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The Effect of Cross-linking on Catalytic Properties of Macroporous Styrene–Divinylbenzene Ion Exchangers

A. MARTINEC, K. SETÍNEK, AND L. BERÁNEK

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences,
165 02 Prague 6-Suchdol, Czechoslovakia

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Gas-phase dehydration of 1-propanol at 130°C has been studied on a series of differently cross-linked sulfonated macroporous styrene–divinylbenzene copolymers. The degree of cross-linking of the catalysts influences the values of the constants of the Langmuir–Hinshelwood kinetic equation and brings about changes in total dehydration rate as well as in the ratio of the products formed by parallel reactions, propene and dipropyl ether. These phenomena are probably due to the extensive and fast permeation of 1-propanol into the polymer mass of the ion exchangers and the slow permeation of both reaction products from the polymer mass; during permeation the ether is transformed to a different extent into propene, which results in changes in selectivity. These conclusions were supported by measurements of 1-propanol dehydration on an ion exchanger containing functional groups only on the polymer surface, by the study of partial poisoning of the ion exchangers with nitrogen-containing bases, and by measurements of the relative sorption ability of the reaction components.

INTRODUCTION

The degree of cross-linking of ion exchangers is one of the important parameters influencing their catalytic activity. Some attention has been already paid to this problem in the literature, particularly in the case of liquid-phase catalytic reactions. The effect of cross-linking of ion exchangers upon their activity in gas-phase reactions has been the subject of only a few works. Prokop and Setínek (*1*) have examined this effect when studying the adsorption of organic substances and the catalytic dehydration of alcohols, and Andrianova (*2*) reported on this effect in a study on the decomposition of formic acid and esterification of acetic acid. Andrianova (*3*), Rodrigues and Setínek (*4*), and Setínek (*5*) have compared the effect of cross-linking for reactions carried out in both gas and liquid phases. The first author (*3*) investigated esterification of acetic acid, the second paper (*4*) dealt with reesterification of ethyl acetate by propanol, and the third one (*5*) studied a series of reesterifications of aliphatic esters by alcohols.

The effect of the degree of cross-linking upon catalytic properties will obviously be different for standard (gellous) and macroporous ion exchangers. Regarding the latter type of ion exchangers, it is known that different contents of divinylbenzene cause changes in their texture, i.e., their specific surface increases with increasing degree of cross-linking. This is undoubtedly connected with the fact that particles of macroporous ion exchangers are composed of spherical microparticles with free space between them which accounts for the porosity of the catalyst. As the content of

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divinylbenzene in the polymerization mixture increases, the specific surface of the polymer increases. Change in specific surface is probably not the only factor through which variation in the degree of cross-linking manifests itself in catalytic properties of ion exchangers.

In this work we studied the effect of the degree of cross-linking upon the selectivity of a gas-phase reaction catalyzed by macroporous ion exchangers. We utilized knowledge of the kinetics of heterogeneously catalyzed reactions in which we used macroporous sulfonated styrene–divinylbenzene copolymers (*6–9*). The same catalysts were employed in the present work. Catalytic properties of the ion exchangers were tested on dehydration of 1-propanol which proved to be a suitable reaction for this purpose. This branched reaction yields two products [propene via reaction (A) and dipropyl ether via reaction (B)] in comparable amounts and renders it possible to examine both catalytic activity and selectivity of the ion exchangers.

$$CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O \quad (A)$$

$$2\ CH_3CH_2CH_2OH \rightarrow (CH_3CH_2CH_2)_2O + H_2O \quad (B)$$

EXPERIMENTAL

Compounds used. 1-propanol p.a. (Lachema) was freed of low-boiling admixtures by rectification. After drying over a molecular sieve it contained 0.03 wt% of water. Dipropyl ether puriss. (Fluka), propene (Schuchardt), methylamine puriss. (Fluka), and pyridine p.a. (Lachema) were used without further purification. Nitrogen (Technoplyn, Ostrava) was dried with a molecular sieve.

