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ALKYLATION OF AROMATICS. KINETICS OF PHENOL ALKYLATION WITH METHANOL

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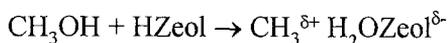
Abstract

A kinetic study of phenol alkylation with methanol in the presence of γ -Al₂O₃ has been carried out. A mechanism involving the reaction of phenol and methanol adsorbed on acid-base pair sites is proposed.

Keywords: Phenol, alkylation, kinetics

INTRODUCTION

Alkylation of phenol with methanol results in a range of products. Some of them, such as anisole, *o*-cresol, *p*-cresol and 2,6-xyleneol, are extensively employed in industry [1]. In previous works [2-4] we found that HY zeolite can catalyze dimethylphenols formation if the contact time is sufficiently long. The study of reaction kinetics allows to propose a mechanism for the reaction. In the first step a methanol molecule is chemisorbed on an acid center of zeolite with methyloxonium ion formation:



Then, a gaseous phenol molecule reacts with adsorbed methanol, giving products of *O*- and *C*-alkylation with selectivity depending on both acid centers density and zeolite structure. It is necessary to point out that under the reaction conditions applied (473 K), phenol is physisorbed in the zeolite structure. The presence of narrow pores (*ca* 7.5 Å) and a reaction temperature close to phenol boiling point (455 K) favors its capillary condensation in the HY framework. Hence, phenol concentration in the proximity of active centers becomes constant in spite of its partial pressure in the gas phase, which explains the observed reaction order equal to zero for all zeolites studied.

The aim of the present work was to extend the investigation of the alkylation reaction on large pore catalysts. Alumina with a mean pore diameter of 80 Å was chosen to study the kinetics of the reaction of methanol with phenol. In this case, the observed kinetics should not be disturbed by phenol capillary condensation.

EXPERIMENTAL

$\gamma\text{-Al}_2\text{O}_3$ (GSF 300, Rhône Poulenc, specific surface area $270 \text{ m}^2 \text{ g}^{-1}$, average pore diameter 80 Å) of 0.063-0.125 mm grain diameter was used as catalyst. Phenol alkylation was carried out under atmospheric pressure in a differential flow reactor. A mixture of phenol, methanol and nitrogen ($P_N=81.04 \text{ kPa}$, $P_{Ph} + P_{Meth}=20.26 \text{ kPa}$) was used as substrate. Prior to the reaction the catalyst (100 mg) was activated under nitrogen flow for 12 h at 773 K, then the reactor was cooled down to the reaction temperature (473 K) and the substrate was introduced. The kinetic orders of phenol alkylation were determined according to the procedure described elsewhere [4]. Liquid reaction products of phenol alkylation were collected in an ice trap at intervals of 30 min and analyzed by gas chromatography (WCOT CPWax 57 CB capillary column, 413 K).

RESULTS AND DISCUSSION

The influence of partial pressure of phenol and methanol on the reaction rate was determined for phenol conversions lower than 5%. At such conditions only primary reaction products, *viz.*, anisole, *o*- and *p*-cresol were detected. The phenol alkylation rates for different partial pressures of the reactants, obtained for three independent measurements as well as calculated reactions orders are shown in Table 1. It was found that the rate of phenol alkylation increases with the rise

of methanol partial pressure (P_{Meth}) and decreases when the phenol partial pressure (P_{Ph}) increases.

Table 1

Kinetics of alkylation of phenol with methanol: r -reaction rate for different phenol (P_{Ph}) and methanol (P_{Meth}) partial pressures; a, b are reaction orders calculated from the rate equation: $r = k P_{Ph}^a P_{Meth}^b$

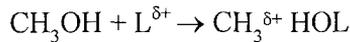
Catalyst	P_{Ph} (kPa)	P_{Meth} (kPa)	r ($10^3 \text{ mol h}^{-1} \text{ g}^{-1}$)			a	b
$\gamma\text{-Al}_2\text{O}_3$	2.0	10.0	1.3	1.5	1.4	-0.2	0.1
	3.3	10.0	1.5	1.4	1.5		
	5.0	10.0	1.4	1.4	1.4		
	10.0	10.0	1.1	1.3	1.1		
	10.0	15.0	1.7	1.8	1.8		
	10.0	30.0	2.1	2.0	2.0		
	10.0	50.0	1.8	1.8	1.8		

The reaction of phenol with methanol is catalyzed by solids of acidic or basic nature. In the presence of solid acids, such as zeolites [2,3,5] Nafion H [6] or silica mounted H_3PO_4 [7], methanol undergoes activation and reacts with gaseous phenol. For catalysts of basic properties, such as MgO for example, it is the phenol molecule which is activated to form phenolate anion capable of reacting with gaseous methanol. In the case of alumina, which possesses simultaneously acidic and basic centers, both reacting species, *viz.*, phenol and methanol could be chemisorbed and thus activated. The mechanism (Hinshelwood or Rideal type) of the reaction can be elucidated from the rate dependence on reactant partial pressures. It was found (see Table 1) that in the case of alumina, reaction orders relating to phenol (a) and methanol (b) are substantially lower than unity and have different signs. One can propose two explanations of these findings. The first one is based on the assumption that due to the low reaction temperature (473 K), close to the boiling point of phenol (455 K), this reactant could be physisorbed in the vicinity of active centers. In such a case the phenol partial pressure near the surface is no longer equal to its partial pressure in the gas phase (P_{Ph}) and should be replaced by physisorbed phenol surface concentration C_{Ph} , which is given by the Langmuir type formula [8,9]:

$$C_{Ph} = \frac{d P_{Ph}}{1 + K_L P_{Ph}} \quad (1)$$

where K_L and d are physisorption parameters.

