Kinetics of toluene methylation over silica modified HZSM-5 zeolites

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Selective alkylation of toluene with methanol is one of the most promising routes to produce para xylene. This subject has been receiving considerable attention as can be ascertained by the number of patents being filed and papers being published. The quintessential factor to success is the design of a catalyst that gives commercially viable conversions and selectivity. Thus, the study of reaction kinetics assumes importance in evaluating catalysts and in optimizing reaction conditions. Zeolites, being economical and environmentally safe, are the sought after catalysts for alkylations. By proper selection of the type of zeolite and its treatment with silica to control pore mouth dimensions and passivation of external acid sites, it is possible to obtain high performance. The kinetic studies help in improving the catalyst design based on the observed stability, toluene conversion, and product purity.

Earlier literature on selective alkylation of toluene relates mainly to the use of HZSM-5 zeolite and its modifications to regulate pore mouth opening. Selective production of p-xylene with unmodified ZSM-5 zeolites was studied by Yashima et al. and Bhat. Chen and Garewood suggested that the selectivity observed in various reactions carried out over ZSM-5 zeolites is not resulting from sharp molecular sieving but from differences in intracrystalline mobility due to steric hindrance. Similarly, Chen et al. observed enhanced formation of p-xylene in the methylation of toluene on HZSM-5 only in larger crystals or after “modifications” of zeolites with phosphorus. Bhat et al. and Beschumann and Rickert also have reported higher para selectivity in larger crystals. Wei proposed a mathematical model representing the kinetics and different diffusivities of the xylene isomers in zeolite crystals. Kaeding et al. have suggested a mechanism for toluene methylation. A second approach reported by Sotelo et al. and Uguina et al., considers that p-xylene is preferentially produced inside the zeolite channels due to diffusional constraints and that acid sites located on the external surface are mainly responsible for isomerization.

In order to enhance the shape selectivity, various methods of modification of the zeolite property were proposed by different authors. Kaeding et al. and Hibino et al. explained the enhancement of the shape-selectivity as a result of the narrowing of pore opening size. Yashima et al., Sayed et al. and Kim et al. explained higher shape selectivity as a result of controlling the acidity. Wang et al. and Das et al. explained higher shape selectivity in terms of inactivation of external surface acid sites.

Kinetic studies of toluene methylation over HZSM-8 and HZSM-5 were reported by Bhat et al. and Mantha et al., respectively. They proposed a kinetic model using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism. Similarly Vaysilitov et al. proposed a power-law model where only toluene alkylation and xylene isomerization were considered. These authors have considered both external and internal surface acid sites of the zeolite crystals to explain the observed product distribution. However side reactions such as methanol dehydration to a number of gaseous products have not been accounted for in all the above cases.
Sotelo et al. studied kinetics of the toluene methylation with both unmodified and modified HZSM-5 zeolites. After fitting various models like LHHW, Eleye-Rideal and power law model for main alkylation reaction, they had chosen the power law model to explain the product distribution obtained though Eleye-Rideal model fitted the data best. They considered the secondary reaction of the methanol and xylenes in the reaction scheme.

Other important aspect of this reaction such as effect of coke deposition, ZSM-5 type catalyst covered with silicate shell, catalysis by Ga(H)ZSM-5 and generation of shape selectivity have also been discussed in literature.

Present study is concerned mainly with the performance of in-house developed catalyst at different operating conditions, formulation of a simple kinetic model that adequately represents the main reactions, its testing and agreement of parameter values with earlier studies. It considers the secondary reactions such as methanol dehydration, toluene disproportionation, p-xylene dealkylation and ethylation of toluene with ethylene.

**Experimental Procedure**

Silica modified ZSM-5 zeolite catalyst used in this study was prepared by the method explained in Das et al. The reaction was carried out at near atmospheric pressures in a fixed bed continuous down-flow glass reactor having a diameter of 2.54 cm. The catalyst was supported on a sintered glass ring. About 1-2 g of catalyst was charged and reactor space above the catalyst was filled with inert glass helices. All chemicals used were of analytical grade.

