accessibility of functional groups for reactants, since also in the case of porous types, where geometrical surface plays a certain role, the catalytic reaction proceeds mainly within polymer mass[5]. Furthermore, changes in the polymer structure can affect also the mobility of functional groups or distance between them.

The present work is concerned with the effect of the degree of the exchange for transition metal and alkali metal ions on the catalytic activity of differently cross-linked sulphonated macroporous styrene–divinylbenzene copolymers in the gas phase isomerization of cyclohexene and dehydration of 1-propanol at 130°C and atmospheric pressure.

EXPERIMENTAL

Compounds used. Cyclohexene was prepared from cyclohexanol (chemical purity grade), as reported[6]. Prior to using, the compound was rectified and the fraction boiling at 82—83°C was used. 1-Propanol (analytical purity grade, Reachim) was rectified and the fraction collected at 82—83°C was further used. After drying with re-annealed $MgSO_4$, the water content in the compound was 0·03 w.%. 1-Methyl-1-cyclopentene (b.p. 74—75°C) and 1-methyl-2-cyclo-pentene (b.p. 64—65°C) were prepared by isomerization of cyclohexene on alumina at 500°C (ref.[7]). The obtained product was repeatedly rectified until pure products have been obtained; their purity was verified by gas chromatography. Propene (analytical purity grade), dipropyl ether (Fluka), sodium hydroxide (analytical purity grade, Lachema), transition metal salts, nitrogen for lamps and electrolytic hydrogen (Technoplyn) were used as obtained.

Catalysts were macroporous styrene-divinylbenzene sulphonated copolymers (MS) and Wofatit Y-37 (VEB Chemie-Kombinat, Bitterfeld, GDR, industrially produced and designed for catalytic purposes). Their properties are summarized in Table I. The known amount of a given ion exchanger was placed into a beaker and wetted with a small amount of distilled water. Then the known amount of the appropriate transition metal chloride (except for $CuSO_4$ and $Fe_2(SO_4)_3$) corresponding to the required partial neutralization of the exchange capacity of the ion exchanger was added. With Fe(III) and Cr(III) salts, several drops of the acid corresponding to the anion of the salts used were always added to hot solution, in order to prevent hydrolysis. Ion exchangers partially neutralized by Na ions were obtained by adding the appropriate amount of 0·1M-NaOH. After standing for 48 h with intermittent stirring, the catalysts were washed with water in a column, until negative reaction on the corresponding anion of the metal salt used was obtained. After re-drying with infralamp, the catalysts were dried in a vacuum drier (cca 5 kPa) for 6 h.

Apparatus and procedure. The apparatus used was a glass flow reactor with fixed catalyst bed which was connected *via* a feeding valve to a gas chromatograph. The starting compound was fed by a linear feeding device to an evaporator, to which also nitrogen dried over molecular sieve was introduced, the flow rate of which was controlled by a manostat and measured by a capillary flow meter. Temperature of the catalyst bed was measured by a thermocouple which was placed in the center of the bed. The reactor was heated electrically and its temperature was controlled by a tyristor regulator. The weighed amount of catalyst, W (g), was placed in the reactor and exposed to a stream of nitrogen at the reaction temperature for 1 h. After that, the starting compound was fed at the rate F (mol/h). After steady state conditions have been established in the reactor, six analyses of the reaction mixture were made. As the measurements were performed in the range of low conversions (to 7% mol), conversion data for the starting compound and the time of its contact were used directly to calculate the values of initial reaction rates.

Analytical methods. Analysis of the reaction mixture in cyclohexene isomerization was carried out on a chromatograph equipped with a flame-ionisation detector with the use of a 1 000 × 4 mm packed with 12% dinonyl sebaccate + 4% diglycerol on Cellite at 80°C and the nitrogen overpressure of 0·03 MPa. In the case of 1-propanol dehydration, the analysis was made on a 2 500 × 4 mm column packed with 25% Carbowax 20 M on Chromosorb at 150°C and the nitrogen overpressure of 0·065 MPa. Calibration was performed by plotting the ratio of molar per cent of the product and the starting compound against the ratio of corresponding peak areas. In the case of cyclohexene isomerization the calibration graph was not linear.
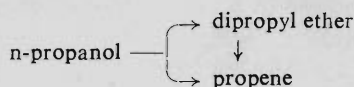
RESULTS AND DISCUSSION

