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Dependence of Esterification Rates on Crosslinking of Ion Exchange Resins Used as Solid Catalysts

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A series of standard and macroreticular sulfonated styrene ion exchangers, with the broadest possible range of divinylbenzene content, were used to study the effects of particle size and crosslinking on reaction rate. The reesterification of ethyl acetate with 1-propanol in liquid and gas phase was chosen as a model reaction. It was found that particle size does not affect significantly reaction rates. The degree of crosslinking exerts a different effect in standard and macroreticular ion exchangers. A comparison of reaction rates on standard ion exchangers with the reaction rate of reesterification catalyzed by soluble *p*-toluenesulfonic acid has proved that the ion exchanger and the soluble catalyst differ only in the accessibility of their functional groups.

Organic ion exchangers have several specific properties as catalysts, one of them being the effect of the amount of crosslinking agent in the macromolecule of polymer on their physical, chemical and catalytic properties. The effect of the content of divinylbenzene in ion exchangers of styrene–divinylbenzene type on the catalytic activity was already studied. In the case of gas phase reactions this problem was investigated by Prokop and Setínek (*1*) who used series of ion exchangers of both standard and macroreticular type in the study of dehydration of aliphatic alcohols. Andrianova (*2*) examined the decomposition of formic acid and its esterification with ethanol on ion exchangers with different degrees of crosslinking and with varying ion exchange capacity. Both authors found that catalytic activity of standard ion exchangers decreases with increasing crosslinking, while the activity of macroporous ion exchangers increases due to their increasing surface. Several studies were devoted to liquid phase reactions catalyzed mainly with standard ion exchangers of varying crosslinking. Czürös and co-workers (*3*) studied Claisen condensation of aromatic aldehydes on a strongly basic anion exchanger of the Zerolit FF-IR type. A number of studies were concerned with esterification and hydrolysis of aliphatic compounds (*4–7*), or with the Prins reaction (*8,9*), on sulfonated ion exchangers. Bafna and Bhale (*10*) reported on the reaction of acetone with iodine, Verkhovskaya and co-workers (*11*) on the reaction of phenol with acetone, and Bodamer and Kunin (*12*) studied the inversion of saccharose. Alkylation of benzene with lower olefins on sulfonated ion exchangers of varying degree of crosslinking was protected by a patent (*13*). In these studies it was stated that the catalytic activity of ion exchangers decreases with increasing crosslinking of copolymer matrix. Different conclusions were reached only by Frilette *et al.* (*14*).

In this work we have made a compari-

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son of a series of standard and macroreticular sulfonated ion exchangers with the broadest possible range of crosslinking. For this reason we have chosen reesterification of ethyl acetate with 1-propanol as a model reaction. This reaction proceeded at an adequate rate and was selective with the above catalysts. The aim of the work was to find the dependence of reaction rates on the degree of crosslinking for different reaction conditions. The same series of ion exchangers was used in the study of the sorption of ammonia (*15, 16*) and aliphatic amines (*17*), which rendered it possible to compare the data on the accessibility and distribution of active sites in adsorption and catalytic reaction.

EXPERIMENTAL METHODS

Catalysts

Styrene–divinylbenzene copolymers with varying amounts of divinylbenzene were swelled with 1,2-dichloroethane and then sulfonated with concentrated sulfuric acid at temperatures below 100°C. After decantation, the ion exchangers were washed with distilled water until they showed a negative test for the presence of sulfate ions; they were predried in air at room temperature and then dried at about 10 Torr and 100 to 120°C for 6 hr. The exchangers were stored in a desiccator over phosphorus pentoxide. Properties and designation of the ion exchangers are given in Table 1. Pore distribution curves of macroreticular ion exchangers are shown in Fig. 1. Liquid phase experiments were performed with 0.09–0.20 mm particles, and gas phase experiments with 0.20–0.30 mm particles.

The chemically pure monohydrate of *p*-toluenesulfonic acid was used without further purification.

Materials

Ethyl acetate, propyl acetate, 1-propanol, and 1,4-dioxane were dried over anhydrous magnesium sulfate and distilled. The absence of impurities was verified by gas chromatography. The compounds contained less than 0.5% water, as determined by Fisher titration.

