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**COMPARISON OF THE KINETICS OF BISPHENOL A SYNTHESIS  
ON PROMOTED AND UNPROMOTED ION EXCHANGER CATALYSTS**

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Previously evaluated kinetics of the synthesis of bisphenol A on ion exchanger catalyst modified by partial neutralization of its acidic groups by 2-mercaptoethylamine was compared with kinetics of this reaction on unmodified ion exchanger. Beside the differences in observed reaction rates, there was found only a small influence of the promoter on the form of the kinetics. The effect of 2-mercaptoethylamine as a heterogenized promoter, corrected for the influence of the diminishing of the concentration of acidic groups due to their neutralization by the promoter, was found to be comparable with the effect of ethylmercaptane as a homogeneous promoter.

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Reaction rate and selectivity of bisphenol A synthesis by acid-catalyzed condensation of acetone and phenol is known to be favourably influenced by the presence of mercapto compounds in the reaction mixture. For this reaction, ion exchanger catalysts containing (after modification by a suitable method) both acidic and mercapto groups bonded to their polymer skeleton<sup>1,2</sup> are applied in the industry. Using this type of catalyst, we have studied the kinetics of bisphenol A synthesis in the wide range of reaction conditions recently<sup>3</sup>. For the characterization of the influence of the introduction of mercapto groups into the ion exchanger catalyst it would be useful to compare the kinetics on the modified catalyst with the kinetics on the ion exchanger containing acidic groups only. The kinetics on an unmodified catalyst was measured by Reinicker and Gates<sup>4</sup> but their results are unsuitable for comparison with our data. They worked at 91°C and our study was performed at 70°C. Another possible source of discrepancies could be the differences in the ion exchanger catalysts used in both studies. Hence, we have now measured kinetic data at 70°C on unmodified ion exchanger from the same batch as that used in our previous work<sup>3</sup> and on a series of modified catalysts prepared from this ion exchanger containing various ratios of acidic and mercapto groups.

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## EXPERIMENTAL

Apparatus, procedure and chemicals used were the same as in the previous study<sup>3</sup>. All experiments were performed at 70°C. Ion exchanger catalyst was gel-type strong acid resin Ostion KSC-1 (Spolchemie, Ústí nad Labem), declared divinylbenzene content 4%, from the same batch as that used previously<sup>3</sup>. Modified catalysts containing also mercapto groups were prepared by contacting the ion exchanger with calculated amount of the solution of 2-mercaptoethylamine hydrochloride (Cilag Chemie, Switzerland). Changes in the values of exchange capacities determined by the titration of modified catalysts confirmed that the desired degree of modification was achieved. Catalyst particle size used was 0.35–0.63 mm and it was verified<sup>3</sup> that in such a case the results were free of the influence of internal diffusion.

## RESULTS AND DISCUSSION

Experiments were performed in a CSTR-type glass microreactor in which the direct measurement of reaction rates was possible. On the unmodified catalyst, 32 values of reaction rates were collected for initial ratios of phenol and acetone concentrations in the range from 4 : 1 to 30 : 1 at conversion of acetone lower than 10%. Eight of these experiments were performed with reaction mixture to which up to 1% of water was added.

The ion exchanger catalyzed synthesis of bisphenol A is very sensitive to the influence of water as the reaction product and hence it is necessary to include the term for water into the kinetic equation even for the description of reaction rates at conversions of acetone lower than 10 mole % (ref.<sup>3</sup>). Experimental data were correlated by the set of kinetic equations shown in Table I. Their selection was based on the experience with the description of kinetics on the modified catalyst<sup>3</sup>.