Catalysts. Preparation of the ion exchanger catalysts was reported earlier (*4*). The macroporous styrene–divinylbenzene copolymers were sulfonated by conc H_2SO_4 at about 100°C in the presence of 1,2-dichloroethane as a swelling agent. In Table 1 are presented some properties of the macroporous ion exchangers used. These were dried at 100°C for 6 hr under a pressure of ca. 5 kPa and were stored in a desiccator over phosphorus pentoxide. For kinetic measurements of dehydration, particles with diameters from 0.3 to 0.5 mm were used. The macroporous polymer containing 60% divinylbenzene was also sulfonated by gaseous sulfur trioxide in a stream of nitrogen at room temperature (denoted as MS-60-S in Table 1). In this way, preponderantly the surface layers of

TABLE 1

Properties of Ion Exchanger Catalysts Used

Designation	Divinylbenzene content[a] (wt%)	Exchange capacity[b] (meq/g)	Specific surface[c] (m^2/g)	Mercury density (g/cm^3)	Helium density (g/cm^3)	R^d (nm)
MS-15	15	3.81	35	0.75	1.36	44.5
MS-25	25	3.80	44	0.61	1.45	44.5
MS-40	40	3.20	120	0.57	1.40	32.0
MS-60	60	3.02	227	0.53	1.45	22.5
MS-60-S	60	0.18	310	—	—	—

[a] Initial content before polymerization.

[b] Determined by acidimetric titration in aqueous medium.

[c] Measured by BET method with the use of *n*-heptane.

[d] The radius of pores corresponding to the maximum on a distribution curve. Pore distribution was measured with a Carlo Erba mercury porosimeter.

the particles were sulfonated. In addition, sulfonation was carried out to a low degree to ensure minimal concentration of sulfonic acid groups within the polymer mass (*10*).

Apparatus and procedure. Kinetic measurements of gas-phase dehydration of 1-propanol were made with a flow apparatus. The reaction mixture leaving the reactor was passed through a loop whose content was fed by means of a six-way valve to the column of a gas chromatograph. The apparatus was also used to measure the sorption of substances by the method of transient regime (*11*). For this purpose the apparatus was equipped with a bypass loop with the aid of which jump changes in concentration of a given substance were evoked in the reactor inlet. Kinetics of 1-propanol dehydration and the sorption of reaction components were measured at a temperature of 130 ± 0.5°C. The weighed amount (W) of the catalyst was always 0.3 g, and the feed rate of the alcohol (F) varied from 0.009 to 0.107 mol/hr. The initial reaction rates r^0 were determined from the slope of the dependence of conversion of the alcohol upon the reciprocal value of its space velocity, this dependence being linear in the range of conversions investigated. The selectivity of the reaction (S) was defined as the ratio of the initial rate of the ether formation to that of the olefin formation (r_E^0/r_O^0).

The partial poisoning of the ion exchangers with methylamine and pyridine was realized by sorption of the vapors of these substances at room temperature. The amount of the sorbed bases (and thus the poisoned fraction of the $-SO_3H$ groups) was determined by measuring the pressure of their vapors and their volume in the sorption apparatus. The poisoned ion exchanger was transferred quantitatively to the reactor in which its catalytic activity was tested.

Analytical method. Gas chromatographic analyses were made on an instrument equipped with a flame-ionization detector at 110°C. The column (140 × 4 mm) was packed with 6% diglycerol and 6% polyethylene glycol on Chromosorb. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

Kinetics of the Reaction

Prior to measurements of the kinetics of dehydration of 1-propanol, it was verified that conversion of the alcohol does not depend upon hydrodynamic conditions in the reactor and that mass transport to the external surface of catalyst particles is not therefore the rate-determining process. Inside the particles of macroporous ion exchangers two types of mass transport are possible, i.e., in pores and in the polymer mass. The first will be called internal diffusion and the second one will be called permeation. The effect of internal diffusion upon reaction rate has been excluded based on the fact that neither the conversion of 1-propanol nor the selectivity of the reaction depended upon the size of the ion exchanger particles. Disintegration of ion exchanger particles does not affect the size of the microparticles from which the particles of ion exchangers are formed and thus does not influence the thickness of the layer through which permeation is taking place. Hence, the effect of permeation cannot be either proved or disproved by this means.