The catalytic activity of partially exchanged sulphonated styrene-divinylbenzene copolymers has been studied with the use of two model reactions: the skeletal isomerization of cyclohexene to 1-methyl-1-cyclopentene (isomer 1) and 1-methyl-2-cyclopentene (isomer 2) and the dehydration of 1-propanol to dipropyl ether and

TABLE I

Properties of ion exchangers used

Designation of ion exchanger	Divinylbenzene content, w.%	Specific surface[a], m^2/g	Porosity[b] %	Exchange capacity meq. H^+/g
MS—10	10	16	13	4·39
MS—15	15	35	45	4·37
MS—25	25	44	58	3·81
MS—40	40	120	59	2·97
MS—60	60	227	53	2·53
Wofatit Y—37	12—15	28	—	4·02

[a] Determined by BET method with nitrogen as the sorbent, [b] calculated from mercury and helium density.

propene. Both reactions were followed at 130°C in the gas phase. Dehydration of 1-propanol was studied under similar conditions earlier[5] and, as confirmed, it proceeds according to the following scheme.

$$
\text{n-propanol} \longrightarrow \left[\begin{array}{l} \longrightarrow \text{dipropyl ether} \\ \qquad \downarrow \\ \longrightarrow \text{propene} \end{array} \right.
$$

The main attention has been paid to the effect of Fe(III) ions, since these ions exhibit the most significant activation effect on the ion exchanger catalyst in the addition of methanol to isobutene[2]. The results of preliminary experiments on cyclohexene isomerization, presented in Table II, show that the catalytic activity of ion exchangers exchanged with Fe(III) and Na ions differs from one another. Especially marked was the decrease in the catalytic activity in the case of Na ions, although the degree of exchange was the same as in the case of Fe(III) ions. This indicates that these ions affect catalytic activity of the ions exchanger in a different manner.

The measurement of the kinetics of cyclohexene isomerization on MS-25 ion exchanger was made with the aim to contribute to its more detailed knowledge. For the reaction temperature used, the value of 52·4% mol was obtained by calculation for the equilibrium concentration of isomer 1 in cyclohexene isomerization. This ensured that the values of initial reaction rates have been obtained in the region sufficiently far from the chemical equilibrium. The results of experiments made with catalyst particles of different size (fractions 0·5 − 0·6 mm and 0·05 − 0·15 mm) showed that the effect of transport phenomena on the reaction course can − under

TABLE II

Activity of partially exchanged MS−25 ion exchanger in the isomerization of cyclohexene at 130°C and cyclohexene partial pressure $p_A = 38·1$ kPa

Ion used for exchange	Neutralized portion of the total exchange capacity %	Initial reaction rate of formation, mol/g kg		Selectivity r_1^0/r_2^0
		isomer 1 r_1^0	isomer 2 r_2^0	
None	0	2·16	0·48	4·50
Fe(III)	30	1·54	0·22	7·00
Fe(III)	50	1·16	0·17	6·82
Fe(III)	80	0·21	0·05	4·20
Fe(III)	100	0·04	0·01	4·00
Na	30	0·09	0·03	3·00
Na	50	0·05	0·01	5·00
Na	80	0·08	0·02	4·00

the conditions used — be neglected. It was found that the catalytic activity of the catalyst with exchanged Fe(III) ions decreases on storring the catalyst for several days. For that reason these catalysts were prepared immediately before kinetic measurements. With regard to the desactivation of these catalysts during the course of the reaction resulting from polymerization of both the starting compound and the products, always fresh samples of the catalyst were weighed and applied to experiments and the analyses of reaction mixtures were made as soon as possible. Examination of the reproducibility of data obtained has shown that the catalytic activity becomes irreproducible at cyclohexene partial pressure higher than 70 kPa, likely due to the capillary condensation of cyclohexene in the pores of the ion exchanger. Hence, the activity of the catalyst was measured only to the partial pressure of 60 kPa.

In the range of partial pressures 3−60 kPa, twenty values of initial reaction rates of formation of isomer 1 and isomer 2 were obtained for the gas phase isomerization of cyclohexene on MS-25 ion exchanger. With both products, the dependence of initial reaction rates on partial pressures shown maximum around 40 kPa. Obtained experimental data were correlated by Marquardt nonlinear regression with kinetic equations of Langmuir-Hinshelwood type. These kinetic equations described different types of the course of the reaction studied: the surface reaction as the rate determing step, the adsorption, either molecular or with dissociation, one or two reacting molecules and one to three active centers necessary to form the activated complex. Experimental data fit best the kinetic equations corresponding to the mechanism involving participation of one (Eq. (*1*)) or two (Eq. (*2*)) cyclohexene molecules in the formation of the activated complex on three active centers (Table III).