TABLE I  
Set of kinetic equations

Eq.	Rate equation	$[Q(K)_{rel}]_{min}^a$
(1)	$r = kc_Ac_P^2/(1 + K_Ac_A + K_Pc_P + K_Wc_W)^2$	0.377
(2)	$r = kc_Ac_P^2/(1 + K_Ac_A + K_Pc_P + K_Wc_W)^4$	0.288
(3)	$r = kc_Ac_P^2/(1 + K_A^2c_A^2 + K_Pc_P + K_Wc_W)^2$	0.717
(4)	$r = kc_Ac_P^2/(1 + K_A^2c_A^2 + K_Pc_P + K_Wc_W)^4$	0.731
(5)	$r = kc_Ac_P^2/(1 + K_Ac_A + K_Pc_P + \sqrt{(K_Wc_W)})^4$	0.291
(6)	$r = kc_Ac_P^2/(1 + K_A^2c_A^2 + K_Pc_P + \sqrt{(K_Wc_W)})^4$	0.731
(7)	$r = kc_Ac_P^2/[(1 + K_A^2c_A + K_Wc_W)(1 + K_Ac_A + K_Pc_P)^2]$	0.450
(8)	$r = kc_Ac_P^2/[(1 + K_A^2c_A + K_Wc_W)(1 + K_Ac_A + K_Pc_P)^4]$	0.393

<sup>a</sup> For the data obtained with unmodified catalyst.

The mathematical treatment by non-linear regression was based on Marquardt algorithm<sup>5</sup>; the sum of squared relative errors  $Q(K)_{rel}$  defined by the relation

$$Q(K)_{rel} = \sum ((r_{exp} - r_{calc})/r_{exp})^2 \quad (9)$$

was minimized.

In the preceding study using the ion exchanger catalyst modified by neutralization of 15% of the acidic groups (optimal degree of modification) by 2-mercaptoethylamine<sup>3</sup> Eq. (4) was the best, only slightly better than Eq. (2). In the present study, the ability of Eq. (4) to describe the experimental data obtained on the unmodified catalyst was much worse than that of Eq. (2). It indicates a small difference in the character of kinetics in these two cases, but nevertheless Eq. (2) seems to be able to describe the kinetic data both on modified and unmodified catalysts. The influence of the form of the adsorption term of water is negligible (compare Eqs (2) vs (5) and (3) vs (6)). The preference for higher value of the exponent in the denominator of a kinetic equation (compare Eqs (1) and (2)) was already observed in the kinetic study on modified catalyst<sup>3</sup>. It is in agreement with the observed dependence of the activity of ion exchanger catalysts of bisphenol A synthesis on the concentration of acidic active centres. Reinicker and Gates<sup>4</sup> did not consider kinetic equations with the exponent in denominator larger than 2. They found as acceptable the kinetic equation (1), but they preferred the equation based on the presumption of the existence of separate hydrophilic and lipophilic phases in ion exchanger catalyst. We found kinetic equations based on such hypothesis (Eqs (7) and (8)) less suitable than Eq. (2).

In Table II, the values of constants of Eq. (2) are shown, determined alternatively by optimization of all four constants of the equation (column A) and by optimization

TABLE II  
Values of constants of rate equation (2) for kinetic data obtained with unmodified catalyst

Constant	A <sup>a</sup>	B <sup>a</sup>
$k$ (dm <sup>3</sup> /kg h mol <sup>2</sup> )	995	347
$K_A$ (dm <sup>3</sup> /mol)	3.46	2.53
$K_P$ (dm <sup>3</sup> /mol)	0.873	0.635
$K_W$ (dm <sup>3</sup> /mol)	11.1	9.82
$[Q(K)_{rel}]_{min}$	0.288	0.408

<sup>a</sup> A Values of all constants were optimized during regression; B the constant  $k$  only was optimized during regression. Adsorption coefficients of acetone, phenol and water were held at values determined in the study on catalyst modified by the neutralization of 15% of acidic groups by 2-mercaptoethylamine<sup>3</sup>.

of constant  $k$  only when adsorption coefficients of acetone, phenol and water were held at values determined in the study on optimally modified catalyst (column B). In the second case, the obtained value of  $Q(K)_{rel}$  was, of course, higher but nearly within the limit permitted according to the Beale's criterion<sup>6</sup> for 95% probability level: critical  $Q(K)_{rel} = 0.399$ . It means that the observed differences in the shapes of the kinetic dependences obtained with modified and unmodified catalysts are comparable with the experimental error. The possibility that the introduction of mercapto groups into the catalyst influences the rate constant only cannot be excluded.