Depending on the value of the $K_L P_{Ph}$ term, the reaction order may vary from unity ($K_L P_{Ph} \ll 1$) to zero ($K_L P_{Ph} \gg 1$). Observed reaction order was equal to -0.2, a value close to zero. This indicates complete saturation of the active sites with phenol. In this case, the phenol partial pressure near the surface remains constant and equal to: $P_{Ph} = d / K_L$. The reaction order relative to methanol was found to be 0.1, which may be caused, similarly as in the case of zeolites [4], by strong methanol adsorption on acid centers. There are two potential sites for methanol adsorption: OH groups and Lewis acid centers. Since the hydroxy groups of alumina are incapable of protonating even such strong bases like pyridine [10], it is improbable that they could interact with methanol, being a weaker base. Hence, Lewis acid centers (L) are the most probable sites for methanol chemisorption on alumina.



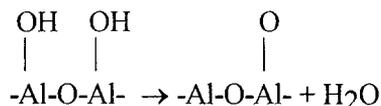
If one assumes that the rate-determining step consists of the reaction of physisorbed phenol with strongly adsorbed methanol, then the following rate equation should describe the experimental data:

$$r = \frac{k d P_{Meth}}{K_L (1 + K_{Meth} P_{Meth})} \quad (2)$$

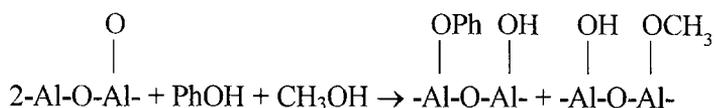
where K_{Meth} denotes the equilibrium constant of methanol adsorption.

The second interpretation of the results is based on our finding that when applying the same experimental procedure to different HY zeolites, the reaction order relative to phenol was found to be exactly equal to zero [4]. Hence, the negative value of reaction order observed in this work for large pore alumina should reflect rather the differences in reaction mechanism than the capillary condensation of phenol. The different signs of reaction orders relative to phenol and methanol (see Table 1) indicate that both reactants adsorb competitively on the same active center. Since on the alumina surface methanol activation

leading to $\text{CH}_3^{\delta+}$ cation is possible only on Lewis acid sites and phenol could interact with basic centers exclusively, one can assume that active center is an acid-base pair site. Such centers are formed as a result of alumina surface dehydration [11]:



Phenol and methanol adsorption on alumina could proceed according to the following scheme:



Phenol has a pK_a close to 10, and thus more pronounced acid-base properties than methanol. Hence, its interaction with acid-base pair sites should determine the number of vacant centers for methanol adsorption. It explains that in a certain region of phenol partial pressure, the observed reaction order relative to phenol may be negative. If one assumes that the surface reaction between strongly adsorbed molecules of phenol and methanol is the rate-determining step, then the rate equation of phenol alkylation could be written as:

$$r = \frac{k P_{\text{Ph}} P_{\text{Meth}}}{(K_{\text{Ph}} P_{\text{Ph}} + K_{\text{Meth}} P_{\text{Meth}})^2} \quad (3)$$

The choice between the above two explanations of the kinetics may be done on the basis of the least-squares fit of experimental data to the two alternative rate equations. To simplify the fitting procedure, eqs 2 and 3 were used in linear forms. The results of fitting procedure are presented in Fig. 1. Calculated correlation coefficients equal to 0.94 and 0.41 for data fit to eqs 3 and 2, respectively, indicate that the mechanism of simultaneous adsorption of phenol and methanol on an acid-base pair site is more probable than the mechanism involving the physical adsorption of phenol.

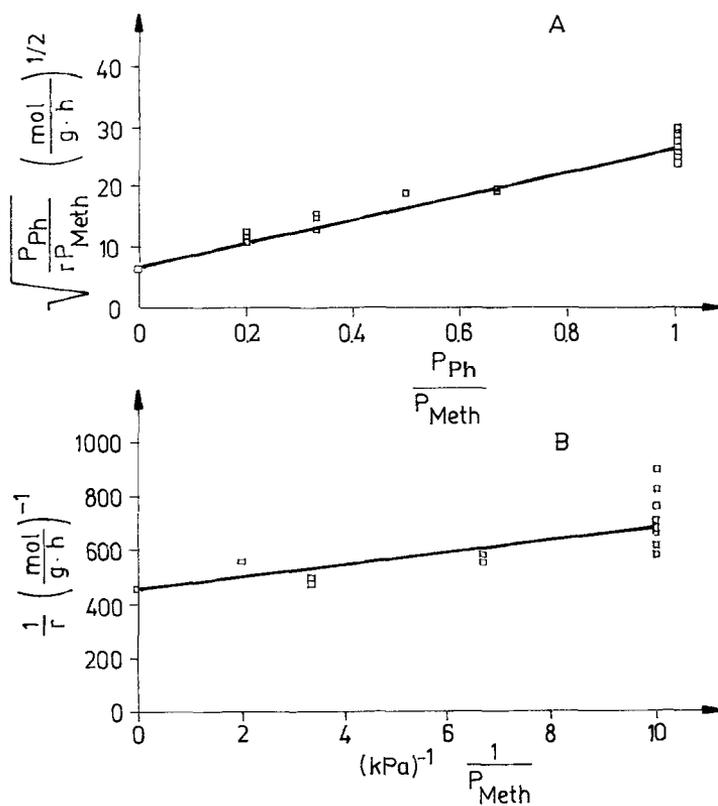


Fig.1. Least-squares fit of experimental data to rate equations 3 (A) and 2 (B)

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