The results of kinetic measurements (Fig. 1) show that the degree of cross-linking does affect catalytic activity. The rate of the olefin and ether formation is highest on the catalyst MS-25 and decreases with further increases in the content of divinylbenzene, in spite of a substantial increase in specific surface in the same direction (compare Tables 1 and 2). This indicates that especially on the less cross-linked ion exchangers the reaction is taking place to a significant extent within the polymer mass. The degree of cross-linking affects also the selectivity of the dehydra-

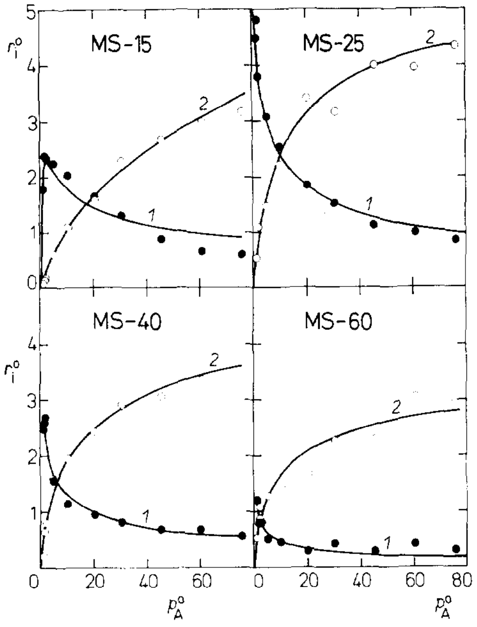

FIG. 1. Dependence of initial reaction rate (moles per hour·kilogram) of product formation upon initial partial pressure (kilopascals) of 1-propanol on ion exchangers cross-linked to different degrees. *1*, Propene, curve calculated according to Eq. (1); *2*, dipropyl ether, curve calculated according to Eq. (2). The points are experimental values.

tion (Table 2, Fig. 2). It increases in favor of the ether with increasing degree of cross-linking and thus with increasing specific surface. The highest selectivity was exhibited, however, by the surface-sulfonated ion exchanger MS-60-S. On the basis of these results it is to be presumed that the inner layers of catalyst particles produce the ether less than do surface layers.

TABLE 2

Rate of Dehydration of 1-Propanol and Selectivity of this Reaction Depending upon the Degree of Cross-linking of Ion Exchanger[a]

Catalyst	r_O^0 (mol/hr·kg)	r_E^0 (mol/hr·kg)	S (r_E^0/r_O^0)
MS-15	2.05	1.10	0.54
MS-25	2.55	2.22	0.87
MS-40	1.15	1.96	1.70
MS-60	0.47	1.48	3.15

[a] $t = 130°\text{C}$, $p_A^0 = 10$ kPa.

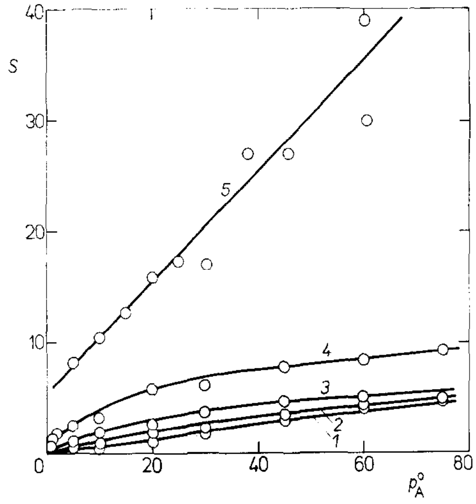

FIG. 2. Dependence of the ratio of the rate of ether to olefin formation, *S*, upon partial pressure (kilopascals) of 1-propanol. *1*, MS-15; *2*, MS-25; *3*, MS-40; *4*, MS-60; *5*, MS-60-S.