Sulfuric acid and 1,2-dichloroethane were of technical purity grade; pure nitrogen contained 0.1% oxygen.

Apparatus and Procedure

The reesterification in the liquid phase with ion exchangers as catalysts and dioxane as diluent was measured at 52°C

TABLE 1
PROPERTIES OF ION EXCHANGERS USED

Ion[a] exchanger	Exchange capacity (meq/g)	Specific surface (m^2/g)	Mercury density (g/cm^3)	Helium density (g/cm^3)	Porosity (%)	Medium pore radius (Å)[b]
SS-2	4.90	<0.1	—	—	—	—
SS-8	4.75	<0.1	1.43	1.45	0.01	—
SS-15	4.38	<0.1	1.39	1.43	0.04	—
SS-25	3.72	<0.1	1.35	1.38	0.02	—
SS-50	1.97	<0.1	1.39	1.45	0.04	—
MS-10	4.00	16	1.27	1.46	13	225
MS-15	3.81	35	0.75	1.36	45	445
MS-25	3.80	44	0.61	1.45	58	445
MS-40	3.20	120	0.57	1.40	59	320
MS-60	3.02	227	0.53	1.45	63	225

[a] SS = Standard sulfonated ion exchangers; MS = macroreticular sulfonated ion exchangers; the number denotes the content of divinylbenzene in percent.

[b] Determined by mercury porosimetry.

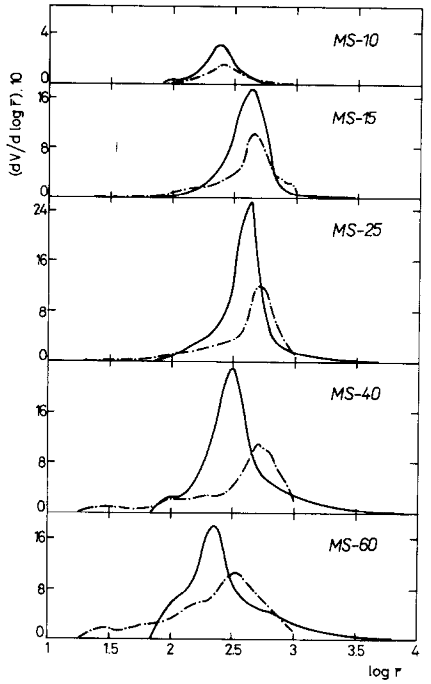

FIG. 1. Pore distribution curve for macroreticular ion exchangers: (—) by mercury porosimetry, (—·) from desorption of *n*-heptane.

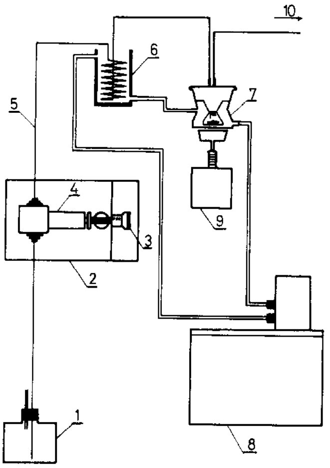

FIG. 2. Ideally mixed glass-tank flow reactor: (1) container of reaction mixture, (2) feeding pump, (3) regulator of pump piston stroke, (4) piston, (5) reaction mixture mains, (6) preheater, (7) reactor, (8) thermostat, (9) magnetic stirrer, (10) removal of product samples.

in an ideally mixed glass-tank flow reactor (about 100 rpm). The correct operation of the reactor was tested by the method suggested by Bennett *et al.* (*18*). The apparatus is schematically shown in Fig. 2. Samples for analysis were removed when steady state conditions were achieved.

The liquid phase reesterification with *p*-toluenesulfonic acid as a catalyst, and 1,4-dioxane as diluent, was measured at 52°C in a three-necked flask equipped with a stirrer, and heated in a temperature-controlled bath. Samples for analysis were removed by using a capillary tube at appropriate time intervals. In all experiments the volume of reaction mixture was kept constant.

The gas phase reesterification was measured in a glass flow reactor at 120°C. The catalyst was previously preheated in the reactor at the reaction temperature for about 1-2 hr in a stream of nitrogen. Liquid reactants were fed to an evaporator, in which they were mixed with nitrogen and then introduced to the reactor. Reaction products were separated from the stream of nitrogen by condensation at −78°C.