Prior to reaction, the catalyst was treated with a hydrogen stream at the desired temperature. A mixture of toluene and methanol was fed using a syringe pump (Sage, Model 362) through vapourizer to the reactor top. The products were collected from the bottom of the reactor after condensation with chilled water. The gases were vented and the liquid product was analyzed using a HP 5890 Series-II gas chromatograph.

There was no significant deactivation during the duration of experiments, as can be seen from Fig. 1. Experiments were carried out at two different catalyst weights but with same w/f ratio to ascertain external mass transfer effects and to select proper range of feed flow rates. The results are shown in Fig. 2. Likewise experiments were carried out with three different sizes of catalyst particles and the results showed almost identical conversions at same conditions indicating absence of macropore diffusional resistance.

Initially reactions were conducted to study the effects of different parameters in the ranges: temperature $350^\circ \text{C}$ to $475^\circ \text{C}$ toluene to methanol mol ratio 1:1 to 12:1, and $\text{H}_2$ to hydrocarbon mol ratio 1:1 to 8:1. Based on these observations, toluene to methanol ratio and $\text{H}_2$ to hydrocarbon ratio were selected as 4 and 2 respectively and further experiments were carried out at different w/f ratios and repeated at three different temperatures, viz 400, 425 and $450^\circ \text{C}$.

**Results and Discussion**

Attempts are made first to study the effects of temperature, toluene to methanol ratio, hydrogen to hydrocarbon ratio and space velocity to select appropriate conditions for obtaining desirable
performance. Varying temperature from 350° to 475°C shows that the toluene conversion increases with increase in temperature as presented in Fig. 3. At lower temperatures both toluene conversion and total xylene selectivity are low though para xylene selectivity is high. At higher temperatures, both toluene conversion and xylenes selectivity increase with a slight reduction in para xylene selectivity. It was also noticed that further increase of temperature results in toluene disproportionation as was observed by the increasing benzene fraction in liquid products. From this, a temperature range of 400-450°C appears to give reasonable conversions with acceptable para xylene selectivity. Fig. 4 shows the effects of varying toluene to methanol ratio from 1 to 12. At lower values of this ratio, total xylenes selectivity is low and this probably indicates various side reactions of methanol. At higher toluene:methanol ratios, the utilization of methanol for alkylation increases and at around a value of 4, the xylenes selectivity approaches about 72% and remains constant thereafter. However the p-xylene selectivity drops slightly with increasing toluene:methanol ratio. Hence further decrease in methanol has adverse effects in terms of p-xylene selectivity and toluene recycle load. The effect of varying hydrogen:hydrocarbon ratio is shown in Fig. 5. While increasing hydrogen concentration in feed reduces the toluene conversion slightly, probably due to dilution, it has a marked influence on total xylenes selectivity and p-xylene selectivity both of which increase. For further studies, a ratio of 2 has been chosen. It was observed that still lower hydrogen concentrations in feed speed up the catalyst deactivation by coke build up. The results of varying WHSV from 1-17 are shown in Fig. 6. Toluene conversion and total xylenes selectivity decrease with increasing WHSV whereas p-xylene selectivity increases. No definite trend in the distribution of higher aromatics could be discerned from the results. Similar results were observed at
other temperatures, viz. 400 and 450°C.

From the large number of chemical species detected in the product stream, it was obvious that many simultaneous reactions were occurring. Here only the main reactions are considered to enable us predict total toluene conversion, conversion to xylenes and para xylene selectivity. It is reported in the literature that p-xylene is the primary product of methylation. As the surface active sites are passivated in the present work, it is assumed that p-xylene isomerization takes place within catalyst channels and the conversion to m- and o-isomers is controlled by the diffusivities which are low due to reduced pore opening size. Consequently, the rate constants obtained are masked by micropore mass transfer resistances. Similarly methanol reacts to produce a number of gaseous products but this reaction is approximated by the dehydration reaction. In addition, all isomers of ethyl toluene are grouped into one species and trimethyl benzenes and higher aromatics are ignored as they were present in traces. The reaction scheme considered is,

Toluene Alkylation: \( C_7H_8 + CH_3OH \rightarrow p-C_8H_{10} + H_2O \) ... (1)

