

## Adsorption-assisted catalysts

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Received 27 June 1996; revised version received 10 December 1996; accepted 20 December 1996

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### Abstract

Possibilities for enhancement of catalytic reaction rate by combining adsorptive (unfunctionalized) and catalytically active (functionalized) domains within the polymer skeleton of ion-exchanger catalysts have been studied. These catalysts were prepared by copolymerization of styrene and divinylbenzene with a functionalized monomer (styrene sulfochloride). For comparison were included also catalysts prepared by partial sulfonation of macroreticular copolymers of styrene and divinylbenzene and conventional, fully sulfonated ion exchangers. Catalytic activity was tested by the measurements of initial reaction rates of hydrolysis of ethyl acetate (5 wt% in water, 60°C) and ethyl benzoate (0.035 wt%, 75°C). With the catalysts prepared by copolymerization of the functionalized and unfunctionalized monomers the reaction rate per equivalent of the acid centers was found to be up to 15-times higher than with conventional ion-exchanger catalysts. With the partially sulfonated resins, this effect was somewhat lower, due to less advantageous distribution of the functionalized and unfunctionalized domains.

**Keywords:** Catalysis; Adsorption; Sulfonation; Styrene sulfochloride

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### 1. Introduction

The applications of polymers as catalyst carriers open up for catalyst preparation potentially powerful methods of organic chemistry. The most significant catalysts of this type are strongly acidic ion exchangers, commercially manufactured by sulfonation of copolymers of styrene (S) and divinylbenzene (DVB). These catalysts are also very good models for studying structure–activity relationships for heterogenized homogeneous catalysts.

In comparison with homogeneously catalyzed reactions, kinetics on heterogeneous catalysts al-

ways includes additional steps of adsorption of reagents and desorption of products. These steps greatly influence the concentration relations in the vicinity of active centers and hence, the overall catalytic activity. For example, it is known that for ester hydrolysis organic ion-exchanger catalysts can be more effective than a soluble acid, due to preferential sorption of the ester by the polymer catalyst [1,2]. In the vicinity of its acidic centers there exists a higher concentration of the key component than in the external homogeneous solution. Independent regulation of adsorption properties of catalysts could be a powerful tool for their optimization.

Unfunctionalized S–DVB copolymers are known as efficient adsorbents and hence it ap-

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appears useful to combine adsorbent and catalyst in one material. In application of such catalysts for reactions in diluted aqueous solutions of organic compounds it can be expected that the adsorption of the organic compounds by the unfunctionalized parts of polymer skeleton will assist the catalytic reaction on the neighboring acidic centers. However, implementation of this task requires very intimate intermixing of the adsorptive (unfunctionalized) and catalytically active (functionalized) domains. In the preparation of strongly acidic ion-exchanger catalysts it is a difficult task. Sulfonation of the S–DVB copolymers always proceeds on a sharp border between the already fully sulfonated and the yet unsulfonated part of polymer skeleton, advancing during the process from the surface toward the interior of the polymer mass [3]. For the gel-type resins where the sulfonation proceeds from the bead surface to the center of the particle, it is evidently impossible to achieve the desired high intermixing of sulfonated and unsulfonated regions by this method. Only in macroreticular materials, where the front of the sulfonation process (at suitable condition) may proceed homogeneously in the whole bead from the pore walls to the polymer mass interior, can a more extensive interface between the functionalized (hydrophilic) and unfunctionalized (hydrophobic) domains be achieved [4].

Better perspective in this direction offers copolymerization of S and DVB with a functionalized monomer. We have investigated this approach to the synthesis of reactive polymers using styrene sulfochloride (SSC) as one of the monomers. It enables us to obtain strongly acidic ion-exchanger catalysts with the active groups more or less evenly spread through the polymer mass. In this paper we report results of tests of activity of this novel type of the strongly acidic polymer catalyst under conditions where the catalytic reaction may be supported by an adsorption assistance due to the presence of lipophilic, unfunctionalized domains in the polymer skeleton. For comparison we have included also catalysts prepared by partial sulfonation of macroreticular

copolymers of styrene and divinylbenzene and conventional, fully sulfonated ion exchangers.

## 2. Experimental

Preparation of functional polymers from *p*-styrenesulfonyl chloride (SSC) as functional monomers was subject of a separate study [5]. In its framework was prepared a series of terpolymers of SSC, styrene (S), ethylvinylbenzene (EVB) and divinylbenzene (DVB) of various composition. SSC-containing copolymers were prepared by radical polymerization (initiated by dibenzoyl peroxide) of the mixtures of SSC, S, tech. DVB and various porogens in a sealed glass ampoule at 80°C. The resulting solid was crushed and extracted by tetrahydrofuran. Sulfochloride groups were converted to  $-\text{SO}_3\text{H}$  groups by hydrolysis in 10% solution of NaOH in 1 : 1 mixture of dioxane and water. More details on the preparation of this type of ion-exchanger catalyst can be found in ref. [5]. For the purpose of the presented work we have selected a group of these polymers with varying ratio of the functionalized (SSC) and nonfunctionalized monomers. Their properties are summarized in Table 1.

