

Alkylation of Phenol with Methanol over Basic X Zeolites

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Abstract: The alkylation of phenol with methanol was studied and a high selectivity for O-alkylation was attained over alkali-metal cation-exchanged X zeolites. The transformation of primary products of the title reaction was also studied over CsX zeolite. On the basis of experimental results, a reaction scheme on CsX zeolite was suggested.

Keywords: Alkylation, phenol and methanol, basic zeolite.

Alkylation of phenol provides many industrial intermediates such as agrochemicals and polymers. The alkylation of phenol with methanol proceeds *via* oxygen (O)-alkylation producing anisole (An) as well as methylanisole isomers (mAn) and ring (C)-alkylation producing mainly cresols (*m.p.o*-Cr) as well as xylenols (Xy). Vapor-phase alkylation of phenol with methanol has been examined over various solid catalysts¹⁻⁵. The catalytic properties and the product selectivity are strongly affected by the structure of catalyst in addition to acidic-basic character. Strong acid catalysts generally produce a mixture of anisole and cresols as well as other secondary methylated products and were deactivated with time due to coking. Basic catalysts or acid-base catalysts selectively produce *o*-cresol and 2,6-xyleneol,ortho-methylates. Weak acid catalysts favour the O-alkylation of phenol. Recently, we have found⁵ that the alkylation of phenol proceeded predominantly through anisole as the unstable intermediate over strong acidic H β zeolite. So far, little attention has been paid to basic zeolite. The aim of this work is to investigate the reaction scheme of phenol alkylation with methanol and the transformation of intermediate anisole and *o*-cresol on alkali-metal cation-exchanged X zeolites.

Experimental

The methylation of phenol (PhOH) with methanol (MeOH) over alkali-metal cation-exchanged X zeolite (Si/Al=1.24) as catalysts was carried out in a flow reaction system at 673K under atmospheric pressure. The catalysts were pretreated *in situ* N₂ flow for 2 h at 773K. The mole ratio of the phenol to methanol was 1:5, and mole ratio of carrier gas N₂ to the reactants (PhOH and MeOH) was 6:1. The contact time was

expressed as W/F_{PhOH} ($W/F_{\text{PhOH}}=148\text{g.h.mol}^{-1}$). The liquid reaction products were collected in an ice trap in a sequence of 30 min and analyzed by gas chromatography.

Results and Discussion

Table 1 activity and product distribution over basic X zeolites at 673K

Catalyst	Conversion (mol%)	Products distribution of Oxygenates (mol%)				
		An	mAn	o-Cr	(m+p)-Cr	Xy+others
NaHX	47.3	3.0	8.5	12.5	6.4	69.6
LiX	64.5	42.3	18.1	13.9	12.4	13.3
NaX	75.3	51.7	18.4	13.9	4.1	11.9
KX	92.5	69.4	20.0	4.9	0	5.7
CsX	93.1	60.4	23.3	7.1	0	9.2

It is observed that acidic strength decreased and basic strength increased on alkali-metal cation-exchanged X zeolites in the order from Li to Cs, and the acidic and basic sites are shown to coexist simultaneously on these zeolite samples. The exchanged alkali metal cation acts as a Lewis acid and the close framework oxygen as a base⁶. The activities and selectivities of alkali-metal cation-exchanged X zeolites in alkylation of phenol with methanol were shown in **Table 1**. Every catalyst has a high activity for the alkylation, increasing acidity trends toward C-alkylation to form cresols and xylenols, increasing basicity trends toward O-alkylation to form anisole and methylanisoles. The order of the activity of alkylation over alkali-metal cation-exchanged X zeolites agrees with that of the basicity of the catalysts. It is indicated that the basicity is essential for the O-alkylation of phenol. The high selectivities for An and mAn are observed for KX zeolite (89.4%) and CsX zeolite (83.7%). The overall yield of An and mAn on CsX zeolite was 77.9% , the other products were cresols (6.6%) and xylenols (8.6%) . At high reaction temperature (748K), a large amount of cresols and xylenols were formed by both primary and secondary C-alkylation reaction (**Table 2**). Because the activation energy of O-alkylation is lower than that of C-alkylation³.

