

## Alkylation of phenol with methanol over ion-exchanged Y-zeolites

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MS received 4 July 1998; revised 21 September 1998

**Abstract.** Alkylation of phenol with methanol was carried out over Lewis acid ion exchanged Y-zeolites, FeY, ZnY, CdY and LaY at temperatures of 523, 573, 623, 673 and 698 K. The products obtained were *o*-cresol, 2,6-xyleneol and anisole. The effects of phenol to methanol mole ratio and Weight Hourly Space Velocity (WHSV) were examined for high phenol conversion and product selectivity. Phenol conversion decreased with increase of temperature over all the catalysts due to coke deposition. Selectivity to *o*-cresol decreased with increase of temperature as it, once formed, became the reactant for formation of 2,6-xyleneol. Selectivity to 2,6-xyleneol increased with increase of temperature indicating high activation energy for its formation. Selectivity to anisole, although formed less than 10% over all the catalysts, decreased with increase of temperature due to its conversion to *o*-cresol and then to 2,6-xyleneol. In addition, selectivity to anisole also decreased with decrease of phenol to methanol feed ratio and WHSV. The study of time on stream showed preferential blocking of strong acid sites by coke deposits and hence these site dependent formations of *o*-cresol and 2,6-xyleneol were greatly reduced but free weak acid site dependent anisole formation increased with time.

**Keywords.** Phenol; methanol; *o*-cresol; 2,6-xyleneol; anisole.

### 1. Introduction

Alkylation of phenol is an industrially important reaction because many alkylated phenols have important applications. For instance, anisole is used as an octane booster for petrol<sup>1</sup>, *o*-cresol in the manufacture of insecticides and herbicides<sup>2,3</sup> and 2,6-xyleneol in the manufacture of poly(2,6-dimethyl)phenyleneoxide<sup>4</sup>, a thermoresistant polymer, used in special grade paints. In general, alkylation of aromatics occurs at a ring position over acidic catalysts and at oxygen over basic catalysts<sup>1,3,5</sup>. Therefore, the choice of suitable catalysts and proper operating conditions are of primary importance in determining the industrial convenience of the process of alkylation of phenol. Several papers and patents have been published over alkylation of phenol with methanol over a variety of catalysts which include phosphates<sup>6</sup>, thoria<sup>7</sup>, vanadiahromia<sup>8</sup>, zeolites Y and X<sup>5</sup>, ZSM-5<sup>9</sup> and hydrotalcites<sup>10,11</sup>. The formation of both ring and O-alkylated products over all these catalysts has been established. NaX and NaY zeolites and their protonic forms have also been used for this reaction. Selective ring or O-alkylation still remains an interesting area of research. In the present study, it has been planned to investigate alkylation of phenol with methanol over Lewis acid

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ion-exchanged *Y*-zeolites, which have not been largely exploited as catalysts for this reaction, and to examine the conditions for maximizing the ring alkylated products.

## 2. Experimental

The parent zeolite NaY (Si/Al = 2.62) obtained from IPCL-CATAD, India, was successively ion-exchanged with 1 M ammonium chloride solution at 348–353 K to obtain its protonic form (91%). The ammonium form was finally converted to H-form by calcination at 673 K for 6 h.

The H-form of *Y*-zeolite thus obtained, was ion-exchanged using 0.1 N solution of respective metal nitrates, Fe(III)<sup>12</sup>, Zn(II)<sup>13</sup>, Cd(II)<sup>14</sup> and La(III)<sup>15</sup> nitrates. The pH of the solutions was maintained between 4.5 and 6 by adding a buffer. 15 ml of metal nitrate solution per gram of zeolite was stirred under reflux at 353 K for 6 h. This mixture was filtered, washed several times with warm water and dried in a hot air oven at 373 K for 12 h. The same exchange operation is repeated thrice. The zeolite was then activated at 723 K for 12 h in a slow stream of dry and purified air. The XRD patterns of parent HY and Lewis acid ion-exchanged *Y*-zeolites are shown in figure 1. The  $2\theta$  values of all the catalysts were in good agreement with the published data, and in addition, the spectra indicated high crystallinity. However, a decrease in relative