Due to the small difference in the character of the kinetic dependences found for unmodified and optimally modified catalyst, the kinetic measurements on ion exchanger catalysts with 5, 10, 20 and 30% neutralization of acidic groups by 2-mercaptoethylamine were performed in limited extent only. With reaction mixtures containing phenol and acetone in molar ratios 2 : 1, 8 : 1 and 30 : 1, 12 values of reaction rates were collected for each catalyst. They were correlated by Eq. (2) with adsorption coefficients of acetone, phenol and water fixed at values from column B of Table II. The results were the values of the constant  $k$  characterizing the differences in activities of these catalysts. The dependence of the values of constant  $k$  on the degree of modification is shown in Fig. 1. For 15% modification, this dependence shows a sharp maximum. Further increase of the modification results in a decrease of catalytic activity due to the diminishing of the concentration of acidic centres by excess 2-mercaptoethylamine. The decline of catalytic activity corresponding to the increase of the degree of modification from 15 to 30% is proportional to 4th power of the fraction of sulfonic groups remaining in the acidic form. This agrees with the dependence of the bisphenol A synthesis rate on the concentration of acidic centres

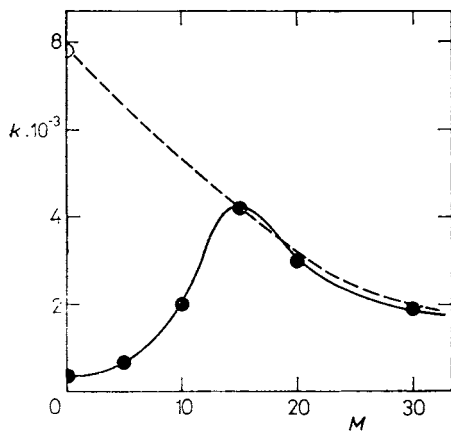


FIG. 1

Dependence of the catalytic activity on the modification of ion exchanger catalyst by 2-mercaptoethylamine. Constant  $k$  of rate equation (2) determined by correlation of experimental data using values of  $K_A$ ,  $K_F$  and  $K_W$  from the column B of Table II ( $\text{dm}^3/\text{kg h mol}^2$ ).  $M$  Fraction of ion exchanger acidic groups neutralized by 2-mercaptoethylamine (%). ● Data obtained with reaction mixture containing phenol and acetone only; ○ activity determined using reaction mixture containing 0.5 wt. % of ethylmercaptane

in the ion exchanger catalysts determined in independent experiments with the catalysts partially neutralized by sodium ions<sup>7</sup>.

The dependence of catalytic activity on the 4th power of the fraction of sulphonic groups remaining after modification in acidic form is shown in Fig. 1 as dashed line. Its extrapolation to the zero modification corresponds well to the activity determined using unmodified catalyst and reaction mixture containing 0.5 wt. % of ethylmercaptane as a homogeneous cocatalyst. This concentration of ethylmercaptane is high enough for the saturation of bisphenol A synthesis requests. Its further increase would have no influence. It seems that the intrinsic activity of the ion exchanger catalyst promoted by the compounds containing mercapto groups is the same, regardless whether the promoter is present as homogeneous cocatalyst or if it is heterogenized by bonding to the ion exchanger.

#### LIST OF SYMBOLS

$c_i$	concentration of compound $i$ , mol/dm <sup>3</sup>
$k$	rate constant (dimensions according to the form of the rate equation)
$K_i$	adsorption coefficient of compound $i$ , dm <sup>3</sup> /mol
$r$	reaction rate, mol h <sup>-1</sup> dm <sup>-3</sup>
$Q(K)_{rel}$	sum of squared relative deviations of reaction rates (Eq. (9))

#### Subscripts

A	acetone
P	phenol
W	water

#### REFERENCES

1. Wagner R. B. (Hercules Powder Company): U.S. 3,172,916 (1965).
2. McNutt B. W., Gammill B. B. (Dow Chemical Company): U.S. 3,394,089 (1965).
3. Jeřábek K., Odnoha J., Setínek K.: Appl. Catal. 37, 129 (1988).
4. Reinicker R. A., Gates B. C.: AIChE J. 20, 933 (1974).
5. Marquardt D. W.: J. Sec. Ind. Appl. Math. 11, 431 (1963).
6. Beale E. M. L.: J. R. Stat. Soc. B 22, 41 (1960).
7. Jeřábek K., Setínek K.: J. Mol. Catal. 39, 161 (1987).

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