

THE EFFECT OF INHOMOGENEITY OF THE POLYMER STRUCTURE ON CATALYTIC ACTIVITY OF ION EXCHANGERS

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It has been shown that using the dependence of catalytic activity of ion exchangers on the degree of sulphonation one can infer on the structure of their polymeric skeleton. Using condensation of phenol and acetone yielding Bisphenol A as a test reaction we have been able to distinguish up to four fractions of active groups in a series of ion exchangers of the gel and macroreticular type affected to a different extent by the structure of the surrounding polymer mass.

Organic ion exchangers have been used both to catalyze reactions of industrial importance, as well as model catalysts for theoretical studies¹. Catalytic activity of polymer ion exchangers has been known to strongly depend on the structure of their polymer skeleton. Classic methods of study of the structure of solid catalysts, such as *e.g.* mercury porosimetry or sorption methods, however, do not provide relevant data. These methods supply information about the external shape of polymeric mass, although the macromolecular skeleton is not rigid, and, owing to the mobility of the polymer chains by the interaction with the reaction medium, the catalytic reaction takes place also on the active groups within the polymer mass.

The structure of the polymer mass has been so far characterized by the content of the crosslinking component as a consequence of the simplified concept assuming uniform distribution of the crosslinking component and identical resistance offered to the transport of the reacting species throughout the polymer mass². This concept, however, is clearly at odds with reality. The most often used polymer skeletons of organic ion exchangers, copolymers of styrene and divinylbenzene, have been known to consume divinylbenzene faster than styrene during their polymerisation and, consequently, initially the reaction yields a more crosslinked polymer³ compared to the product from the final stages of that process. Another cause of nonuniformity in the crosslinking of the polymer structure is the existence of polymer chains with one free end, the growth of which has been terminated before the free end is attached by the crosslinking component to another chain. In case of macroreticular ion exchangers such a heterogeneity has been proven within the polymer mass also quantitatively⁴.

From the standpoint of permeability the polymer mass thus cannot be regarded as homogeneous and the true situation in the process of the reaction is apparently more complex than so far believed. The rate of transport of the reacting components is given on the one hand by the length of the path between the active group and the surface of the particle of the ion exchanger, and, on the other hand, by the permeability of the medium along this path which may be different for individual sections of this path. It seems that the structure of the polymeric mass in the vicinity of the active centers may be of greater importance for the rate of transport of the reacting species between the active center and the bulk phase than its distance from the surface of the

grains. The often reported finding is the negligible effect of the grain size of the ion exchanger on the rate of the catalytic reaction, even in those cases when the reaction rate could be eventually influenced by transport phenomena. This has been shown very convincingly by Jiráček and co-workers⁵. Based on the selectivity changes these authors observed considerable influence of diffusion on the reaction which could not have been reduced by decreased grain size of the ion exchanger.

For the assessment of suitability of a given ion exchanger as a catalyst it would be therefore desirable to have at the disposal data on the distribution of active groups within the ion exchanger as these are accessible from the bulk phase. In order to obtain information of this kind an attempt has been made to utilize the dependence of catalytic activity on the degree of sulphonation of the ion exchanger. Sulphonation of copolymers of styrene and divinylbenzene has been known to be controlled by the rate of transport of the sulphonating agent⁶. It is therefore influenced by the structure of the polymer and it may be assumed that at the beginning of the sulphonation the active groups are introduced into the most easily accessible and most permeable sites, while later on into less and less readily accessible sites within the polymer. In order to test catalytic activity of partially sulphonated ion exchangers we have adopted the method of initial reaction rates of condensation of phenol and acetone yielding Bisphenol A (diane). This reaction is sensitive to the changes of the polymer skeleton of the ion exchanger catalyst⁷.

EXPERIMENTAL

Chemicals. Phenol (Loba-Chemie) was purified by distillation, acetone (Lachema) was dried over a molecular sieve. Ethylmercaptan *purum* (Fluka), sulphuric acid *p.a.* (Lachema) and 1,2-dichloethane *purum* (Fluka) were used without additional purification.