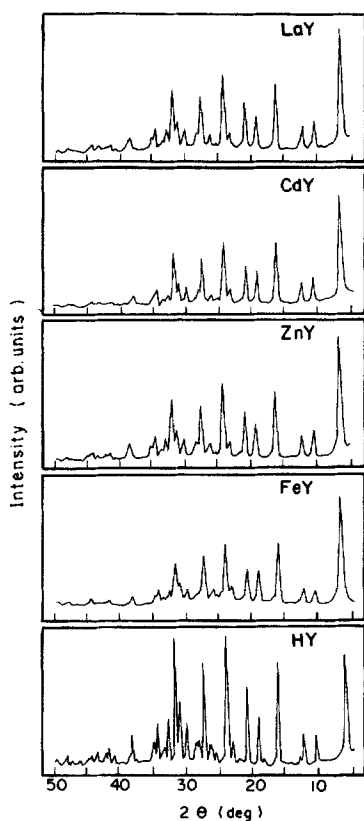


Figure 1. XRD patterns of HY and ion-exchanged HY zeolites

**Table 1.** Composition and characteristics of Lewis acid ion-exchanged *Y*-zeolites

Catalysts	Unit cell composition	Si/Al	Percentage of exchange (%)	Surface area m <sup>2</sup> /g	TPD of NH <sub>3</sub>	
					Weak acid sites m.mol/g	Strong acid sites m.mol/g
HY	H <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub> (AlO <sub>2</sub> ) <sub>53</sub>	2.62	Nil	650	—	—
FeY	Fe <sub>14</sub> H <sub>11</sub> (SiO <sub>2</sub> ) <sub>139</sub> (AlO <sub>2</sub> ) <sub>53</sub>	2.62	78	620	0.35	1.18
ZnY	Zn <sub>17</sub> H <sub>19</sub> (SiO <sub>2</sub> ) <sub>139</sub> (AlO <sub>2</sub> ) <sub>53</sub>	2.62	64	609	0.54	0.59
CdY	Cd <sub>15</sub> H <sub>23</sub> (SiO <sub>2</sub> ) <sub>139</sub> (AlO <sub>2</sub> ) <sub>53</sub>	2.62	60	595	0.59	0.33
LaY	La <sub>12</sub> H <sub>14</sub> (SiO <sub>2</sub> ) <sub>139</sub> (AlO <sub>2</sub> ) <sub>53</sub>	2.62	73	590	0.30	1.19

intensities was observed in all the ion-exchanged *Y*-zeolites compared to the parent zeolite HY, which might be due to the distortion of frameworks by the exchanged metal ions. All these materials were estimated by wet chemical analysis, and characterized by Brunauer, Emmette and Teller (BET) and Temperature Programme Desorption (TPD) and the data obtained are given in table 1.

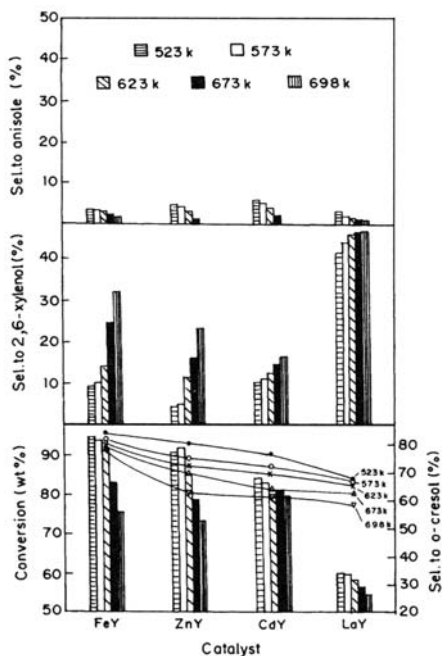
Methylation of phenol was carried out in a fixed bed continuous down flow reactor made up of a quartz tube, 40 cm in length with an internal diameter of 1 cm. About 1 g of each catalyst was taken in the reactor and the reaction mixture was fed into it by a motor driven syringe pump at predetermined flow rates. The liquid product collected for 15 min of each run which normally covered 1 h was discarded and only the product collected after these 15 minutes was analysed. The analysis of the products was done in a Hewlett-Packard gas chromatograph (5890 A) equipped with a Flame Ionisation Detector (FID) using a SE30 column. Nitrogen was used as a carrier gas, flown at a rate of 20 ml per minute. After completion of each run, the reactor system was flushed with nitrogen to remove the adsorbed molecules and regenerated at 748 K in a current of CO<sub>2</sub> free air for 6 h.

### 3. Results and discussion

Alkylation of phenol with methanol was carried out over ion-exchanged *Y*-zeolites, FeY, ZnY, CdY and LaY, at 523, 573, 623, 673 and 698 K atmospheric pressure. Maintaining phenol to methanol mole ratio as 1:3, the reaction was run at WHSV of 2.9, 4.8 and 6.7 h<sup>-1</sup>. The products obtained significantly were *o*-cresol, 2,6-xyleneol and anisole. The other ring alkylated products identified by GC-MAS analyser were of insignificant quantity and hence they are not presented and discussed. The effects of temperature, WHSV and time on stream on phenol conversion and product selectivity were studied and the data obtained are discussed in the following sections.

