Methylation of toluene over MnAPO-11 and ZAPO-11

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Methylation of toluene with methanol in the vapour phase has been studied over MnAPO-11 and ZAPO-11. The reactions were carried out in a fixed bed reactor in the temperature range of 250-400ºC. p-Xylene is produced in greater concentrations than the other products. The selectivity for p-xylene is a function of acidity, specific surface area of the catalyst, reaction temperature and toluene to methanol ratio. ZAPO-11 was found to be more active than MnAPO-11. Maximum conversion (25.8%) was observed at 400ºC over ZAPO-11. The selectivity to p-xylene was found to increase with time on stream possibly due to partial reduction in the pore size of the catalyst by coke deposition.

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Electrophilic alkylation of aromatics can be carried out by a variety of reactants such as olefins, alcohols and halogenated hydrocarbons¹. p-Xylene and o-xylene represent two important starting materials for the production of various polymers. Particularly, p-xylene is in high demand for oxidation to terephthalic acid. Methylation of toluene was initially investigated over various cationic forms of Zeolite-Y²,³. Chen et al⁴. have shown that small crystals of ZSM-5 zeolite yield an equilibrium mixture of xylenes, while significantly higher p-xylene selectivity (about 50%) can be obtained using relatively large ZSM-5 crystals. The elimination of active sites on the zeolite external surface has been shown⁴,⁵ to yield a catalyst exhibiting p-xylene selectivities greater than 80%. Yashima et al⁶. suggested that high yields of p-xylene are obtained, due to the restricted transition state selectivity; A high para-selectivity can be achieved by preventing the isomerization of primarily formed p-xylene⁷. Although methylation of toluene and toluene disproportionation has been extensively studied over zeolites, studies with zeotype are scarce. In the present study, attempts have been made to synthesize AlPO-11 based molecular sieves by Zn and Mn substitution in the framework, and evaluate their performance at various reaction conditions in the methylation of toluene.

Experimental Procedure
The catalysts, MnAPO-11 and ZAPO-11 were synthesized as described elsewhere⁸,⁹ from gel compositions of 0.1 MnO: Al₂O₃: P₂O₅: DPA: 40 H₂O and 0.1 ZnO: Al₂O₃: P₂O₅: DPA: 40 H₂O, respectively. The gels were crystallized in teflon-lined autoclaves in static conditions at 200ºC for 22 h. Then, the solids were filtered, washed with deionised water, dried, and finally calcined at 550ºC for 8 h to remove the template present in the sample. The chemical composition of the calcined samples, BET surface area (m²/g) and acidity (mmol/g) respectively, for the samples are given below: MnAPO-11- 0.067 MnO: 0.933 Al₂O₃: 1 P₂O₅, 174, 0.2; ZAPO-11- 0.07 ZnO: 0.93 Al₂O₃: 1 P₂O₅, 181, 0.24.

Coke content measurement
The amount of coke formed in the reactions was measured ex situ. The coke content was measured after 1 h run and after 4 h, under the same reaction conditions. The spent catalyst was calcined at 500°C for 2 h, in a stream of air, under atmospheric pressure. The weight loss was measured, and from the difference in weight, wt% of coke content was calculated. The results obtained by this method match with the results obtained by TGA method.