Methanol Dehydration: \( 2 CH_3OH \rightarrow C_2H_4 + 2H_2O \) ... (2)

Disproportionation: \( 2 C_7H_8 \rightarrow p-C_8H_{10} + C_8H_6 \) ... (3)

Dealkylation: \( p-C_8H_{10} \rightarrow C_7H_8 + GP \) ... (4)

Isomerization to meta: \( p-C_8H_{10} \rightarrow m-C_8H_{10} \) ... (5)

Isomerization to ortho: \( p-C_8H_{10} \rightarrow o-C_8H_{10} \) ... (6)

Ethylation of Toluene: \( C_7H_8 + C_2H_4 \rightarrow C_9H_{12} \) ... (7)

For the integral reactor with 1:0.25 mole ratio of toluene and methanol feed, the moles of different species present at any point where toluene conversion is \( X_T \) and methanol conversion is \( X_M \) and toluene conversion to any aromatic species is \( X_P \) are expressed in terms of conversions as,

- Moles Toluene = \( 1 - X_T \)
- Moles Methanol = \( 0.25 \times (1 - X_M) \)
- Moles p-Xylene = \( X_{PX} \)
- Moles m-Xylene = \( X_{MX} \)
- Moles o-Xylene = \( X_{OX} \)
- Moles Water = \( X_M \)
- Moles Gaseous product = \( 1.25 \times X_{GP} \)
- Moles Ethyl Toluene = \( X_{ET} \)

Using these relations, partial pressures of the species are expressed as below for hydrogen to hydrocarbon ratio of 2:1 and at total pressure of 1 atmosphere for the actual experimental conditions.

\[
P_T = (1 - X_T)/A
\]

\[
P_M = 0.25 \times (1 - X_M)/A
\]

\[
P_{PX} = X_{PX}/A
\]

\[
P_{MX} = X_{MX}/A
\]

\[
P_{OX} = X_{OX}/A
\]

\[
P_R = X_R/A
\]

\[
P_{ET} = X_{ET}/A
\]

\[
P_{GP} = 1.25 \times X_{GP}/A
\]

where \( A = 3.75 + 1.25 \times X_{GP} \).

Here \( X_{GP} \) is defined as moles of gaseous product formed per 1 mol of toluene and 0.25 mol methanol fed and \( A \) gives the total number of moles including hydrogen. The corresponding rate equations are:

Rate of disappearance of toluene:

\[\frac{dX_T}{dT} = k_1 P_T P_M + k_3 (P_T)^2 + k_7 P_T P_{GP} - k_4 P_{PX}\] ...

Rate of disappearance of methanol:

\[\frac{dX_M}{dT} = k_1 P_T P_M + k_2 (P_T)^2 \] ...

Rate of formation of p-xylene:

\[\frac{dX_{PX}}{dT} = k_1 P_T P_M - k_3 P_{PX} - k_4 P_{PX} - k_6 P_{PX} \] ...

Rate of formation of o-xylene:

\[\frac{dX_{OX}}{dT} = k_6 P_{PX} \] ...

Rate of formation of m-xylene:

\[\frac{dX_{MX}}{dT} = k_5 P_{PX} \] ...

Rate of formation of ethyl-toluene:

\[\frac{dX_{ET}}{dT} = k_3 P_T P_{GP} \] ...

Rate of formation of benzene:

\[\frac{dX_R}{dT} = k_2 0.5 (P_T)^2 \] ...

Rate of formation of gaseous product:

\[\frac{dX_{GP}}{dT} = k_2 0.5 (P_M)^2 + k_6 0.5 P_{PX} \] ...