Experimental initial reaction rates of formation of both the olefin and the ether were correlated by a set of kinetic equations of the Langmuir–Hinshelwood type which were derived using different assumptions about the mode of 1-propanol adsorption and surface reaction. The optimal values of the constants of these equations were computed by nonlinear regression procedure BSOLVE (*12*). From the order of fitness of these equations to experimental data, no conclusions have been drawn concerning the mechanism of the reaction. In Table 3 is presented the dependence of the constants of Eqs. (1) (olefin formation) and (2) (ether formation) upon the degree

TABLE 3

Values of Constants of Kinetic Equations at Different Degrees of Cross-linking

Catalyst	Eq. (1)		Eq. (2)	
	k (mol/hr·kg)	K_A (kPa^{-1})	k (mol/hr·kg)	K_A (kPa^{-1})
MS-15	18.04	0.45	12.03	0.02
MS-25	39.68	2.17	7.49	0.15
MS-40	24.33	2.69	5.88	0.17
MS-60	11.04	5.15	4.07	0.31
MS-60-S	0.03	0.065	0.23	0.045

of cross-linking. These equations, with the assumed powers $\frac{1}{2}$, 2, and 3, were found to fit the experimental data well. A similar dependence has been found for the constants of all the kinetic equations used.

$$r_O^0 = 8kK_Ap_A^0/[1 + (1 + 8K_Ap_A^0)^{\frac{1}{2}}]^3 \quad (1)$$

$$r_E^0 = kK_Ap_A^0/[1 + (K_Ap_A^0)^{\frac{1}{2}}]^2 \quad (2)$$

The value of the rate constant k in the numerator of kinetic equations of the Langmuir–Hinshelwood type depends upon the amount of functional groups which are accessible during the reaction. Hence, its dependence on the degree of cross-linking has been presumed. It is surprising, however, that the value of the constant K_A in the denominator of these equations increases substantially with increasing cross-linking. Several works (*9*, *13*, *14*) have shown that in the case of ion exchanger catalysts the constant in the denominator of kinetic equations of the type mentioned above can be identified with the equilibrium constant of adsorption of a given substance on the functional groups of the ion exchanger. An increase in its value would mean that the chemical properties of functional groups of the ion exchanger change with the degree of cross-linking. However, Jeřábek (*15*) has verified by means of sorption of ethyl acetate that the adsorption coefficient and therefore also chemical properties of sulfonic acid groups do not depend upon the degree of cross-linking. This discrepancy, as well as the unusually high adsorption coefficient of 1-propanol (ca. 5 kPa^{-1}), indicated that in the dehydration of 1-propanol the adsorption coefficient of the alcohol includes, in addition to the occupation of catalyst sites, another inhibition effect of the alcohol.

Sorption of Organic Bases

The results of measurements of catalytic activity of the ion exchangers partially poisoned by methylamine from the gaseous phase are shown in Fig. 3. The isotherms of poisoning exhibit two distinctly separated

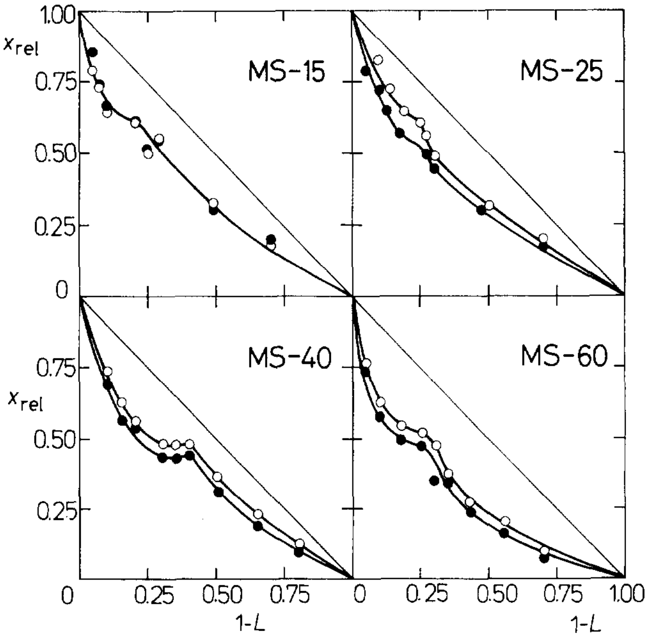

FIG. 3. Isotherms of poisoning by methylamine. x_{rel}, the ratio of the conversion on partially poisoned to the conversion on unpoisoned ion exchanger; $1 - L$, the poisoned fraction of the total exchange capacity of the ion exchanger. t = 130°C, p_A^0 = 10 kPa. ●, propene; ○, dipropyl ether.