Polymers. The used polymers were styrene-divinylbenzene copolymers in the porous form (macroreticular) containing 60, 40 or 10% of divinylbenzene (marked MS-60, MS-40 and MS-10) and standard, non-porous copolymers containing 12.8 or 2% of divinylbenzene (marked SS-12, SS-8 and SS-2). With the exception of MS-10 and SS-12, which were products of Spolek pro chemickou a hutní výrobu, Ústí nad Labem, the rest of copolymers were products of Výzkumný ústav syntetických pryskyřic a laků, Pardubice.

Sulphonation. It was important that the course of sulphonation of copolymers depend as little as possible on the grain size and hence that the sulphonation take place equally well on the surface of the grains as in their interior. In the preparation of the porous copolymers the permeation of sulphuric acid into the bulk of the grains was facilitated by the porosity of the polymer. Sulphonation of the standard, non-porous polymers was carried out after swelling in 1,2-dichloethane. As has been found by analysis of the sulphur concentration profile on the surface of a cut through the ion exchanger grains by the electron microprobe⁸, the sulpho groups in this case are introduced into the bulk volume of the grain from the very beginning. In addition, the process is under a strong influence of the microstructure of the polymer rather than that of the grain size. The sulphonation was carried out in the usual way using 90% sulphuric acid. The degree of sulphonation was regulated by appropriate choice of the reaction time (between 0.5 to 5 hours). The degree of sulphonation shall be expressed in terms of the exchange capacity of the ion exchanger found by titration.

Apparatus and method. The initial reaction rates of condensation of acetone and phenol were measured in an ideally mixed flow glass-tank microreactor 6 cm³ by volume of similar construction as that used by Rodriguez and Setínek⁹. The reaction rates were measured at 70°C and the molar ratio of phenol to acetone was 8 : 1. In accord with the recommendation from the patent literature, 0.5% by mass of ethylmercaptan was added to the reaction mixture. To expedite establishment of the steady state the catalyst (0.05 to 2 g) was swelled in acetone prior to the reaction; the excess acetone was vacuumed away before the onset of the reaction. The reactor was filled with the reaction mixture and immersed in the thermostated bath the temperature of which was held constant to within $\pm 0.1^\circ\text{C}$. The flow rate of the reaction mixture ranged between 10 and 40 cm³/hour. The samples of the products were drawn only after at least 20 cm³ of the reaction mixture has passed through the reactor. This, as has been verified, is sufficient to reach the steady state. The experimental conditions were chosen such as to keep conversion below 10% (related to acetone) and it has been established that under such circumstance the experimental reaction rates are independent of the degree of conversion. The resulting value of the catalytic activity for each catalyst was always an average of at least 3, typically, however, of 5 to 7 measurements. The reaction products were analyzed by HPLC in a 4.1 \times 50 mm column filled with 10 μ Porasil (Pierce Eurochemie); the carrier phase was heptane with 15% of ethyl acetate¹⁰.

RESULTS AND DISCUSSION

Catalytic activity depends generally on concentration of active sites. In order that the results of measurements of catalytic activity on the degree of sulphonation may be interpreted as the effect of the structure of the polymer mass only, it was necessary to assume that regardless of the degree of sulphonation there was always only one sulpho group per benzene ring in all spots reached by sulphuric acid. This is in accord with the earlier finding that the overall rate of sulphonation of ion exchanger is

TABLE I
Initial Reaction Rates of Condensation of Phenol and Acetone for the Fully Sulphonated Ion Exchanger SS-8 at 70°C

Grain mm	Initial reaction r^0 , nmol/hg _{cat}
0.09 — 0.23	31.6
0.315 — 0.64	29.1
0.8	31.6

TABLE II
Specific Initial Reaction Rate of Condensation of Acetone and Phenol on the Most Easily Accessible Sulpho Groups at 70°C

Catalyst	Initial reaction rate nmol/h g _{cat}	Exchange capacity mequiv./g	Specific initial reaction rate r^0 nmol/h mequiv.
SS-2	34.4	2.49	13.8
SS-8	3.97	0.19	20.9
SS-12	1.0	0.15	6.7
MS-10	3.75	0.25	15.0
MS-40	5.8	0.32 ^a	18.1
MS-60	9.8	0.52 ^a	18.8

^a Calculated number of sulpho groups.

controlled by the penetration of the sulphuric acid into the bulk of the polymer and the rate of the sulphonation proper is much higher. Partially sulphonated polymers should thus not differ in the concentration of the sulpho groups only in the fraction of the sulphonated polymer mass.