Characterisation
MnAPO-11 and ZAPO-11 were characterised by X-ray diffraction (XRD), ²⁷Al NMR, ³¹P NMR, ICP-MS, BET and acidity in order to study the structure, chemical composition and surface area. The XRD patterns were recorded on Siemens D 500
diffractometer using Cu K$_{\alpha}$ radiation in the scan range of $2\theta = 5$ to 50$^\circ$ with a scan rate of 1$^\circ$ per min. Figure 1 shows the XRD pattern of MnAPO-11 and ZAPO-11. It may be seen from the XRD pattern that these catalyst samples are crystalline, and do not contain detectable impure phases. The $^{27}$Al and $^{31}$P NMR spectra of the calcined catalysts are shown in Figs 2 and 3. MAS-NMR spectra indicate the isomorphic substitution of Zn and Mn in the framework of aluminophosphate molecular sieves. Strong signals are observed at 35.21 (ZAPO-11) and 34.93 ppm (MnAPO-11) for aluminum and at –30.20 (ZAPO-11) and –28.46 ppm (MnAPO-11) for phosphorus. They are characteristic of the tetrahedral environment of aluminum and phosphorus in the lattices. The spinning side bands in the $^{31}$P NMR indicate that the Zn and Mn are incorporated in the framework. The chemical analysis of these catalysts was performed by using ICP-MS optima 4300 DV spectrometer. The metals are substituted in the framework of the catalyst as revealed by the chemical composition. Acidity measurements were carried out by $n$-butylamine-TPD method$^{10}$ using Seiko SSC 5200H thermal analysis system attached to a TG/DTA 220 module. About 50 mg of calcined catalyst in each run was activated at 500°C for 1 h in a flow of air and then the system was kept in vacuum (~ 10$^{-4}$ torr) at the same temperature. The catalysts were subsequently cooled down to room temperature and allowed to adsorb $n$-butylamine. The amine adsorbed catalyst was kept in vacuum at room temperature to remove the excess amine from the catalyst surface. Thermal desorption measurements were made on the catalyst and from the weight loss, acidity was determined. The acidity values obtained by this method show good agreement with the
calculated values obtained from the chemical composition. ZAPO-11 is more acidic than MnAPO-11, indicating greater substitution of Zn in the framework of ZAPO-11 than Mn in MnAPO-11. BET surface area measurements were carried out in Micromeritics pulse chemisorb 2700 using nitrogen as adsorbent at 97 K. Initially the samples were degassed at 473 K for 2 h in a current of oxygen. Helium was used as carrier gas and TCD used as detector. The surface area, chemical composition, acidity, $^{27}$Al NMR, $^{31}$P NMR and XRD pattern of these catalysts are similar to those shown in previous reports and are characteristic of AlPO$_4$-11 molecular sieves$^{8,9}$, and indicate Mn and Zn are incorporated in the framework.

**Methylation of toluene**

Methylation of toluene with methanol over MnAPO-11 and ZAPO-11 was studied at 250, 300, 350 and 400ºC, with toluene to methanol ratio of 1:2, and weight hourly space velocity of 2 h$^{-1}$. The reaction was carried out in a fixed-bed continuous down flow glass reactor of 40 cm length and 1 cm internal diameter. About 1 g of the catalyst was employed in the study. The reaction mixture was fed into the reactor by a motor driven syringe pump at different flow rates. After each run, the catalyst was regenerated in situ by passing CO$_2$-free, dry air through the reactor at 500ºC for 6 h in order to remove the deposited coke and to restore the original activity of the catalyst. The reaction products were identified using Shimadzu gas chromatograph mass spectrometer (GCMS-QP5000). The products of the reaction were found to be $p$-xylene, $m$-xylene, $o$-xylene and Heavies (1,2,4- and 1,3,5-trimethylbenzene). The definitions of conversion ($C$), and yield ($Y_i$) are given below.

\[
C (\text{wt}\%) = \frac{\text{Wt}\% \text{ of toluene reacted}}{\text{Wt}\% \text{ of toluene fed}} \times 100
\]

\[
Y_i (\text{wt}\%) = \frac{\text{Wt}\% \text{ of ith product}}{\text{Wt}\% \text{ of toluene fed}} \times 100
\]

**Results and Discussion**

**Influence of temperature**

The influence of temperature on the activity and product distribution is presented in Table 1. The data suggest that the reaction temperature has a marked effect on the conversion of toluene and the product distribution. As expected, the toluene conversion increases with temperature over both the catalysts. The conversion, which is found to be more for ZAPO-11 relative to MnAPO-11, parallels their acidity and surface area.

The effect of temperature on product yield was examined over MnAPO-11 and ZAPO-11 and the results are presented in Table 1. The total product yield was found to increase with increase in temperature. The distribution of the reaction products for xylene isomers is strongly influenced by the channel geometry and the transport of individual xylene isomers into channel structure.

Formation of $p$-xylene with high selectivity may be due to its free diffusion through the pores. The observation that $para$-xylene is formed in greater amount than other isomers indicates that the alkylation proceeds on the acid sites inside the catalyst channels, where the formation of $para$ isomer is favoured. Also the diffusion coefficient for $p$-xylene, with the smallest kinetic diameter$^{11,13}$, $D=6\times10^{-12}$ cm$^2$/s, is two or three orders of magnitude higher than those for the bulkier isomers, viz., $o$-xylene ($D=6\times10^{-14}$ cm$^2$/s) and $m$-xylene ($D=7\times10^{-15}$ cm$^2$/s). The higher diffusivity of $p$-xylene in the channels of MnAPO-11 and ZAPO-11 compared to

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Conversion (wt %)</th>
<th>Product yield (wt%)</th>
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<tbody>
<tr>
<td></td>
<td>$p$-xylene</td>
<td>$m$-xylene</td>
</tr>
<tr>
<td>MnAPO-11</td>
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<tr>
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<td></td>
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<td>8.21</td>
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<td></td>
<td>350</td>
<td>24.07</td>
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<td></td>
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<td>25.78</td>
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and \( \text{o- and m-xylene} \) ensures that the \( \text{p-xylene} \) is removed much faster from the channel system than the other isomers. Moreover, the rate of conversion of \( \text{o- and m-xylene} \) to \( \text{p-xylene} \) is expected to be higher compared to the rate at which they diffuse out of the channel system. The diffusion rate of xylene isomers is sufficiently high such that the formation of heavier components does not take place appreciably.