TABLE 4

Amount of Reaction Components Sorbed on Differently Cross-linked Catalysts[a]

Catalyst	1-Propanol (mol/g)	Dipropyl ether (mol/g)	Propene (mol/g)
MS-15	1.40	0.02	0.09
MS-25	1.54	0.40	0.13
MS-40	1.51	0.88	0.17
MS-60	1.39	0.66	0.16

[a] $t = 130°\mathrm{C}$, $p_A{}^0 = 10$ kPa.

regions whose existence can be explained in the following way. Methylamine first occupies the functional groups located on pore walls and is uniformly distributed on them, since they are equally accessible. This results in a nonlinear curve (the first part of the isotherm) which can be expressed approximately by a power-type equation, since dehydration of alcohols involves several sites in the rate-determining step (*8*, *9*, *13*). Further deactivation takes place only after all the surface groups have been poisoned and methylamine begins to penetrate to the inner layers of the polymer mass.

The measurements of the catalytic activity of the ion exchangers poisoned by pyridine have revealed that the poisoning of a thin layer of the polymer mass (approximately 25% of the functional groups, which corresponds to 10% of the radius of the microparticles constituting a particle of macroporous ion exchanger) completely inhibits the reaction. This means that the reaction components of the dehydration of 1-propanol are no longer capable of penetration through the poisoned zone. Thus, the resistance to permeation increases by the sorption of substances within the polymer mass, an important role being played by the size of the molecules of the substance sorbed. Pyridine with relatively bulky molecules is able to suppress permeation completely, while permeation is still realized through the layer poisoned by methylamine.

Sorption of Reaction Components

Measurements of the sorption of reaction components by the method of transient regime at the reaction temperature (Table 4) have shown that 1-propanol is sorbed much more than are the reaction products and that the amount of the alcohol sorbed does not depend essentially upon the degree of cross-linking of the ion exchanger. This means that 1-propanol permeates through the polymer mass much more easily than do the reaction products. In contrast to 1-propanol, the reaction products are obviously sorbed in the surface layers of ion exchanger microparticles.

Permeability of the Polymer Mass of the Catalyst

All the facts discussed so far can be interpreted in a consistent way. First, one should take into account that the reaction proceeds not only on pore walls, i.e., on the surface of microparticles, but also in microparticles, i.e., within the polymer mass of the ion exchanger. Under these circumstances, the rate of permeation of the reaction components through the polymer mass is an important factor influencing the overall catalytic activity of the ion exchangers. As far as the reaction rate to permeation rate ratio is concerned, three cases are to be expected:

I. Permeation of substances is much slower than the rate of the reaction. The reaction then proceeds only on the walls of pores of macroporous ion exchanger, and the activity is proportional to specific surface (i.e., to the number of the groups readily accessible from gas phase). Selectivity of the reaction is not affected by permeation.

II. Permeation of substances proceeds much faster than does the reaction. In such a case the reaction occurs in the polymer mass as a whole; concentration gradients are not formed and the activity does not depend upon the specific surface of the ion exchanger. The selectivity of the reaction is not influenced by permeation.

III. Permeation and reaction proceed at comparable rates. In this case concentration gradients are formed in the polymer mass or only a certain layer of the polymer mass is catalytically active. Selectivity of the reaction can be influenced by permeation.