Differences between the theoretical exchange capacity (derived from the nominal SSC content) and the actual capacity determined after the hydrolysis showed that it was possible to hydrolyze to a high degree only those polymers with the low amount of the unfunctionalized polymer mass (SSC-F). In the polymers containing a higher proportion of unfunctionalized monomers, only a fraction of the sulfochloride groups were accessible to hydrolysis in water. Evidently, the unfunctionalized styrenic polymer, unable to swell in water, envelopes some of the sulfochloride group domains and prevents their hydrolysis [5].

The catalysts functionalized by partial sulfonation included for a comparison were prepared by sulfonation of macroreticular copolymer of S and DVB (10 mol% DVB) by 94% sulfuric acid without preswelling, at temperatures 40°C for 6 h and at 60 for 3 h. These catalysts are designated S/DVB-P1 and S/DVB-P2. By sul-

Table 1

Properties of the ion-exchanger catalysts prepared by copolymerization of SSC with nonfunctionalized comonomers (S, EVB and DVB)

Catalyst	SSC content <sup>a</sup> (mol %)	DVB content <sup>a</sup> (mol %)	Theoretical exchange capacity (mmol/g)	Actual exchange capacity (mmol/g)
SSC-A	23	4	1.86	0.47
SSC-B	37	35	2.58	1.20
SSC-C	41	18	2.89	1.53
SSC-D	43	8	3.05	1.84
SSC-E	46	4	3.23	2.14
SSC-F	89	6	5.01	4.24

<sup>a</sup> 100 – (SSC + DVB) = S + EVB.

Table 2

Exchange capacities of the partially sulfonated and commercial ion-exchanger catalysts

Ion exchanger	Exchange capacity (mmol/g)
S/DVB-P1	0.59
S/DVB-P2	1.60
S/DVB-P3	5.03
Lewatit SC104	5.10
Lewatit SC108	5.10
Lewatit SC108	4.90
Lewatit SC118	4.72

fonation of the same polymer at 90°C for 3 h was obtained practically fully functionalized catalyst S/DVB-P3. In this study were also included representatives of conventional, commercial ion-exchanger catalysts, gel-type low-crosslinked Lewatit SC104 and medium-crosslinked Lewatit SC108, and macroreticular medium-crosslinked Lewatit SPC108 and high-crosslinked Lewatit SPC118. The exchange capacities of these ion exchangers are shown in Table 2.

Before catalytic experiments, all the resins were converted to the acidic form by a column washing, first with 10% hydrochloric acid and then with distilled water. To eliminate possible differences in water content, the resins were dried overnight at 110°C and kept in a closed vessel over phosphorus pentoxide.

Catalytic activities of the ion-exchanger catalysts were tested by measurements of reaction rates of hydrolysis of ethyl acetate (5 wt% in water, 60°C) and ethyl benzoate (0.035 wt% in water, 75°C) in a flow-trough stirred (CSTR)

glass reactor (volume 7 cm<sup>3</sup>). Catalyst charge was 0.05–0.1 g and the reaction mixture was fed at constant rate in the range 10–20 cm<sup>3</sup>/h. Steady-state of reactor operation was achieved usually within 1–2 h after the start of an experiment. Analysis of reaction mixture from the ethyl acetate hydrolysis was performed by gas chromatography, using a 1.2-m column filled with Porapak N, working at 150°C (Chrom 6, Laboratorni přístroje, Praha). Reaction mixture from the hydrolysis of ethyl benzoate was analyzed by HPLC, with mobile-phase methanol–water (2:1), column 150 × 3 mm filled with Separon SGX C18 and spectrophotometric detection at 254 nm. In all experiments the conversion of esters was kept low (less than 10%) and hence it was possible to interpret the data obtained as initial reaction rates.