Analytical Methods

Reaction products were analyzed chromatographically on a 0.4 × 350 cm column filled with 15% dinonyl sebacate on Celite at 76°C, using nitrogen as a carrier gas. The injection port temperature was 150°C.

RESULTS AND DISCUSSION

Liquid Phase

We first measured initial reaction rates of the liquid phase reesterification of ethyl acetate with 1-propanol in dioxane at a temperature of 52°C on ion exchangers of varying particle size and of varying cross-linking (Table 2). The composition of the reaction mixture was identical with that for which the highest reaction rate was obtained in the gas phase reaction (*19*). It was found that the particle size of catalyst does not strongly influence the reaction rate. The moderate increase of the reaction rate with decreasing particle size of standard ion exchangers is most probably due to their increasing geometrical surface.

TABLE 2
INITIAL REESTERIFICATION RATES FOR THE ETHYL ACETATE–1-PROPANOL–DIOXANE SYSTEM

	Initial reaction rate (mole/hr kg_{cat})[a]		
	Particle size (mm)		Powder approx
Catalyst	0.50–0.31	0.31–0.16	0.05 mm
SS-2	18.57	19.55	19.92
SS-8	8.90	9.46	8.94
SS-15	2.06	2.40	2.00
SS-25	0.66	0.68	0.92
SS-50	0.18	0.26	0.37
MS-10	3.88	4.44	6.01
MS-15	3.60	3.85	4.19
MS-25	3.35	3.60	3.42
MS-40	4.13	4.51	4.38
MS-60	4.59	4.38	4.33

[a] Composition of the reaction mixture in molar fractions: ethyl acetate, 0.4; propanol, 0.4; dioxane, 0.2; reciprocal space velocity of ethyl acetate, 5.8×10^{-3} kg_{cat} hr/mole.

With macroreticular ion exchangers, whose specific surface is not essentially changed on shattering, the size of particles does not affect the reaction rate.

With standard ion exchangers, the initial reaction rate is strongly dependent on the crosslinking of the copolymer (Fig. 3, curves 1 and 2). In this case only a small amount of active groups resides on polymer surface, and is then directly accessible from the liquid phase. The change of reaction rate should be therefore due to the different accessibility of sulfonic acid groups located within the gel, in differently crosslinked ion exchangers. Swelling of ion exchangers increases with decreasing crosslinking, i.e., molecules from the liquid phase penetrate more easily through the mass of polymer to the sulfonic acid group located below the surface. Since, in agreement with experiments with catalyst samples of varying particle size we do not presume that reaction rate is decreased by diffusion, it is necessary to assume the existence of two different regions in the polymer mass of the ion exchanger. In one of these regions sulfonic acid groups are easily accessible, and in the other they are inaccessible. Since reaction rate is only very little influenced by particle size, these two regions have to be uniformly distributed within the ion exchanger and they should then form space inhomogeneity of the polymer mass. The total volume of the accessible region in the volume unit of the polymer mass of the ion exchanger depends on the crosslinking of the exchanger in such a way that the number of accessible functional groups increases with decreasing content of divinylbenzene. We as-

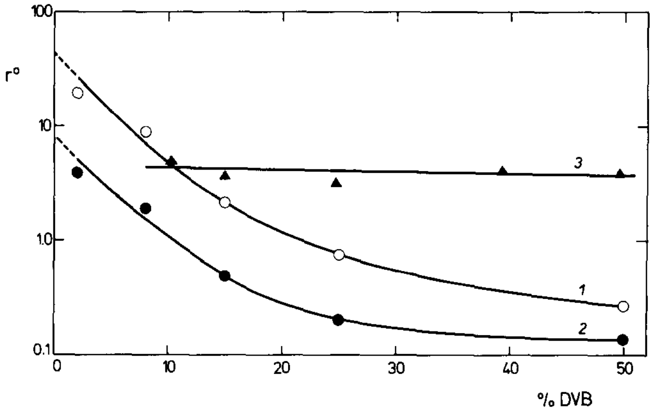

FIG. 3. Dependence of initial reaction rate of reesterification in dioxane on crosslinking of ion exchangers: (1) initial reaction rate [mole/hr kg_{cat}], on standard ion exchangers; (2) initial reaction rate [mole/hr mole of sulfonic acid groups] on standard ion exchangers, (3) initial reaction rate [mole/hr · kg_{cat}] on macroreticular exchangers.

sume that reactants penetrate readily through swelled polymer mass to accessible sulfonic acid groups and that, on the other hand, they cannot reach sulfonic acid groups in the inaccessible region.