In order to study the transformation of intermediate An and Cr on CsX zeolite, the reaction of An and Cr on CsX zeolite were carried out. When An alone was used as reagent a large amount of PhOH was formed (**Table 2**). An was disproportionated to form mAn and PhOH. The latter is present in excess over the stoichiometric amount, which may be attributed to the dealkylation of An. Increase the selectivity of Cr could be due to the isomerization of An. The reaction of An with MeOH (1:1) over CsX zeolite demonstrates that An readily undergoes methylation to mAn. Decrease the selectivity of PhOH may be due to the rapid further alkylation of PhOH produced with MeOH. The alkylation of PhOH by An leads to Cr as main product, which shows that An as alkylating agent compared with MeOH effectively undergoes C-methylation to give Cr. Meanwhile, PhOH inhibits the disproportionation and dealkylation of An. The reaction of o-Cr and MeOH only gives (m+p)-Cr and Xy. (m+p)-Cr were obtained by the isomerization of o-Cr, but the O-alkylation of o-Cr does not occur. Thus, we suggest that An is produced from the O-alkylation of PhOH with MeOH. mAn can be formed by the

C-methylation and disproportionation of An. *o*-Cr is formed mainly from C-alkylation of PhOH or An.

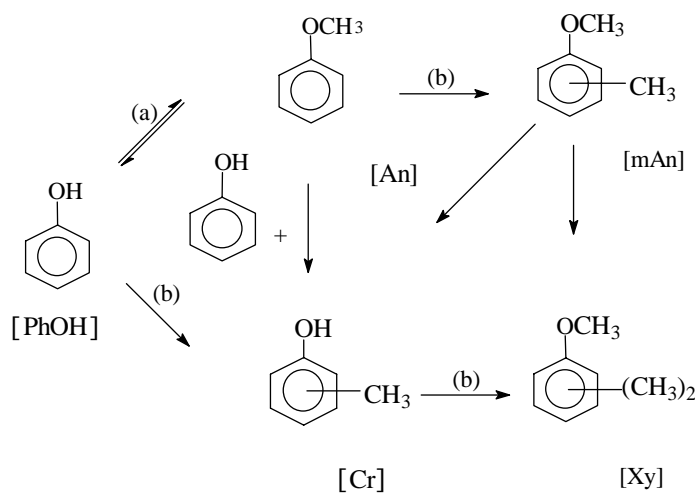
Table 2 product distribution in the transformation of phenol and anisole over CsX zeolite at 673K

Reactant (mol ratio)	Conv. (mol%)	product distribution of oxygenates (mol%)					
		PhOH	An	mAn	<i>o</i> -Cr	(<i>m+p</i>)-Cr	Xy+others
PhOH/MeOH=1/5	93.1	—	60.4	23.3	7.1	0	9.2
PhOH/MeOH=1/5 ^a	88.6	—	15.0	12.5	13.8	7.3	51.4
An	35.9	59.6	—	21.1	11.5	1.7	6.2
An/MeOH=1/1	51.0	33.3	—	30.4	17.1	3.0	16.2
An/PhOH=1/1	21.7	19.5	—	26.5	37.0	9.5	7.5
<i>o</i> -Cr/MeOH=1/1	54.8	0	0	0	—	80.7	22.9

^areaction at 748K

Based on the above results, the reaction pathway for the alkylation of PhOH with MeOH on CsX zeolite can be depicted as shown in **Figure 1** wherein the reaction proceeds predominantly through O-alkylation to give An rather than C-alkylation to give Cr and Xy. An is an unstable primary product and further is transformed into other products, such as mAn and Cr.

Figure 1. Reaction scheme of PhOH alkylation with MeOH on CsX zeolite.



(a) O-alkylation, (b) C-alkylation

Acknowledgment

The work was supported by the National Natural Science Foundation of China.

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Received 7 December 1998

Revised 22 July 1999

Erratum.

CCL Vol. 10, No. 9, pp. 778, **Figure 1** should appear as follows:

Figure 1. Response of electroosmosis to radial voltage using different buffers at 0.01mol/l. An anode-to-cathode flow was set as positive.