From the results described in the present work it follows that the dehydration of 1-propanol is taking place within the polymer mass and does not therefore belong to group I. Catalytic activity decreases with increasing specific surface of the ion exchanger, and the selectivity of the reaction varies with the degree of cross-linking (influencing permeability). Hence, the reaction cannot be classified as belonging to group II. It belongs to group III. Its rate is comparable to the rate of permeation, and concentration gradients are formed in the polymer mass, or only a certain layer of the polymer mass is efficient (reaction zone). The thickness of this layer must increase with increasing permeability. In harmony with this, the catalytic activity increases with decreasing degrees of cross-linking. In the dehydration of 1-propanol the permeation of the products from the inside of the polymer mass to pore walls is obviously rate determining, since permeation of 1-propanol is faster. Under these conditions the molecule of dipropyl ether is not released immediately to the gas phase after its formation, and during permeation to pore walls it has the opportunity to react further. We have found experimentally that dipropyl ether reacts on the ion exchangers at 130°C to form propene and 1-propanol according to reaction (C).

$$(CH_3CH_2CH_2)_2O \rightarrow CH_3CH_2CH_2OH + CH_3CH{=}CH_2 \quad (C)$$

TABLE 5

Initial Rate of the Reaction of Dipropyl Ether [Reaction (C)] at Varying Partial Pressures[a]

p_E^0 (kPa)	5.1	10.1	20.3	30.4	40.5
r^0 (mol/hr·kg)	2.29	1.93	1.70	1.37	1.64

[a] Catalyst, MS-40; t = 130°C; space velocity of the ether, 58.8 mol/hr·kg.

The values of the initial reaction rate of this reaction on the MS-40 ion exchanger are presented in Table 5. From comparison of these data with those of Table 2 and Fig. 1, it becomes evident that dipropyl ether reacts at a rate which by its order of magnitude is comparable to the rates of 1-propanol conversion to the ether and to the olefin. The assumption about its transformation during permeation through the polymer mass is thus justified. The successive reactions of dipropyl ether explain the earlier-discussed lower selectivity of the inner layers of the polymer mass of the ion exchanger. If we exclude permeation of dipropyl ether through the inner layers of the polymer mass by using the surface-sulfonated ion exchanger MS-60-S, we obtain the highest selectivity with respect to ether formation (Fig. 2). It should be noted that on poisoning the surface groups of the ion exchangers by methylamine the selectivity with respect to ether formation is not reduced (Fig. 3), as could have been expected from the greater efficiency of the surface layers with respect to ether formation. This fact is explicable by the above-mentioned concept of the reaction zone. By poisoning a certain layer of the polymer mass with methylamine, the reaction zone is only shifted deeper into the microparticle of the polymer mass, and the selectivity is not changed.

The high value of the constant in the denominator of the kinetic equations indicates that the alcohol exerts a strong inhibiting effect. From the study of the poisoning of catalysts by pyridine, it followed that the adsorption of pyridine in the polymer mass decreases the permeability of the reaction components of the dehydration of 1-propanol. The adsorbed 1-propanol should decrease permeability in

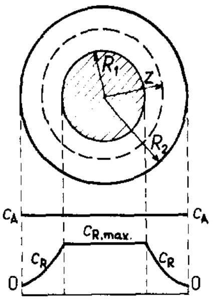

FIG. 4. Cross section of the ion exchanger microparticle (schematic). R_2, microparticle radius; R_1, radius of inactive nucleus; z, geometrical coordinate; c_A and c_R, concentrations of the alcohol and the product in the polymer mass, respectively.

a similar way. As the concentration of 1-propanol within the polymer mass increases, the permeability of dehydration products probably decreases and their concentration gradients become more important. Because of this, the thickness of the active layer of the polymer mass of the ion exchanger diminishes (the nucleus within the microparticles of the polymer mass, which is saturated by the products and thus inactive, enlarges). This inhibiting effect of the alcohol should manifest itself more distinctly on the more highly cross-linked ion exchangers which possess a more tightly knit macromolecular skeleton. This inhibition by the alcohol is obviously demonstrated by the high value of the constant in the denominator of the kinetic equations and by its increase with the degree of cross-linking. In the case of the surface-sulfonated ion exchanger, the permeation of the products through the polymer mass cannot influence the reaction, and the mentioned inhibiting effect of 1-propanol does not occur. The value of the adsorption coefficient of 1-propanol determined kinetically (in hundredths of a reciprocal kilopascal) corresponds to this expectation, in accordance with literature data on adsorption of the alcohol on ion exchangers (*13*, *14*).

