

POSSIBILITIES OF DECREASING ABSORPTION OF WATER IN ION-EXCHANGER CATALYSTS

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Possibilities of decreasing the ability of strong-acid ion-exchanger catalysts to retain water were investigated in a case study of bisphenol A synthesis for to diminish effects of water as reaction product on the kinetics of the catalyzed reaction. It was found that partial thermal desulfonation or neutralization of about 30–40% acid groups with 2-aminoethanethiol can produce catalysts which exhibit, in the presence of technologically significant concentration of water, a higher activity in bisphenol A synthesis than conventional ion-exchanger catalysts.

Key words: Polymer supported catalysts; Sulfonates; Desulfonation; Ion exchangers; Water adsorption; Bisphenol A.

Strong-acid ion exchangers can replace soluble acids as catalysts in many industrially important reactions. Heterogenization of the homogeneous catalysts makes possible to minimize wastes and replace batch reactors with continuously operated flow-through reactors. Ion exchangers has been used as catalysts in a number of industrial processes^{1,2}. Reactions performed using ion-exchanger catalysts proceed in swollen polymer gel, *i.e.* is in a phase where the reactant composition is inherently different from that in the fluid phase. This specific feature was recognized already by Helfferich³, who proposed using corrective factors in description of reaction kinetics on ion-exchanger catalysts, expressing the difference in concentration of a reaction component inside the resin and in the outer fluid phase. Recently this aspect was brought up by Morbidelli and coworkers⁴, who studied liquid-phase esterification in a batch system. They found that effects of ion-exchanger catalysts are not restricted to an increase of the reaction rate. Due to selective absorption of reactants into the resin, in the batch system it is possible to shift the equilibrium conversion. They proposed using this phenomenon for optimization of the corresponding processes but they did not discuss possibilities how the partition of reactants between the fluid and the resin phase could be actively controlled. For the optimization of a catalytic process, such a tool would be highly desirable.

The affinity of the polymer network to various types of solvents may depend very strongly on its functionalization. Before functionalization, the styrene–divinylbenzene

backbone of a future ion exchanger resin is lipophilic, while the sulfonated strong-acid ion-exchanger catalysts are highly hydrophilic. We have already tested possibilities of combining the ability of a lipophilic porous polymer to concentrate organic compounds from dilute aqueous solutions with the catalytic activity of strongly acidic groups attached to the polymer⁵. Industrially quite important would be a method, which could decrease the ability of a strong-acid ion-exchanger catalyst to retain water. Catalytic activity of strong-acid resin catalysts is influenced quite substantially by the presence of water. In a study of dehydration of *tert*-butyl alcohol on strong-acid ion exchangers, Gates⁶ found that while in non-aqueous environment it is catalyzed by the matrix-bound $-SO_3H$ groups *via* the general acid catalysis mechanism, in the presence of water, a much slower mechanism of specific acid catalysis by hydrated protons is operating. In reactions where water is one of the products, water generally acts as a very strong inhibitor. In the Langmuir–Hinshelwood-type kinetic equation for synthesis of bisphenol A by condensation of acetone and phenol, this is expressed by the value of water adsorption coefficient two orders of magnitude higher than that for any other of the reaction partners⁷. For such a reaction having water as one of its products could be advantageous to diminish the ability of the ion-exchanger catalyst to retain water. In principle, this could be achieved by displacement of a part of the strongly hydrophilic acidic sulfonic groups. Sulfonic groups could be either completely removed or neutralized with a lipophilic cation, such as organic amine. In any case, such an operation will also decrease the amount of the catalytically active acid centers and the overall result will depend on the balance of both effects.

We have investigated a few possible approaches to the decrease of the hydrophilic character of strong-acid ion-exchanger catalysts. Properties of the modified catalysts were tested as catalysts in the synthesis of bisphenol A by condensation of acetone and phenol. The goal was to evaluate whether there exists a possibility to produce a modified ion exchanger catalyst able to provide a useful advantage over the conventional one.

EXPERIMENTAL

The starting material for all the modifications was a strong-acid ion exchanger Ostion KSC-1 (Spolchemie, Usti nad Labem). This is a gel-type sulfonated resin crosslinked with about 4% divinylbenzene, having an exchange capacity of 5.28 meq/g. Before use, it was purified by three-fold cycling between the $[NH_4]^+$ and $[H]^+$ forms, followed by washing with deionized water.