Sulphonation of macroporous copolymers may in some cases cause considerable changes of their specific surface area measured in the dry state. As it would be difficult to distinguish in the process of evaluation of the dependence of the catalytic activity on the degree of sulphonation the effect of these changes from that of the structure of the polymer, only those samples were taken for measurement which exhibited the same specific surface area. Its value for a series of ion exchangers MS-10 was equal $11.6 \pm 0.6 \text{ m}^2/\text{g}$ and for the series of ion exchanger MS-40 $137 \pm 7 \text{ m}^2/\text{g}$. In the series MS-60 we were unable to prepare sulphonated samples of the specific surface area acceptably identical and confined therefore ourselves in this case to a comparison of catalytic activity of the fully sulphonated sample of MS-60 (spec. surface area $225 \text{ m}^2/\text{g}$).

The aim of this work has been to characterize the effect of the macrostructure of the polymer mass on the catalytic activity of ion exchangers and the experimental results thus should be independent of the size of the catalyst grain. This assumption was tested on the nonporous catalysts SS-8 sulphonated to full capacity, which was at our disposal in sufficiently widely ranging size of the catalyst grain and, unlike the majority of the remaining exchangers was sufficiently mechanically strong as to remain undamaged by the impeller in the reactor (Table I).

The review of the found dependences of catalytic activity on the degree of sulphonation is given in Fig. 1. For low crosslinked non-porous ion exchangers SS-2 the catalytic activity grew almost linearly with increasing exchange of the ion exchanger up to full sulphonation of the polymer. For medium crosslinked non-porous catalysts SS-8 and macroreticular exchangers MS-10 the catalytic activity grew with the degree of sulphonation up to very high exchange capacity, although not linearly and neither did it reach comparably high value as in the case of SS-2 ion exchanger. For catalysts with high degree of crosslinking, namely SS-12 and MS-40, the catalytic activity is low and does not change appreciably over a wide interval of exchange capacity.

The course of the dependence of catalytic activity on the degree of sulphonation for the exchangers with a high degree of crosslinking, SS-12 and MS-40, suggests that the catalytic reaction took place on the active groups in the most easily accessible parts of the polymer mass which had been sulphonated first but formed only a small portion of the supporting skeleton. The acidic groups deposited by progressing sulphonation into less readily accessible parts of the polymer apparently did not participate in the reaction, and accordingly, the activity of the ion exchanger no longer grew with increasing capacity. For the MS-40 series of catalysts the condensation

of phenol and acetone apparently no longer takes place within the polymer mass and catalytic function retain only the surface acid groups because the mean value of the catalytic activity of the exchangers of this series related to a unit surface ($0.043 \text{ mmol/hour m}^2$) is identical with the similar value calculated for the MS-60 ion exchanger ($0.044 \text{ mmol/hour m}^2$).

The shape of the dependence of the catalytic activity on the degree of sulphonation for the series SS-8 and MS-10 demonstrates a greater variety of the character of the influence on the catalytic activity by the polymeric structure of the carrier skeleton. The catalytic activity grew up to high degrees of sulphonation, and hence probably all active sites within the whole polymeric mass took part in the reaction although not necessarily always with the same efficiency. Differentiation of the dependence of the catalytic activity on the degree of sulphonation for the series of exchangers MS-10 enabled 4 fractions of the active groups to be distinguished (Fig. 2). Only a very small portion of the active groups introduced at the beginning of the sulphonation (7%) exhibited high catalytic activity. The following fraction of the acidic groups (13%) functioned only with 65% efficiency in comparison with the former fraction. The active groups introduced in the subsequent stages of sulphonation exhibited a substantially lower activity; 35% of the groups has an efficiency 17% and the last fraction, encompassing 55% of all groups, functioned with 5% mean efficiency only. The course of the dependence of catalytic activity on the degree of sulphonation