For differently crosslinked ion exchangers, the values of initial reaction rates of formation of both isomers were measured at three partial pressures of the reactant, which were uniformly distributed in the studied region (15·1; 40·4; 60·8 kPa). The same procedure was also to determine these data for the ion exchangers which were partially neutralized with Fe(III) ions to 30, 50 and 80% of their original exchange capacity. Initial reaction rates so obtained showed in all cases a similar trend to the rates obtained for MS-25 ion exchanger. This demonstrates that changes in the

TABLE III

Kinetic equations for cyclohexene isomerization and their constants

No	Equation	Rate constant k, mol/h kg	Adsorption coefficient K_A, kPa^{-1}	Number of experimental points, n	Sum of squared deviations Q
(*1*)	$r^0 = kK_A p_A/(1 + K_A p_A)^3$	12·0	0·012	28	0·590
(*2*)	$r^0 = kK_A p_A^2/(1 + K_A p_A)^3$	0·065	0·055	28	0·257

crosslinking of the ion exchanger and partial pressure do not alter the mechanism of the reaction. Therefore, the activity of the catalysts under study can be compared with the use of initial reaction rates determined at one partial pressure of cyclohexene.

From Fig. 1 it is seen that the reaction rate of both isomerization products increases with increasing crosslinking, in agreement with the results reported in our previous works[8,9]. This fact is obviously due to the greater specific surface of the higher crosslinked catalysts, which ensures that the greater number of functional groups becomes available for the interaction with the reactant. As the form of the dependence of both isomers (Fig. 1a,b) is analogous, also the selectivity of the reaction does not depend on the degree of crosslinking.

The effect of partial exchange on the activity of individual catalysts is different for Fe(III) ion and Na ion. The logarithmic dependences of initial reaction rate r^0 on the concentration of unexchanged acid functional groups in the ion exchanger ($c_{rel} = c$ of the unexchanged SO_3H/c of the total amount of SO_3H) gave a linear relationship both for Fe(III) ions and Na ion, which were not fulfilled only by data for the catalysts exchanged from 80% with Fe(III) ion. The results concerning the formation of both isomers have been treated in a similar way. The relations obtained can be expressed by Eq. (3).
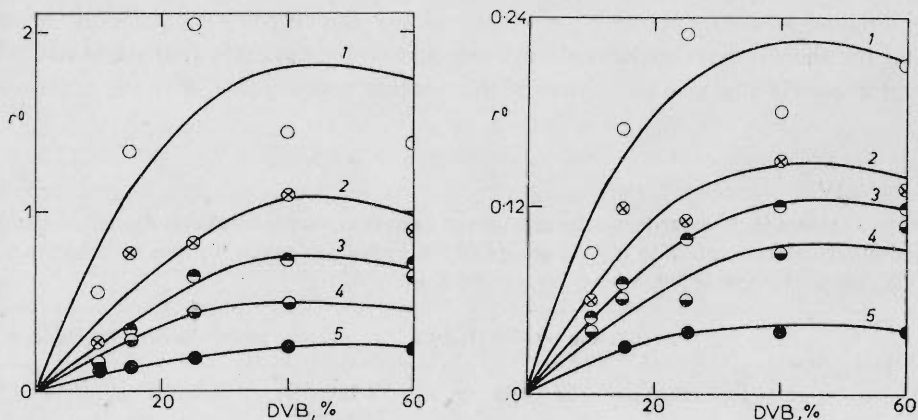
$$\log r^0 = a + b \log c_{rel} \tag{3}$$

Table IV presents the values of slopes of straight lines (b), with the exclusion of points for the polymers exchanged from 80% with Fe(III) ion, the data obtained from initial reaction rates of formation of isomer 2 being given in parentheses.

With regard to the same mechanism for all the catalysts, obtained initial reaction rates should be proportional to the rate constants. In this case the slope of straight lines (b) (Eq. (3)) can be related to the apparent number of active centers required for formation of the activated complex. From Table IV it becomes clear that obtained values of the slopes can be divided into three groups. For the MS-10, 15 and 25 catalysts exchanged by Fe(III) ions they have a value of approx. 2, for MS-40 and 60 catalysts they equal to approx. 0·9 and for the catalysts exchanged by Na ions these values are close to 6. In the case of formation of isomer 2, the proportions of these three groups remain similar, the absolute values of the slopes are, however, somewhat lower.