#### 3.1 Effect of reaction temperature

In the beginning, the effect of temperature on phenol conversion and product selectivity was examined for phenol to methanol mole ratio equal to 1:3 and WHSV 2.9 h<sup>-1</sup>. The results obtained are illustrated in figure 2 with lines and bars representing phenol conversion and product selectivity respectively. Phenol conversion decreased with increase of temperature over all the catalysts due to blocking of active sites by coke<sup>3</sup>. Although the catalysts were designed to favour ring alkylated products, namely

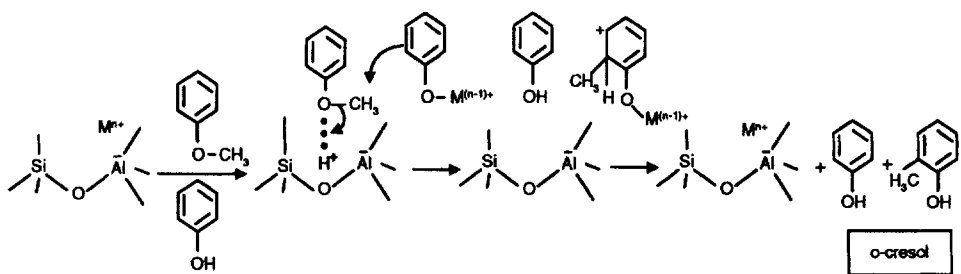
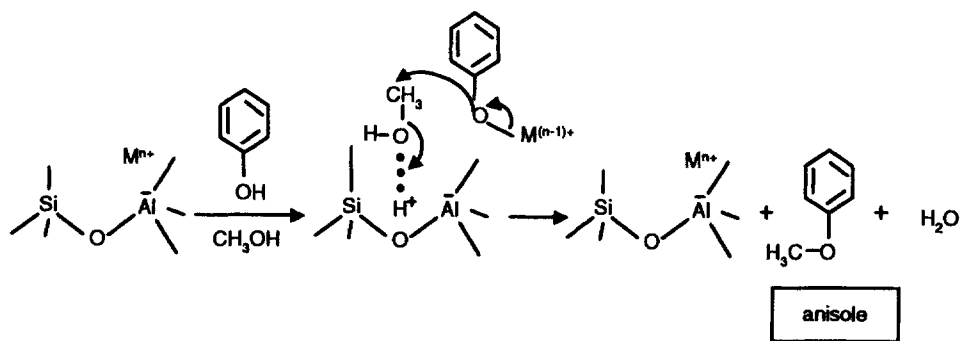
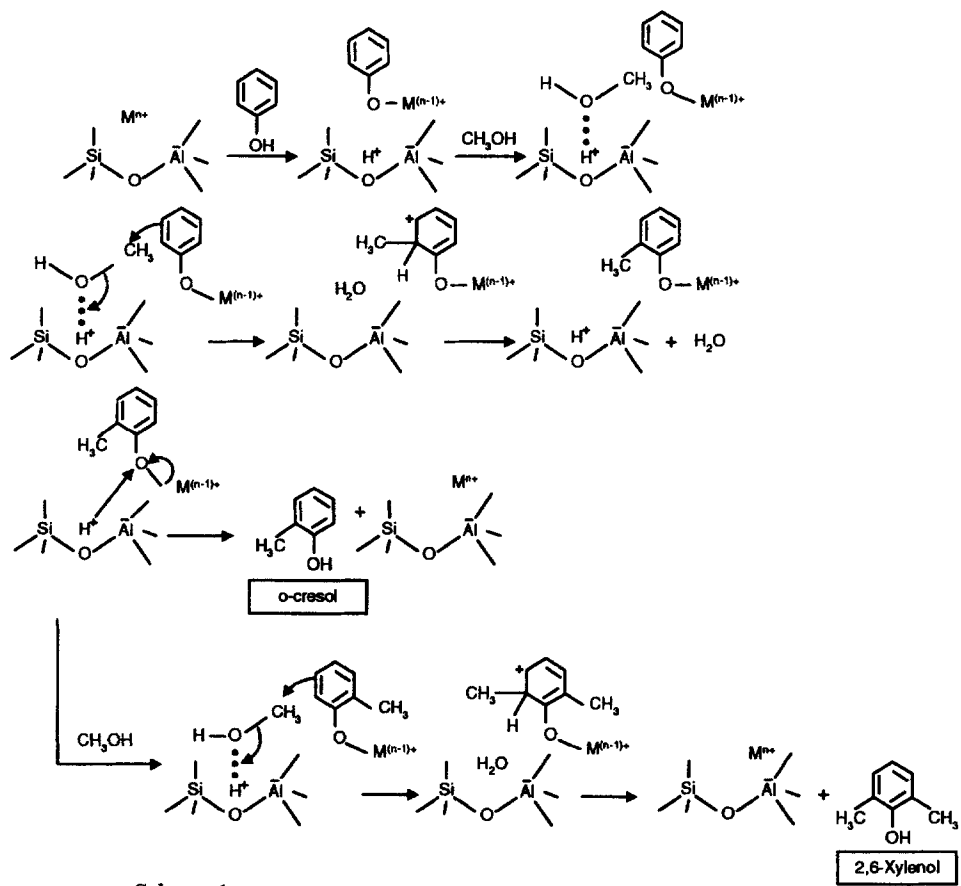