### 3. Results and discussion

Initially, the catalytic activity of the examined catalysts was tested in hydrolysis of acetate dissolved in water in relatively high concentration, 5 wt%, approaching its saturated concentration (6.6 wt%) at the reaction temperature (60°C). Comparison of the measured initial reaction rates for the all examined catalysts is shown in the second and third columns of Table 3. The catalytic activity expressed per unit of exchange capacity both for the SSC-containing and partially sulfonated catalyst significantly increases with the decrease of the exchange capacity. In this outcome could be recognized a possible positive effect of the presence of unfunctionalized,

Table 3

Reaction rate of hydrolysis of ethyl acetate (5 wt% ethyl acetate in water, 60°C) and ethyl benzoate (0.035 wt% ethyl benzoate in water, 75°C)

Catalyst	Reaction rate			
	Ethyl acetate		Ethyl benzoate	
	mmol/h·g	mmol/h·mmol	μmol/h·g	μmol/h·mmol
<i>SSC-containing catalysts</i>				
SSC-A	9.2	19.6	25.1	53.4
SSC-B	12.2	10.2	48.6	40.5
SSC-C	13.4	8.8	32.9	21.5
SSC-D	11.5	6.3	21.3	11.6
SSC-E	13.8	6.4	28.8	13.5
SSC-F	11.5	2.7	21.0	5.0
<i>Partially sulfonated S-DVB</i>				
S/DVB-P1	4.9	8.3	13.4	22.7
S/DVB-P2	11.0	6.9	40.3	25.2
S/DVB-P3	13.9	2.8	14.0	2.8
<i>Commercial ion exchangers</i>				
Lewatit SC-104	22.7	4.5	9.5	1.9
Lewatit SC-108	18.4	3.6	9.8	1.9
Lewatit SPC-108	17.8	3.6	17.8	3.6
Lewatit SPC-118	12.2	2.6	8.0	1.7

lipophilic, domains in the polymer catalyst skeleton. However, compared in terms of activity per unit of catalyst mass, the activity of partially functionalized resins is generally lower than the activity of the fully functionalized conventional ion exchangers.

These results are neither too good nor they are conclusive evidence for the assistance of the adsorption to the catalytic reaction on the polymer carrier. The better specific activity of the low-capacity ion-exchanger catalyst could, especially in the case of the partially sulfonate polymers, be the result of better accessibility of the active centers in therein [4]. Most of the SSC-containing catalysts do not exhibit any appreciable macroporosity and existence of a preferential adsorption of lipophilic compounds on these materials requires more conclusive evidence. Therefore, it was decided to test the sorption properties of these catalyst separately. Separate assessment of adsorption of reactants on catalysts is difficult and therefore the tests were made using a nonreactive sorbate. We have previously investigated adsorption of furfural from aqueous solutions on various adsorbents based on styrene

and divinylbenzene copolymers [6]. On these polymers furfural is adsorbed via lipophilic interaction only on the polymer surface and does not penetrate into the polymer mass. We decided to use this sorbate for testing of adsorption properties of selected representatives the investigated catalyst. For comparison was included also a typical lipophilic polymer adsorbent Amberlite XAD-2 (Rohm and Haas S.A., France). Measurements were performed at room temperature and the adsorption was evaluated from the material balance of the starting amount of furfural and the amount present in solution above the polymer in equilibrium. Details of the procedure are given in [6]. Results of the adsorption measurements are shown in Table 4.

The polymers containing few or no unsulfonated, lipophilic domains (SSC-F and Lewatit SPC-118), sorbed no furfural. Significant furfural adsorption was found only on the polymers containing substantial amount of unfunctionalized polymer mass (catalysts SSC-A and SSC-C). The adsorption measurements produced evidence that lipophilic domains intermixed with strongly acidic regions in ion-exchanger cata-

Table 4

Adsorption of furfural from water on selected examined catalysts and Amberlite XAD-2

Sorbent	BET surface area (m <sup>2</sup> /g)	Furfural equilibrium concentration (wt%)	Adsorption (g/g)
SSC-A	140	4.6	0.18
SSC-C	<1	4.9	0.08
SSC-F	<1	5.0	0.0
Lewatit SPC118	45	5.0	0.0
Amberlite XAD-2	340	4.3	0.21

lyst really can act as adsorbent attracting organic compounds from aqueous solution. The amount of furfural adsorbed on the catalyst SSC-A even approaches that adsorbed by the specialized adsorbent resin Amberlite XAD-2. For a material with a substantial surface area this is not too surprising. More unusual is the relatively good adsorption capacity of the catalyst SSC-C, which in the dry state has no appreciable porosity (BET surface area). As it was already mentioned, the previous study of furfural adsorption on styrene-type polymers [6] showed that furfural is adsorbed only on the surface of these materials and does not penetrate into their interior. Investigation of morphology of the SSC-containing polymer by inverse steric exclusion chromatography indicated that these polymers have mostly a block copolymer morphology consisting of intermixed separate lipophilic and hydrophilic domains [5]. The observed SSC-C capacity for furfural can be explained only on the base of an idea that the water-swollen hydrophilic domains serve in the otherwise nonporous material as transport channels for the sorbate, and the sorption occurs on the outer surface of the lipophilic, unfunctionalized regions. It means that the adsorption assistance to the catalytic reaction is limited only to the acidic centers located at the interface of the both domains. That is probably a reason why in the ethyl acetate hydrolysis the effect of the adsorption assistance was not too distinct. At the relatively high concentration of ethyl acetate in the reaction medium, the normal reaction in the interior of the lipophilic domains was high enough to diminish the relative importance of the rate enhancement at the hydrophilic-lipophilic interface.