Lipophilization by partial neutralization with organic amines: All the amines were obtained from Fluka, Switzerland and were used as delivered. In a typical neutralization experiment with primary amines the wet ion exchanger in the acid form was suspended in water–methanol mixture (1 : 1, by volume) containing amine in an amount corresponding to about 15% of the resin exchange capacity. The resin and solution were kept in contact overnight, then the resin was filtered off, washed with water and dried overnight at 105 °C. The actual degree of the neutralization of the acid groups was determined from the change in the resin acid capacity resulting from the partial neutralization. For

neutralization with tertiary amines, the solvent was dioxane. Neutralization with 2-aminoethanethiol (cysteamine) was performed in water.

Lipophilization by thermal desulfonation: A glass beaker with suspension of the resin in water was heated in a stainless-steel autoclave to 200 °C at autogenous pressure for 5–20 h. After removing from the vessel, the resin was washed with deionized water and dried overnight at 105 °C. The actual degree of the neutralization of the acid groups was determined from the change in the resin acid capacity.

Tests of the catalytic activity: Synthesis of bisphenol A [2,2-bis(4'-hydroxyphenyl)propane] at 85 °C using acetone and phenol in molar ratio 1 : 8 (the optimum molar ratio for the reaction kinetics) was performed using the stirred glass microreactor (volume 5 cm³) described, together with the operating procedure, elsewhere⁷. Conversion of acetone was evaluated from the molar ratio of phenol and bisphenol A determined using HPLC (ref.⁷). Selectivity of the synthesis of bisphenol A was better than 94% and for the evaluation of the catalyst activity the formation of other by-products was neglected.

The tests were performed in two different arrangements. For measurements of reaction rates of acetone, the reactor was operated in a flow-through regime with a constant, low rate of the reaction mixture. These measurements were performed under conditions, when the acetone conversions were lower than 10%. The obtained data could be then considered initial reaction rates. For evaluation of integral data, *i.e.*, the dependence of the conversion on space time, the reactor was operated in the flow-through regime only in the beginning, until the steady state was established. The flow of the reaction mixture was then stopped and the reactor started to operate in the batch regime. This arrangement eliminated the most serious problem of the batch experiments with ion-exchanger catalysts, *i.e.* the influence of changes in the catalyst properties in the initial period of the contact of the resin with the reaction environment.

Sorption of water: Sorption measurements were performed as an independent characterization of the ability of the modified resins to retain water. The dry resin was contacted with acetone to which a known amount of water was added. The resin was left in contact with the solution overnight at the laboratory temperature. The equilibrium concentration of water in the solution above the resin was determined by gas chromatography. The amount of water sorbed by the resin was calculated from the difference between the starting and equilibrium concentration of water in acetone above the resin. The results represent the resin phase excess of water in comparison with the water concentration in the solution above the resin.

RESULTS AND DISCUSSION

In Table I reaction rates of bisphenol A synthesis are shown, measured in a series of ion-exchanger catalysts partially modified (neutralized) with various amines using reaction mixtures with different water contents. For comparison, the values for the unmodified resin are also shown. As the modification decreased also the amount of the acid centers, it is not surprising that at low concentrations of water in reaction mixture, the reaction rate is always lower on the modified than on the unmodified catalysts. A positive effect of the modification could be expected only at higher conversions, when the concentration of water as one of the products would be more significant. Therefore, the measurements of reaction rates of the bisphenol A synthesis were also performed with reaction mixtures containing controlled additions of water, simulating the situation naturally occurring at higher conversions of acetone. The added amount of water was either 1.05 or 1.8 wt.%. In the reaction mixture with the starting acetone–phenol molar

ratio 1 : 8, these water concentrations would be achieved at acetone conversions 45 and 80%, respectively. As expected, the decrease in the reaction rate due to the increase in the concentration of water is the strongest in the case of the unmodified catalyst. Partial neutralization of the catalyst with organic amines actually seems to diminish the ability of the resin to retain water, as the decrease in the reaction rate with increasing concentration of water in the reaction mixture is significantly not as pronounced on the modified as on the unmodified catalysts. However, even at the highest water concentration in the resins modified with primary amines, the positive effect of lower water retention can, at the maximum, compensate the negative influence of diminishing the amount of acid centers. Partial neutralization with tertiary amines at higher concentrations of water can increase the catalytic activity of the modified catalysts above that of the unmodified one, but the difference is not too spectacular. For obtaining a practically useful performance, it is necessary to make either the effect of hydrophobization more efficient or the effect of diminishing the amount of acid centers less harmful.