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Table 1—Results of optimization programme for various models

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Type of Model</th>
<th>Value of the objective function (at temp.=425°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>LHHW model with methanol adsorption controlling</td>
<td>2.111930</td>
</tr>
<tr>
<td>2.</td>
<td>LHHW model with surface reaction controlling</td>
<td>2.222417</td>
</tr>
<tr>
<td>3.</td>
<td>LHHW model with p-xylene desorption controlling</td>
<td>2.326689</td>
</tr>
<tr>
<td>4.</td>
<td>Eilley-Rideal model with methanol adsorption controlling</td>
<td>0.707808</td>
</tr>
<tr>
<td>5.</td>
<td>Eilley-Rideal model with surface reaction controlling</td>
<td>0.689453</td>
</tr>
<tr>
<td>6.</td>
<td>Eilley-Rideal model with p-xylene desorption controlling</td>
<td>0.752543</td>
</tr>
<tr>
<td>7.</td>
<td>Power-Law model</td>
<td>0.728438</td>
</tr>
</tbody>
</table>

A non-linear regression programme based on Box-Complex method with fourth order Runge-Kutta algorithm for solution of above differential equations was employed to estimate the kinetic constants by minimising the sum of squares of errors:

$$\sum \sum (X_{n,m} - X_{n,m\text{cal}})^2$$

where, $X_{n,m}$ is the conversion of species $n$ in the $m^{th}$ experiment and $X_{n,m\text{cal}}$ is that predicted with given parameter values.

Results of this and other few models tried for data fitting are shown in Table 1. Though Eilley-Rideal mechanism with surface reaction controlling fits the experimental data better, the simple stoichiometric model is selected for further work for its simplicity. Table 2 presents the values of rate constants at different temperatures and the Arrhenius parameters are shown in Table 3.

The activation energy obtained here for toluene methylation matches well with that reported by the Sotelo et al., and is slightly less than 71.5 kJ/mol reported by Wang et al. and 79.8 kJ/mol reported by Mantha et al. Activation energies obtained here for p-xylene isomerization to m-xylene and o-xylene are higher than the corresponding values reported by Li et al. and Mantha et al., using an unmodified HZSM-5 catalyst, but are lower than corresponding values reported by Uguina et al. for Mg, Si-modified ZSM-5. However, activation energies of toluene alkylation, methanol dehydration and toluene disproportionation are only high enough to indicate the temperature sensitivity of a chemical reaction. In isomerization and ethyl toluene formation reactions diffusion limitation appears to be controlling the rates due to the controlled size of pore openings. The kinetic model was used to predict total toluene conversion and conversion to p-xylene at different WHSV and the results are shown in Fig. 7. Similar
evaluation was made varying hydrogen to hydrocarbon ratio, the results of which are shown in Fig. 8. However prediction of methanol conversion is not satisfactory as under the experimental conditions nearly the entire quantity of methanol disappears in reaction and its estimation in product stream is difficult.

**Conclusion**

Performance of a silica modified HZSM-5 catalyst for alkylation of toluene with methanol has been studied using a fixed bed reactor. The results show a steady performance under envisaged operating conditions with acceptable conversions and selectivities. Effects of various parameters are investigated and a simple stoichiometric model representing the main reactions is proposed. The rate constants are evaluated and goodness of fit is tested. However, the actual process is complex involving several reactions and intrachannel mass transfer effects. It is also observed that though methanol conversion is complete, its utilization for alkylation is less. Further work is needed for more accurate representation of this process.

**Nomenclature**

- $A$ = Total no. of moles present in the reaction mixture based on 1 mole toluene fed.
- $E$ = Activation energy, kJ/mol.
- $F$ = Molar flow rate, g mol/hr.
- $H$/HC ratio = Hydrogen to hydrocarbon ratio, g mol/g mol.
- $k_i$ = reaction rate constant, $i = 1$ to 7.
- $k_v$ = Pre-exponential factor.
- $P_i$ = Partial pressure of component $i$, atm.
- Tol / MeOH ratio = Toluene to methanol ratio, g mol/g mol.
- $W = \text{Weight of catalyst, gm.}$
- $W/F$ = Space time, g hr/gmol.
- $X_i$ = Conversion of component $i$ in $i^{th}$ experiment.
- $X_i$, cal. = Calculated conversion of component $i$ for $i^{th}$ experiment.
- $T$ = Space time variable g hr/g mol.

**Compounds**

- B = Benzene
- E.T. = Ethyl Toluene
- G.P. = Gaseous product
- M = Methanol
- PX = Para-xylene
- OX = Ortho-xylene
- MX = Meta-xylene
- T = Toluene

**References**

Articles