Therefore, it was decided to perform the catalytic tests at conditions more favorable for the 'visibility' of the adsorption assistance effect, that is, with a less soluble reactant, whose low concentration in the liquid phase would make the 'normal' reaction very slow. In the fourth and fifth columns of Table 3 are shown the results of the tests of catalytic activity of the examined catalysts in hydrolysis of ethyl benzoate dissolved in water at concentration 0.035 wt% at temperature 75°C.

At this low concentration of the reactant, the influence of the presence of unfunctionalized lipophilic polymer in the catalyst was much stronger. Almost all the incompletely functionalized catalysts are more active than the conventional commercial types, even if compared in react rates per unit of mass. In the expression per unit of exchange capacity this difference is much greater.

In Fig. 1 are plotted the reaction rates of ethyl benzoate hydrolysis against the content of the nonfunctionalized, lipophilic components of the catalyst. In this figure are included results for both the catalysts prepared from SSC as functional monomer (empty symbols) and partially sulfonated resins (full circles). Data for the catalysts prepared by copolymerization of SSC with S, EVB and DVB, can be correlated with the fraction of nonfunctional monomers regardless of the DVB content. It shows that the presence of lipophilic domains in the catalyst skeleton has a dominant influence. Under the experimental conditions used, the morphology of the polymer mass seems to be of little importance. It is also illustrated by the similarity of the activity

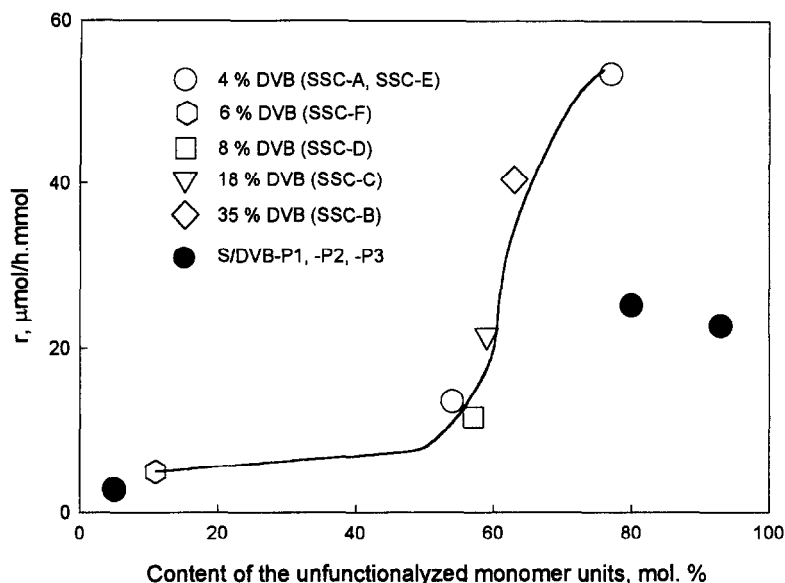


Fig. 1. Dependence of reaction rates of ethyl benzoate hydrolysis (0.035 wt% ethyl benzoate in water, 75°C) on the molar content of the unfunctionalized monomer units in various examined polymer catalysts.

of the highly functionalized catalysts SSC-F and S/DVB-P3, regardless of morphology differences which between materials of so different derivation must exist. However, at low functionalization degrees the partially sulfonated catalysts S/DVB-P1 and S/DVB-P2 are clearly inferior to the catalysts prepared by copolymerization of the functionalized monomer. Copolymerization makes possible to achieve better intermixing of the functionalized and unfunctionalized domains than it is possible to get by sulfonation of the prepared polymer.

It was demonstrated that modification of adsorption properties of polymer-based catalysts could be used for their tailoring for specific reaction conditions. At extremely low reactant concentration levels the assistance of adsorption-active domains in the polymer catalysts skeleton can bring substantial increase of their activity. The magnitude of this effect shown in this study is not probably insufficient for an economically effective practical application. On the other hand, this study was only the first in a preliminary assessment of possibilities of modifications of adsorptive properties of polymer catalysts and there

was no intention to perform an optimization. To find the most effective composition and morphology of an optimal adsorption-assisted polymer catalyst will require further substantial effort which should be connected with a specific process for which such catalyst would be developed.

### Acknowledgements

Support for one of the authors (K.J.) during his stay in France from the TEMPRA programme administered by the Région Rhône-Alpes is gratefully acknowledged. This work was supported in part by Grant No. 104/94/0749 from the Grant Agency of the Czech Republic.

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