Instead of modifying hydrophilic sulfonic groups, it should be more efficient simply to diminish their amount, as the polymer skeleton itself is lipophilic. However, to achieve the desired goal, the sulfonated and unsulfonated domains would have to be intermixed very intimately⁵. It is difficult to achieve such distribution by partial sulfonation of the polymer skeleton⁸, due to poor accessibility of the originally lipophilic polymer to the hydrophilic sulfonating agent. A synthetic approach based on polymerizing a mixture of functionalized and unfunctionalized monomers⁹ would be too costly. Thermal desulfonation of water-swollen resin offers a technologically feasible route to a polymer with the random distribution of sulfonated and unsulfonated domains. The results of the catalytic activity tests of the thermally desulfonated resins are shown in

TABLE I

Influence of the degree of the sulfonic group modification in the ion-exchanger catalysts on the reaction rates of bisphenol A synthesis at different additions of water to the reaction mixture (acetone-phenol molar ratio 1 : 8, 85 °C, acetone conversion < 10%)

Modifier	Degree of modification %	Reaction rate, mmol/h g		
		0 wt.% water	1.05 wt.% water	1.80 wt.% water
None	0	5.8	1.4	1.1
Methylamine	19	2.5	1.1	0.6
Decylamine	23	3.2	1.1	0.8
Octadecylamine	20	4.2	1.2	1.1
Methyl(dioctyl)amine	12	3.7	1.6	1.5
Tripropylamine	22	2.6	1.3	1.3

Table II. In this table are also shown values of the water adsorption coefficient evaluated from the dependence of the reaction rates on the concentration of water, using the kinetic equation (1) and the following supposition on values of the other constants in the equation: The values of adsorption coefficients for acetone and phenol $K_a = 2.53 \text{ dm}^3/\text{mol}$ and $K_p = 0.635 \text{ dm}^3/\text{mol}$, respectively, were taken from a kinetic study¹⁰ and were considered not to be influenced by desulfonation. From this study, the value of the rate constant k for the unmodified resin catalyst was also taken. For the modified catalysts, the value of the rate constant k was adjusted according to the differences in the reaction rates determined on the unmodified and modified catalysts, without addition of water.

$$r = \frac{kc_a c_p^2}{(1 + K_a c_a + K_p c_p + K_w c_w)^4} \quad (1)$$

The data in Table II show that the thermal desulfonation can decrease the adsorption of water in the ion-exchanger catalysts quite significantly. At water contents in the reaction mixture higher than 1 wt.% (corresponding to the technologically important conditions at acetone conversions higher than 40%), the thermally desulfonated resin exhibited higher catalytic activity than the unmodified resin. It means that at these conditions the positive effect of the diminished retention of water offset the negative influence of the lowering of number of the acid sites.

Another way of obtaining technologically feasible ion-exchanger catalyst with a reduced retention of water is to use a modifier useful also for the catalyzed reaction. It is well known that both the activity and selectivity of the ion-exchanger catalyst for bisphenol A synthesis is greatly improved by partial neutralization of the sulfonic groups with cysteamine (2-aminoethanethiol) (ref.¹¹). This partial neutralization also diminishes the retention of water in the resin, as shown by the measurements of equilibrium

TABLE II

Influence of thermal desulfonation of the ion-exchanger catalysts on the reaction rates of bisphenol A synthesis at different additions of water to reaction mixture (acetone-phenol molar ratio 1 : 8, 85 °C, acetone conversion < 10%)

Reaction time h	Degree of desulfonation %	Reaction rate, mmol/h g			K_w^a dm^3/mol
		0 wt.% water	1.05 wt.% water	1.80 wt.% water	
0	0	5.8	1.4	1.1	7.2
14	8	2.5	1.5	1.3	6.6
30	23	3.2	2.0	1.6	4.3