The dependence of reaction rate on the degree of crosslinking of standard ion exchangers can be extrapolated to the ion exchanger without divinylbenzene (SS-0). The latter exchanger should be soluble and all of its sulfonic acid groups should be accessible. From this assumption, it follows that only about 50% of the total amount of sulfonic acid groups of the exchanger SS-2, and only about 0.5% of the sulfonic acid groups of the exchanger SS-50, take part in catalytic reaction. The parallel nature of curves 1 and 2 in Fig. 3 confirms further that differences in the exchange capacity of ion exchangers do not substantially affect this dependence. The extrapolated value of the initial reaction rate for SS-0 (43 mole/hr kg_{cat} or 8.5 mole/hr mole of sulfonic acid groups) is close to the value found in the homogeneous reaction catalyzed by *p*-toluenesulfonic acid under the same conditions (48 mole/hr kg_{cat} or 9.4 mole/hr mole of sulfonic acid groups). This result shows that the catalytic activity of the sulfonic acid group bonded to polymer skeleton is identical with the activity of the sulfonic acid group of soluble *p*-toluenesulfonic acid. Therefore, the same reaction mechanism can be expected to operate in both homogeneous and heterogeneous reesterification. This assumption was confirmed in our previous work (*20*). The obtained results also seem to indicate that the assumption of Helfferich (*21*) about different concentration of reactants in the solution and in the gel cannot be applied in our case.

With the macroreticular ion exchangers, the reaction rate changes only to a small extent with crosslinking (Fig. 3, curve 3) and the values are always higher than those determined for standard ion exchangers of the same crosslinking. As the proper polymer mass is the same in both standard and macroreticular ion exchangers, the relations established with standard ion exchangers should be valid also for macroreticular ion exchangers. Macroreticular ion exchangers are, however, porous and their surface changes with crosslinking (Table 1, Fig. 1), and then the number of directly accessible sulfonic acid groups also changes. For that reason the crosslinking of copolymer acts in two opposite ways: on increasing crosslinking the accessibility of active centers within the ion exchanger mass decreases, similarly to standard ion exchangers, but at the same time their surface markedly increases, which enables a greater number of active groups to be directly approached from the liquid phase. A combination of these two effects results in the reaction rate being little dependent on the crosslinking of macroreticular ion exchangers.

By using the specific activity of sulfonic acid groups found in the homogeneous system and the percentage of active groups

TABLE 3

CALCULATED AND EXPERIMENTAL VALUES OF INITIAL REESTERIFICATION RATES FOR MACRORETICULAR ION EXCHANGERS[a]

Catalyst	r_t^0 (mole/hr kg_{cat})	Percentage of surface $-SO_3H$ groups (%)[b]	r_s^0 (mole/hr kg_{cat})	r_e^0 (mole/hr kg_{cat})
MS-10	36.52	3	1.09	5.56
MS-15	34.78	7	2.43	4.00
MS-25	34.69	12	4.16	3.36
MS-40	29.22	19	5.55	3.78
MS-60	27.57	25	6.89	4.02

[a] r_t^0 = initial reaction rate calculated under the assumption that all sulfonic acid groups of the ion exchanger participate in catalytic reaction (the reactivity of 1 mole of sulfonic acid groups = 9.4 mole/hr); r_s^0 = initial reaction rate calculated under the assumption that only surface sulfonic acid groups react; r_e^0 = experimental initial reaction rate of reesterification in dioxane.

[b] Values recorded by Prokop and Setínek (*16*).

on the surface of the ion exchangers, which was determined in studies of adsorption and desorption of ammonia and organic bases (*1*, *16*), we have calculated hypothetical values of initial reaction rates of reesterification under the assumption that only surface active groups participate in the reaction (Table 3). The values for MS-10 and MS-15 are lower than the experimental values. This confirms again that besides surface sulfonic acid groups, also some sulfonic acid groups located within the gel of ion exchangers take part in the catalytic reaction. Calculated values for MS-25, MS-40, and MS-60 are higher than the experimental values, which shows that not all of the surface groups are accessible. Very small pores might be sealed by swelling of the ion exchanger in the reaction mixture, resulting in a decrease of the number of directly accessible sulfonic acid groups, compared to the value found with the dry ion exchanger.