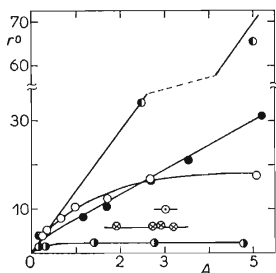


FIG. 1

Initial Reaction Rate of Condensation of Phenol and Acetone r_0 (nmol/h g_{cat}) as a Function of the Degree of Sulphonation A (mequiv./g) for Various Polymer Skeletons SS-2 ●, SS-8 ●, SS-12 ○, MS-10 ○, MS-40 ○, MS-60 ○.

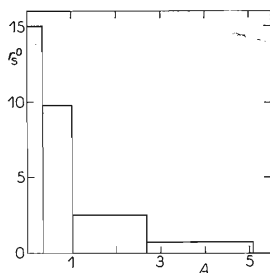


FIG. 2

Specific Initial Reaction Rate of Condensation of Phenol and Acetone r_s^0 (nmol/h . mequiv.) for Sulpho Groups Introduced into the Polymer MS-10 at Various Stages of Sulphonation A (mequiv/g)

for the series of ion exchangers SS-8 points at the existence of two types of active groups. The first, small portion, represented by the initial steep part of the above discussed dependence, was introduced in the initial stages of the sulphonation into the highly permeable part of the polymer mass. The rest of the active groups, with corresponding essentially linear part of the catalytic activity versus degree of sulphonation curve, is apparently located in the less permeable parts of the polymer and function with lesser activity than the former group. Mutual comparison of the shapes of the dependences of catalytic activity on the degree of sulphonation for the series of ion exchangers SS-8 and MS-10 suggests that formation of the macroreticular structure probably altered the distribution of the crosslinking component in the polymer mass. The portion of the highly permeable component of the polymer has increased although at the expense of the permeability of the rest of the polymer mass.

The steep and almost linear increase of catalytic activity with the degree of sulphonation up to high exchange capacities for the series of exchangers SS-2 seems to suggest that in this case the rate of the catalytic reaction should be little affected by the transport phenomena and that all sulpho groups exhibit similar efficiency.

We have compared catalytic activities of most readily accessible sulpho groups on all skeletons examined. For this comparison we have selected from the series SS-2, SS-8, SS-12 and MS-10 the least sulphonated polymers, which were assumed to possess at this stage of sulphonation the active groups in the most readily accessible parts of the polymer mass only, and compared their catalytic activity related to a unit of titration exchange capacity. For the ion exchangers MS-40 and MS-60 the catalytic activity was related to the exchange capacity of only surface groups to which we had arrived by the following reasoning. The fully sulphonated copolymer of the styrene and divinylbenzene had an exchange capacity 5.2 meq/g and skeletal density 1.4 g/cm³. From this follows that the volume corresponding to a single sulpho group is 0.37 nm³. Simulating the surface of the macroreticular exchanger as a layer of cubes of this volume, then 1 m² of this layer contains 4.6 µeq acidic groups. With a random orientation, however, only one half of these groups is directed toward the pore, and, consequently, the surface exchange capacity should then be 2.3 µeq/m², i.e. 0.32 mequiv./g for the exchanger MS-40 and 0.52 mequiv./g for MS-60.

Thus computed values of catalytic activity related to a unit amount of acidic groups are shown in Table II. It is seen that with the exception of the exchanger SS-12 these data do not differ appreciably. This suggests that these data do represent only those sulphogroups which are accessible without appreciable influence of transport phenomena either because they are located in the most permeable parts of the polymer mass (exchangers SS-2, SS-8 and MS-10) or because they have become accessible by the porosity of the polymer (MS-40 and MS-60). The fraction of the well accessible acidic groups in the ion exchanger, however, strongly depends on its polymer structure. For the polymer, crosslinked by 12% of divinylbenzene, this

fraction was probably so low that even on a very poorly sulphonated polymer the reaction was influenced by transport phenomena. Consequently, specific catalytic activity related for the least sulphonated member of the series SS-12 is substantially lower than for other ion exchangers.

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