From the foregoing discussion it follows that the formation of the activated complex is affected both by the degree of catalyst crosslinking and by the type of the ion used for exchange. With regard to the lower slopes for the catalysts exchanged by Fe(III) ion it seems likely that this ion can − at least in some cases − participate in the formation of the activated complex, while Na ion has not such possibility.

The activity of Wofatit Y-37 ion exchanger was examined similarly as was the activity of the above MS catalysts. This ion exchanger was exchanged only to 10% of its initial exchange capacity, similarly to our previous work[2]. Conditions used in experiments and results obtained are presented in Table V.

The exchange by Fe(III) and Cr(III) ions to 10% of the exchange capacity leads to minimal activity decrease, the values of the slopes being significantly smaller than for the catalysts exchanged by other ions. This indicates that these two ions exhibit specific effect on the course of the reaction under study. With the other ions,

TABLE IV

Values of slopes (b) of logarithmic dependences of initial reaction rates of cyclohexene isomerization on relative concentration of acid groups of ion exchangers (Eq. (3)); data without brackets are for isomer 1, those in parentheses correspond to isomer 2

Ion	Neutralization by Fe(III) ions			Neutralization by Na ions	
	$p_A = 15\cdot2$ kPa	$p_A = 30\cdot4$ kPa	$p_A = 60\cdot8$ kPa	$p_A = 30\cdot4$ kPa	$p_A = 60\cdot8$ kPa
MS−10	1·97 (0·97)	1·92 (0·97)	2·02 (1·22)	−	−
MS−15	2·32 (0·99)	1·94 (1·17)	1·93 (1·06)	6·57 (4·84)	5·75 (4·69)
MS−25	2·20 (0·97)	1·42 (1·16)	1·88 (1·76)	6·84 (4·90)	5·81 (4·86)
MS−40	0·94 (0·53)	0·78 (0·56)	0·72 (0·60)	4·90 (4·22)	4·38 (2·38)
MS−60	0·92 (0·57)	0·92 (0·43)	0·64 (0·69)	5·26 (4·65)	5·02 (4·22)

reaction rates and the slopes of straight lines are similar to the MS catalysts exchanged to 30% of their exchange capacity and thus the specific effect of the ion itself is minimal or none. As both ions exhibiting enhanced catalytic effect are threevalent, it seems likely that the valency of neutralizing ion influences the formation of the activated complex. Furthermore, the results have indicated that the most important effect of ions can take place in the region of 10% exchange of the toal capacity of the ion exchanger.

The second model reaction studied analogously to the above discussed cyclohexene isomerisation using the above series of ion exchanger catalysts was dehydration of 1-propanol at 130°C. The results obtained are given in Table VI. It can be stated that these results support conclusions derived by Martinec[5], especially as far as selectivity changes with ion exchangers crosslinking are concerned. In the dehydration of 1-propanol the activity of the catalysts partially exchanged with Fe(III) ions did not change on storing. However, the catalysts showed the same difference as in the isomerization reaction as far as the effect of Fe(III) and Na ions is concerned. Thus, also in this reaction which differs significantly from cyclohexene isomerization, Fe(III) ions influence specifically formation of the activated complex, whereas Na seems to be quite ineffective. As the slopes of logarithmic dependence of initial reaction rates on relative concentrations of acid functional groups of ion exchangers are close to the values obtained for cyclohexene isomerization, it seems likely that the effect of Fe(III) ions does not depend on the type of chemical reactions. In the case of dehydration of 1-propanol this is supported also by essentially the same change

TABLE V

Activity of Wofatit Y—37 ion exchanger exchanged to 10% of its total exchange capacity by metal ions in the isomerization of cyclohexene at 130°C and cyclohexene partial pressure $p_A = 50$ kPa

Ion used for exchange	Initial reaction rate of formation mol/g kg		Selectivity r_1^0/r_2^0	Slope b (Eq. (3))	
	isomer 1 r_1^0	isomer 2 r_2^0		isomer 1	isomer 2
None	1·64	0·18	9·11	—	—
Fe(III)	1·71	0·19	9·00	−0·40	−0·51
Cr(III)	1·57	0·17	9·23	0·41	0·54
Co(II)	1·28	0·15	8·53	2·35	1·73
Ni(II)	1·07	0·12	8·90	4·05	3·85
Cu(II)	1·16	0·15	7·73	3·30	1·73
Zn(II)	1·72	0·16	8·87	1·37	1·12
Na(I)	0·67	0·10	6·70	8·50	5·58