Simplified Model of Performance of the Catalyst

Whether the apparent value of the adsorption coefficient of the alcohol in the Langmuir–Hinshelwood equation can be increased due to slow permeation of the product from microparticles of the ion exchanger can be verified by using a simplified model of the performance of the catalyst. In deriving this model we will assume only one of the two parallel reactions of the alcohol, e.g., formation of the olefin, and introduce the assumption that there are concentration gradients in the microparticle which can lead to the formation of a certain region within the microparticle that does not participate in the reaction since it is fully saturated by the products. For the sake of simplicity we will further assume that the boundary between the inactive nucleus of the spherical nonporous microparticle and its external layer (in which the reaction is taking place) is sharp. The reaction zone is thus delineated by the radii R_1 and R_2 (Fig. 4). On account of the great permeability of 1-propanol, its concentration c_A is the same at each place of the reaction zone. The product concentration c_R decreases from the value $c_{R,max}$ on the boundary between the reaction zone and the inactive nucleus to a value of $c_R = 0$ on the external surface of microparticles (the particle is surrounded by pure 1-propanol). A further simplifying assumption is that the reaction rate is the same at each point in the reaction zone, i.e., it is independent of the product concentration. This situation is schematically depicted in Fig. 4. The density of the permeation flux of the product (moles per square centimeter·second) through the reaction zone is proportional to the concentration gradient of the product in the reaction zone along the radius of the microparticles $[-B(dc_R/dz)]$, analogous to the Fick law; the constant of proportionality B is the permeation coefficient.

Now one can calculate the value which the reaction rate will acquire in the microparticle of the ion exchanger at various partial pressures of the alcohol in the gas phase if this rate is influenced by slow permeation of the product from the polymer mass. The pairs of r–p_A values can be then treated by a simple Langmuir–Hinshelwood equation, and the constants obtained can be compared with those found by treatment of the data not influenced by permeation. The procedure will be demonstrated on the ion exchanger MS-60 as an example. From Fig. 3 it can be deduced that, of the total exchange capacity V, around 30% of the functional groups are readily accessible on the surface of the microparticle, and the reaction proceeds on these groups without being affected by permeation. The remaining 70% of the functional groups are located within the polymer mass. The total experimental reaction rate is then the sum of the rate on the surface functional groups (which equals 0.3 Vr where r is the reaction rate related to unit exchange capacity V) and the rate within the reaction zone which is set by the radii R_1 and R_2. This zone does not contain, however, the remaining 0.7 V of functional groups, but only that part which is given by the ratio of the volume of the reaction zone, $(\frac{4}{3})\pi(R_2^3 - R_1^3)$, to that of the whole microparticle, $(\frac{4}{3})\pi R_2^3$, i.e., 0.7 V $[1 - (R_1/R_2)^3]$. The total reaction rate r_{tot} is expressed by the relation

$$r_{tot} = 0.3Vr + 0.7Vr[1 - (R_1/R_2)^3]. \quad (3)$$

In order for the total reaction rate at different partial pressures of the alcohol around a microparticle to be calculated, the dependence of the size of the reaction zone (i.e., the value of the R_1/R_2 ratio) upon the partial pressure of the alcohol around the microparticle should be determined. By integration of the steady mass balance of the product (the rate of formation of the product equals the rate of its withdrawal by permeation), which is expressed by the relation

$$(\tfrac{4}{3})\pi(z^3 - R_1^3)c_S r = -B \cdot 4\pi z^2 (dc_R/dz) \quad (4)$$

(c_S is the concentration of functional groups in unit volume of the reaction zone), with the use of the boundary conditions $c_R(R_1) = c_{R,\max}$ and $c_R(R_2) = 0$, the following equation has been obtained:

$$(\tfrac{1}{3})c_S r(R_1/R_2)^3 - (\tfrac{1}{2})c_S r(R_1/R_2)^2 + (\tfrac{1}{6})c_S r - Bc_{R,\max}/R_2^2 = 0 \quad (5)$$