**Figure 2.** Alkylation of phenol with methanol, mole ratio 1:3 and WHSV  $2.9 \text{ h}^{-1}$ .

*o*-cresol and 2,6-xylene, O-alkylated product namely anisole was also obtained. A close look at the selectivity of products indicates decrease of *o*-cresol and anisole selectivity and increase of 2,6-xylene selectivity with increase of temperature. Decrease of *o*-cresol selectivity with increase of temperature would virtually be due to its conversion to 2,6-xylene, a high activation energy demanding product<sup>1</sup>. Anisole selectivity decreased with increase of temperature due to its conversion to *o*-cresol. The formation of *o*-cresol, 2,6-xylene and anisole requires the co-existence of both Lewis acid and basic sites<sup>16</sup> in the catalysts as illustrated in the reaction schemes 1, 2 and 3.

As shown in scheme 1, phenol is dissociatively adsorbed on the Lewis acid site, and its proton is released to the adjacent basic site. Methanol is adsorbed on to the Bronsted acid site, and this adsorption increases the electrophilic character of its methyl group. Although dissociative adsorption of phenol on Lewis acid site decreases the positive charge of the latter by one unit, the resulting single coordinated ionic complex cannot migrate away from its usual position to the adjacent free basic sites in the zeolite due to its interactions with the bridging oxygens in its environment. At this time, there is an electrophilic attack of methyl at the *ortho* position of phenol to produce *o*-cresol.

Once the *o*-cresol is formed it would be retained in the dissociated form on the coordination sphere of La(III) ion and very weakly retained over Fe(III), Zn(II) and Cd(II) ions. This difference might be due to high coordination capability of La(III) ion compared to Fe(III), Zn(II) and Cd(II) ions. Hence, reaction of dissociatively adsorbed *o*-cresol with one more Bronsted acid adsorbed methanol to produce 2,6-xylene is more favoured over LaY zeolite than FeY, ZnY and CdY zeolites. If the magnitude of ion-exchange rather than coordination capability is expected to control the 2,6-xylene selectivity, then FeY and LaY should have exhibited the same value as both have



almost the same amount of ion-exchange and acidity as shown in table 1. Increase of temperature increased the selectivity of 2,6-xyleneol, because dissociative adsorption<sup>16</sup> of *o*-cresol on Lewis acid site, which is required for 2,6-xyleneol formation, is more favoured as the temperature is raised. The reaction scheme 2 illustrates formation of anisole from Bronsted acid adsorbed methanol and Lewis acid adsorbed phenol. Anisole selectivity, although generally less over all the catalysts, is high over FeY, ZnY and CdY zeolites compared to LaY zeolite as shown in figure 2. This difference indicates less nucleophilicity for phenolic oxygen when phenol is adsorbed onto La(III), and more nucleophilicity when phenol is adsorbed onto Fe(III), Zn(II) and Cd(II) ions. In addition, selectivity to anisole decreased with increase of temperature illustrating part of its conversion to *o*-cresol (scheme 3). It was observed in the study that when phenol to methanol mole ratio was varied as 1:5 and 1:7, anisole selectivity was not found to increase appreciably over all the catalysts and at all temperatures (data not shown).