^a Adsorption coefficient of water.

sorption of water by the ion-exchanger catalysts from an acetone–water mixture (Table III). For technological application, neutralization of 15% of the sulfonic groups of the ion-exchanger catalyst¹¹ has been recommended, which corresponds to the maximum promotion effect evaluated, however, at low conversion levels¹⁰. The reaction rates determined with ion-exchanger catalysts modified to various degrees with cysteamine are shown in Table IV. Modification of the catalyst by neutralization of 15% of its acid groups with cysteamine is an optimum for the initial stages of the reaction, when the water concentration is low. At the water concentration in the reaction mixture around 1 wt.%, the reaction rate, using catalysts modified by neutralization of 30 or 40% of the acid groups, becomes similar to that achieved with the 15% modified catalyst, so far considered being the optimum. At water concentration 1.8 wt.%, corresponding at industrial conditions to the final stages of the catalytic process, the catalysts promoted with

TABLE III

Dependence of the equilibrium sorption of water from acetone on the fraction of the sulfonic groups in the ion-exchanger catalyst Ostion KSC-1 neutralized with cysteamine (equilibrium water concentration in acetone above the resin 2.06 ± 0.06 wt.%)

Fraction of the sulfonic groups neutralized with cysteamine	Water sorption, g H ₂ O/g resin
0	0.147
0.05	0.136
0.15	0.142
0.30	0.123
0.40	0.086
0.60	0.089

TABLE IV

Influence of the degree of neutralization of the ion-exchanger resin catalysts with cysteamine on the reaction rate of bisphenol A synthesis at different additions of water to the reaction mixture (acetone–phenol molar ratio 1 : 8, 85 °C, acetone conversion < 10%)

Degree of modification %	Reaction rate, mmol/h g		
	0 wt.% water	1.05 wt.% water	1.80 wt.% water
15	70.1	9.2	3.5
30	35.3	8.5	5.5
40	32.9	7.7	4.2

excessive amount of cysteamine appear to be clearly superior to that modified conventionally.

The results of the measurements of reaction rates in the reaction mixture containing deliberate additions of water were confirmed by pseudo-batch experiments in which the reactor worked in integral mode (see Experimental) and the increase in the water concentration followed the increase in the conversion. Conversions achieved at different space times W/F with the catalysts modified by neutralization of different portions of the sulfonic groups with cysteamine are compared in Table V. The modification of 15% of the sulfonic groups with cysteamine produces the catalyst with the highest activity in the initial stages of the reaction. With this catalyst, for the space time $W/F = 130$ g h/mol, the highest conversion was achieved. In the further stages of the reaction, the situation becomes different. A higher degree of the modification decreases the sensitivity of the catalyst towards water as one of the products and at W/F around 300 g h/mol, it is possible to obtain a higher conversion with a catalyst having 40% of the acid groups modified with cysteamine.

CONCLUSIONS

There was found that desulfonation or neutralization of ion-exchanger catalyst with cysteamine can produce catalysts, which, due to lowered water retention, exhibit in presence of water for bisphenol A synthesis higher activity than the conventional ones. For technological application in a process, where water is one of the products (such as bisphenol A synthesis), it should be advantageous to use the catalysts with low water retention in a part of the reactor, where the concentration of water is high due to an advanced conversion. In such a case, the catalyst bed would consist of two parts. The input portion should contain conventional ion-exchanger catalysts and the catalyst with water retention ability decreased by thermal desulfonation or "overmodification" with

TABLE V

Conversions in bisphenol A synthesis catalyzed by ion-exchanger catalyst modified by neutralization of the sulfonic groups with cysteamine achieved at various space times W/F (acetone-phenol molar ratio 1 : 8, 70 °C)

Degree of modification, %	W/F , g h/mol	Acetone conversion, %
15	130	62
	320	70
30	130	48
	313	73
40	130	57
	330	82

cysteamine would be used for the rest of the catalyst charge. It is possible to estimate that for bisphenol A synthesis, the input part with the conventional charge should amount to about 30–40% of the overall mass of the catalyst bed. This technological solution is the subject of a patent application¹².

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