From the results of the study of poisoning by pyridine it can be concluded that the permeation resistance of the polymer mass increases with the amount of another substance sorbed, i.e., with the partial pressure of this substance. The permeation coefficient B of the product in the reaction zone thus decreases obviously with increasing partial pressure of the alcohol. We have assumed that this follows an exponential dependence according to the equation

$$B = B^0 \exp(-ap_A), \quad (6)$$

where B is the permeation coefficient, B^0 is the permeation coefficient at zero partial pressure of 1-propanol, and a is a constant. To express the dependence of the reaction rate on the partial pressure of the alcohol we have used the simple kinetic equation

$$r = kK_A p_A/(1 + K_A p_A)^2. \quad (7)$$

By combining Eqs. (5)–(7), the relationship between the R_1/R_2 ratio and the partial pressure of the alcohol in the gas phase was obtained and solved numerically for estimated values of the parameters B^0, a, c_S, $c_{R,\max}$, and R_2 and of the constants of rate Eq. (7) (see the legend to Fig. 5). With the use of Eq. (3) total reaction rates were calculated for a set of selected partial pressures of the alcohol in the gas phase. The results are graphically represented in Fig. 5. The reaction rates influenced by permeation (curves 2 and 3) are distinctly lower than those without the effect of permeation (curve 1). Curves 2 and 3 have their maxima shifted to the lower values

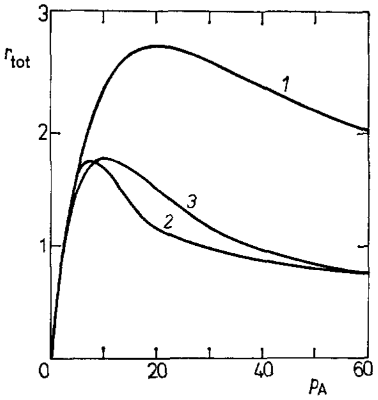

FIG. 5. Calculated dependence of reaction rate r_{tot} (moles per hour·kilogram) upon partial pressure (kilopascals) of the alcohol. Parameters used in Eqs. (3), (5), (6), and (7): $V = 3$ mol/kg; $c_S = 4.5$ mmol/cm^3 of ion exchanger mass; $c_{R,max} = 0.1$ mmol/cm^3 of ion exchanger mass; $R_2 = 1 \times 10^{-6}$ cm; $k = 1 \times 10^{-3}$ mol/s·mol of SO$_3$H; $K_A = 0.05$ kPa^{-1}. *1*, Calculated without permeation effect ($R_1/R_2 = 0$); *2*, the effect of permeation is expressed by parameters in Eq. (6): $B^0 = 4 \times 10^{-15}$ cm^2/s, $a = 0.276$ kPa^{-1}; *3*, parameters: $B^0 = 1 \times 10^{-15}$ cm^2/s, $a = 0.115$ kPa^{-1}.

of the partial pressure of the alcohol, similar to the experimental curves of the olefin formation shown in Fig. 1. By regression treatment of curve 3 in Fig. 5 by means of the Langmuir–Hinshelwood Eq. (7), the following values of the constants k and K_A were obtained: $k = 7.7$ mol hr^{-1} kg^{-1} (10.8 mol hr^{-1} kg^{-1} in the absence of permeation effect), and $K_A = 0.13$ kPa^{-1} (0.05 kPa^{-1} in the absence of permeation effect). It is seen that the K_A values increased 2.6 times on account of the permeation effect. This increase in K_A agrees qualitatively with the experimental results. This means that the concepts used in deriving the above model, although considerably simplified, are close to the real situation.

Dehydration of 1-propanol in the gas phase catalyzed by macroporous sulfonated styrene–divinylbenzene copolymers is therefore an example of the system in which the reaction rate is comparable with the rate of permeation of the reaction components through the polymer mass. The rate of formation of products is affected by mass transport whose rate depends on the degree of cross-linking of the ion exchanger copolymer. That is why this affects both the activity and the selectivity of the catalyst.

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