### 3.2 Effect of WHSV

The influence of WHSV on phenol conversion and product selectivity was examined by giving its values as 2.9 and 4.8 h<sup>-1</sup>. The data obtained are illustrated in figures 2 and 3. Phenol conversion and *o*-cresol and 2,6-xyleneol selectivities decreased but anisole selectivity increased with increase of temperature over all the catalysts. Although phenol or *o*-cresol was dissociatively adsorbed and hence better retained on the Lewis acid site, Bronsted acid adsorbed methanol could not be retained longer to react with Lewis acid adsorbed phenol or *o*-cresol, and hence increase of WHSV decreased phenol conversion, and selectivity to *o*-cresol and 2,6-xyleneol. Anisole selectivity increased with increase in WHSV, because when methanol itself was shown to have less residence time on the Bronsted acid site with increase in WHSV, the preformed anisole would still poorly be retained, and hence its conversion to *o*-cresol, through the reaction sequence

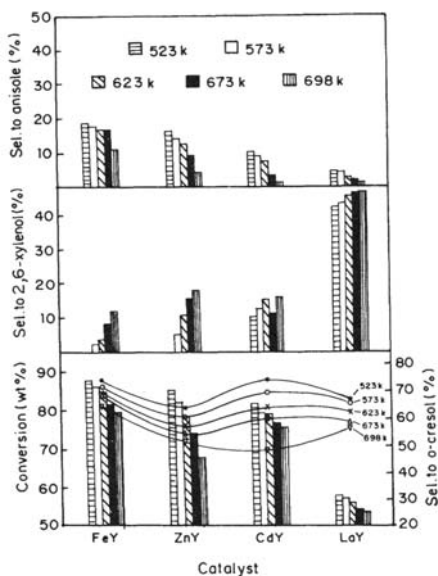
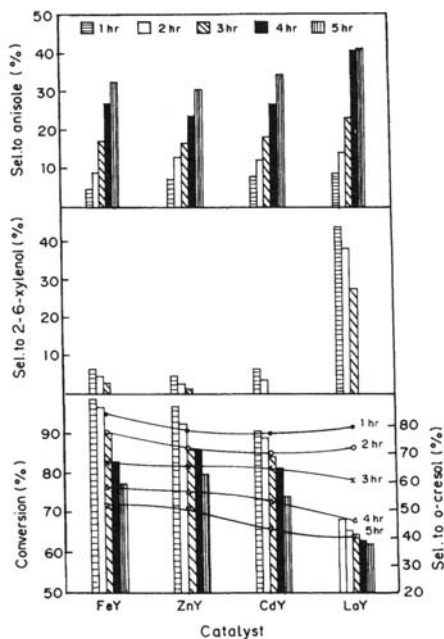


Figure 3. Alkylation of phenol with methanol, mole ratio 1:3 and WHSV 4.8 h<sup>-1</sup>



**Figure 4.** The change in product selectivity with time on stream at temperature 523 k, phenol to methanol mole ratio 1:3 and WHSV  $2.9 \text{ h}^{-1}$

as illustrated in the reaction scheme, is highly unfavourable. So, once the anisole was formed, it can better escape rather than react with another Lewis acid adsorbed phenol to produce *o*-cresol. So, the study of influence of WHSV indicated that low WHSV would be advantageous to maximise phenol conversion and ring alkylated products.

### 3.3 Influence of time on stream

Changes in catalytic activities in the alkylation of phenol with methanol over ion-exchanged Y-zeolites with time on stream was investigated at 523 K with phenol to methanol mole ratio 1:3 and WHSV  $2.9 \text{ h}^{-1}$ . The results obtained are illustrated in figure 4. Phenol conversion decreased with time for all the catalysts and the magnitude of decrease was found to be almost similar for all of them. The selectivity to *o*-cresol decreased with time over all the catalysts. Selectivity to 2,6-xylene decreased with time and it was not observed after 2 or 3 h. Selectivity to anisole increased with time over all the catalysts. During the early hours of time as the more active acid sites were free, there was high conversion of anisole into *o*-cresol, but during the later stages of time, as the active sites were blocked by coke deposits; anisole remained without being transformed to *o*-cresol, and hence anisole selectivity increased with increase in time. Among all the catalysts LaY retained more activity towards 2,6-xylene up to 3 h but no selectivity was found after the third hour because of blocking of these sites by coke.

## 4. Conclusion

Alkylation of phenol with methanol over Lewis acid ion-exchanged Y-zeolites showed formation of both ring and O-alkylated products, but the selectivity to the latter was

found to be less than 10% over all the catalysts. Selectivity to *o*-cresol decreased with increase of temperature and hence low reaction temperature would be more advantageous when one aims for ring alkylation. Selectivity to 2,6-xyleneol, increased with increase in temperature, indicating high energy of activation for its formation. Selectivity to 2,6-xyleneol, high activation energy demanding ring alkylated product increased with increase in temperature but coke formation at high temperature limits its selectivity. In addition, for ring alkylated products low feed ratio and WHSV would be more suitable than high values. Among the Lewis acid metal ions La(III) favoured 2,6-xyleneol whereas other ions favoured *O*-cresol.

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