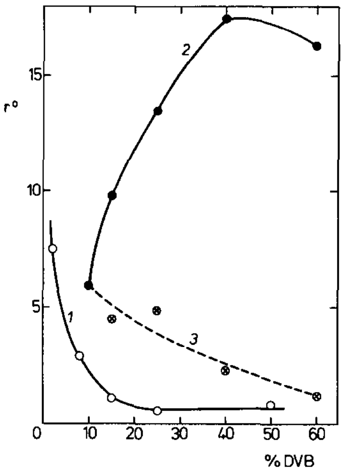

FIG. 4. Dependence of initial reaction rate of gas phase reesterification on crosslinking of ion exchangers: (1) standard ion exchangers; (2) macroreticular ion exchangers; (3) reaction rate on surface equaling to the surface of MS-10 ion exchanger. Temperature, 120°C; partial pressure of reactants, 0.5 at (ester–alcohol ratio, 1 : 1). Reciprocal space velocity for macroreticular, and standard ion exchanger was 7.24×10^{-3} and $11.9 \times 10^{-3}/\mathrm{kg_{cat}}$ hr/mole, respectively.

Gas Phase

The dependence of the initial reaction rate of the gas phase reesterification on the crosslinking of standard and macroreticular ion exchangers is shown in Fig. 4. On standard types, the course is similar as in liquid phase. Absolute values of reaction rates in liquid phase are higher than in gas phase, and differ substantially for the less crosslinked samples, although these differences are small for SS-25 and SS-50. For samples SS-2 to SS-15 the reaction rate in liquid phase is increased by the higher volume concentration of reactants and also by the greater accessibility of sulfonic acid groups within the gel due to swelling in the reaction mixture. The swelling of samples SS-25 and SS-50 in both media is small, and therefore only the sulfonic acid groups residing on geometrical surface of ion exchangers particles are available for catalytic reaction.

The dependence of the initial reaction rate of the reesterification with macroreticular ion exchangers on the degree of crosslinking is different in liquid and gas phase. The swelling in the gas phase occurs only to a very small extent, and the reaction rate increase is proportional to the increase of ion exchanger surface. The exception is MS-60, where the effect of its surface is not so great due to a retarding effect of very fine pores (see Fig. 1). When the reaction rate is expressed with respect to the surface of the ion exchanger MS-10, then the shape of the curve is similar to that found with standard types, where the influence of surface is eliminated (Fig. 4, curve 3).

Kinetics of Reesterification on Ion Exchangers with Varying Amount of Divinylbenzene

We have measured the initial reaction rates of the liquid phase reesterification of ethyl acetate with 1-propanol in dioxane at

52°C, using ion exchangers MS-10 to MS-60 and concentrations of reaction components ranging from 0.24 to 10.51 mole/liter. The kinetic equations were obtained by the method of nonlinear regression and were found to be identical for all the catalysts tested. These equations assume interaction of the alcohol with the catalyst as a primary step of the catalytic transformation, a surface reaction of the formed complex as rate determining step, and the interaction of the solvent with the catalyst [cf. Setínek and Rodriguez (*20*), where the kinetics of ethyl acetate reesterification with 1-propanol in dioxane and cyclohexane and ethyl acetate reesterification with methanol in dioxane, catalyzed by ion exchanger MS-25 and soluble *p*-toluene sulfonic acid were studied. The kinetic reaction course was analogous with both homogeneous and heterogeneous catalyst. Cyclohexane behaved as an inert solvent, while dioxane interacted with the catalyst. Methanol being less basic towards 1-propanol, did not participate in the reaction rate controlling step.]. From these results it follows that neither the difference in phases (liquid vs gas), or the degree of crosslinking of ion exchangers affect the mechanism of the reaction studied. The values of the constants of kinetic equations obtained with differently crosslinked ion exchangers are not discussed, since they were influenced by experimental errors of kinetic experiments.

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