TABLE VI

Activity of MS catalysts partially exchange by metal ions in dehydration of 1-propanol at 130°C and 1-propanol partial pressure $p_p = 10$ kPa

Ion exchanger	Ion used for exchange	Degree of exchange %	Initial reaction rate mol/h kg		Selectivity r_E^0/r_0^0	Slope b (Eq. (3))	
			olefin r_0^0	ether r_E^0		olefin	ether
MS—15	none	0	6·88	5·72	0·83	—	—
MS—25	none	0	5·09	5·14	1·01	—	—
MS—40	none	0	6·18	7·90	1·28	—	—
MS—60	none	0	1·07	3·93	3·67	—	—
MS—15	Fe(III)	30	5·21	4·28	0·82	0·78	0·81
MS—25	Fe(III)	30	3·35	3·04	0·91	1·17	1·47
MS—40	Fe(III)	30	1·98	3·38	1·70	3·19	2·38
MS—60	Fe(III)	30	0·76	2·73	3·58	0·96	1·02
MS—15	Na	30	0·66	0·93	1·40	6·57	5·09
MS—25	Na	30	1·38	1·64	1·19	3·66	3·20
MS—40	Na	30	0·40	1·12	2·79	7·68	5·48
MS—60	Na	30	0·32	1·62	5·06	3·38	2·52

TABLE VII

Activity of Wofatit Y—37 ion exchanger exchanged to 10% by metal ions in dehydration of 1-propanol at 130°C and 1-propanol partial pressure $p_p = 10$ kPa

Ion used for exchange	Initial reaction rate mol/h kg		Selectivity r_E^0/r_0^0	Slope b (Eq. (3))	
	olefin r_0^0	ether r_E^0		olefin	ether
None	7·54	5·83	0·77	—	—
Fe(III)	6·95	5·07	0·73	0·77	1·32
Cr(III)	6·09	4·01	0·66	2·03	3·59
Co(II)	5·72	3·92	0·68	2·62	3·77
Ni(II)	5·74	3·81	0·55	2·59	5·75
Zn(II)	7·07	5·05	0·71	0·61	1·36
Cu(II)	5·39	4·01	0·74	3·18	3·55
Na	3·36	2·71	0·81	7·67	7·27

in the selectivity of the reaction in dependence on the degree of crosslinking for the acidic and partially exchanged catalysts.

Similarly as in isomerization of cyclohexene, also the activity of Wofatit Y-37 ion exchanger was measured for the original unexchanged catalyst and the ion exchanger partially exchanged with a series of metal ions. The results are presented in Table VII.

In accordance with MS catalysts also in this case there exists a difference between the catalysts partially exchanged by transition metal ions and by sodium. With the catalysts exchanged by Fe(III) and Zn(II) ions, the slopes of linear logarithmic dependences of initial reaction rates on relative concentrations of acid groups of the ion exchanger have smaller values. With respect to the smaller number of experimental data obtained, it was not possible to draw any conclusions from this difference.

It seems that transition metal ions exchanged on sulphonated styrene-divinyl-benzene copolymer catalysts exhibit also other than solely neutralization effect. This was demonstrated by their higher catalytic activity relative to the catalysts exchanged by catalytically inactive Na ions. The character of this action of transition metal ions can be ascribed tentatively to either one of the two processes. The first one is the direct participation of transition metal ions (especially Fe(III) ions) in formation of the activated complex and the second involves the effect of these ions on the properties of polymer catalyst mass which leads to the indirect improvement of transport of reactants. For that reason the attention was paid to the dependence of the catalytic activity of exchanged ion exchangers on the degree of crosslinking of their polymer mass. In the case of isomerization of cyclohexene, the slopes of linear logarithmic dependences of initial reaction rates on relative concentrations of acid functional groups were smaller for the higher crosslinked catalysts. In dehydration of 1-propanol this trend has not been observed; the effect of crosslinking on the activity of partially exchanged catalysts depends obviously on the type of chemical reaction and further verification of this assumption with the use of other model reactions would be profitable. Concerning the specific effect of individual transition metal ions on the catalytic activity of studied catalysts, experimental data obtained so far do not allow to draw any reliable conclusions.

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