### Influence of feed ratio

The influence of the toluene to methanol mole ratio on the conversion and product yield is shown in Table 2. An increase in toluene conversion is observed when the toluene to methanol ratio is increased from 1 to 2. At higher toluene to methanol ratios a decrease in the conversion is observed. The increase in conversion from feed ratio 1 to 2 indicates that the optimum ratio is 1:2. The decrease in conversion of toluene at higher feed ratios may be due to (i) dilution of toluene with increase in methanol concentration and (ii) complete coverage of catalyst surface with methanol, keeping toluene entirely in the vapour phase facilitating water and formaldehyde formation. The formation of \( \text{o-xylene} \) in higher concentration relative to \( \text{m-xylene} \) could be due to the free diffusion of \( \text{o-xylene} \) compared to \( \text{m-xylene} \).

### Influence of weight hourly space velocity

Table 3 shows the influence of WHSV on conversion and product distribution. A perusal of the data reveals the following.

(i) Conversion of toluene and selectivity to \( \text{p-xylene} \) are found to be high at lower WHSV (1 and 2) than higher WHSV (3 and 4).

(ii) In case of MnAPO-11 the conversion at WHSV 1 and 2 is nearly the same while a slight drop (about 2%) in conversion is observed when the space velocity increased from 1 to 2 h\(^{-1}\) in case of ZAPO-11.

(iii) At a given WHSV ZAPO-11 exhibits a better conversion and selectivity to \( \text{p-xylene} \).

(iv) A decrease in the heavies content with WHSV is observed irrespective of the catalyst.

(v) Among the \( \text{o- and m-isomers} \), the selectivity to \( \text{ortho} \) isomer is higher as discussed earlier.

From these results it appears WHSV 2 h\(^{-1}\) is better in terms of conversion, selectivity to \( \text{p-xylene} \) and formation of heavier components.

### Influence of time-on-stream

Table 4 presents the effect of time on stream on the conversion and yield of products. These results point...
out that a strong deactivation of catalyst may occur with time on stream. The rapid decrease in activity of the catalysts with stream may be due to (i) the microporous nature of the catalyst which offers diffusional constraint for the products and (ii) blocking of active sites by coke. A decrease in yield for all the products with time on stream is observed. The catalyst can be regenerated with air in a conventional manner to remove coke deposits and restore the lost activity.

### Conclusion

The MnAPO-11 and ZAPO-11 catalysts were synthesized. The catalysts used for methylation of toluene with methanol in the vapour phase exhibited good conversion. The products were ortho, meta and para-xylene. The activity of these catalysts is due to the Brønsted acid sites generated by isomorphous substitution of metal in the framework. An important observation in this study is the increase in coke content and decrease in conversion with time-on-stream. It may be due to a gradual reduction in the pore size of the catalyst by coke deposition.

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### References


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**Table 4**—Effect of time on stream on the conversion and product yield

| Temperature=400°C; WHSV=2 h⁻¹; Feed ratio=1:2 (toluene:methanol) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Catalysts       | Time (h) | Conversion (wt%) | p-xylene | m-xylene | o-xylene | heavies | Coke (wt%) |
| MnAPO-11        | 1        | 20.32            | 11.9     | 3.1      | 4.2      | 1.12    | 1.8            |
|                 | 2        | 13.93            | 8.7      | 1.8      | 2.9      | 0.53    | --             |
|                 | 3        | 8.14             | 4.6      | 1.1      | 2.1      | 0.34    | --             |
|                 | 4        | 4.23             | 2.8      | 0.4      | 0.9      | 0.13    | 8.6            |
| ZAPO-11         | 1        | 25.78            | 12.8     | 4.5      | 7.1      | 1.38    | 1.6            |
|                 | 2        | 17.61            | 9.5      | 2.9      | 4.5      | 0.71    | --             |
|                 | 3        | 12.18            | 5.7      | 2.2      | 3.8      | 0.48    | --             |
|                 | 4        | 5.61             | 3.4      | 0.6      | 1.4      | 0.21    | 8.3            |