Chapter 7

Isopropylation of Benzene

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Friedel–Crafts alkylation reaction with heterogeneous mesoporous catalysts have provided insight into the trends in which activity and selectivity are mostly considered. The isopropylation of benzene catalyzed by solid acids is of significant industrial and pharmaceutical interests. The corrosive nature of traditional Friedel-Crafts catalysts provide some environmental problems due to the formation of large amount of harmful wastes. Mesoporous solid acid catalysts will be effectively catalyze various Friedel-Crafts reactions since they have been shown to exhibit outstanding catalytic behaviour in several acid-catalyzed reactions. The present study has undertaken the isopropylation of benzene over various transition metal incorporated SBA-15 mesoporous catalysts. The investigations revealed that the catalytic activity and product distribution are sensitive to various reaction parameters and can be related to the acidity of the systems. Another possible reason of the increased activity may be attributed to the porous structure of the molecular sieve made it possible for the diffusion of reactants to active sites.
7.1 Introduction

Friedel–Crafts alkylation reactions are found to be an important reaction for attaching alkyl chains to aromatic ring. Friedel–Crafts alkylation reaction of aromatics is of substantial industrial and pharmaceutical significance [1]. Alkylation reactions have been usually carried out in the presence of Lewis acids or organometallic reagents using alkyl halides as alkylation agents. In the presence of strong acids, alcohols and alkenes can also serve as sources of electrophiles in Friedel–Crafts reactions. Recent reports reveal that solid phosphoric acid and Friedel–Crafts catalysts like AlCl₃ and BF₃ can be used in the synthesis of many fine chemicals and pharmaceutical intermediates [2]. But more than stoichiometric amount of AlCl₃ is required in many cases and giving poor selectivity because of degradation, polymerization and isomerization. The traditionally used Lewis acids are not easily separable after reaction and causes large amount of acid waste generation [3, 4]. Solid acid catalysts are important candidates for Friedel-Crafts alkylation reactions since various industrially important reactions are reported using solid acids [2, 5–8].

The use of environmental friendly catalysis involving the use of solid catalyst should lead to minimum pollution and waste. In recent years the preparation of solid acid catalysts is extended to mesoporous molecular sieves, which minimize the diffusion limitation with small zeolite pores. Mesoporous molecular sieves after incorporation of various metals as active sites have become promising catalysts and have been shown to exhibit outstanding catalytic behaviour in several acid-catalyzed reactions [9–11]. Large pore diameter with less diffusion constraint of these mesoporous solids eliminates further alkylation and deactivation by coke formation. Moreover, the mesoporous catalysts can provide spatial environment for the reactants in
the channels as that in the homogenous solution phase which leads to the formation of products.

A variety of solid acid catalysts have been examined and few have been employed for alkylation of various aromatics since 1960. Olah et al. studied isopropylation of benzene and toluene with isopropylbromide as alkylation agent and AlCl₃ as catalyst [12]. Many researchers reported the production of aromatics and petrochemicals such as xylene, ethylbenzene, cumene and linear alkylbenzenes using solid acids like zeolitic materials through Friedel-Crafts alkylation reactions [13–16]. A recent work by Cheng et al claimed a Mobil patent for cumene production over MCM-56 and MCM-22 [17]. Clark et al. found that montmorillonites supporting zinc and nickel catalysts are active towards Friedel– Crafts alkylation reaction [18–20]. Intensive research in the field revealed Zeolites X and Y are more active for alkylation of benzene with olefins than amorphous silica-alumina [21, 22]. The advantages of some other solid catalysts, which make them applicable for alkylation, have been reported extensively [23–26]. Qiaoxia Guo and coworkers investigated the synergetic effects of the MoCl₅ and molecular sieve (HZSM-5 and TS-1), and the Lewis acidity of FeCl₃, ZnCl₂, or AlCl₃ using the alkylation reaction of benzene derivatives [27].

The Friedel-Crafts alkylation of aromatics catalyzed by solid mesoporous acids is of significant interest in the fields of organic chemistry. Acidic mesoporous heterogeneous catalysts, having Bronsted or Lewis acid centers have substantial acid strengths and are capable of replacing homogenous bulk acids. Here we studied vapour-phase isopropylation of benzene using 2-propanol as alkylation agent over transition metals (W, Ti, Zr, V, Mo, Co, Cr) incorporated mesoporous SBA-15 catalysts. The product cumene serves as precursors for the coproduction of phenol and acetone. The results concerning the optimization of the reaction conditions are presented here.
In the isopropylation reaction isopropanol gets chemisorbed on the Bronsted acid sites of the catalyst to yield isopropyl cation. Electrophilic reaction between isopropyl cation and benzene yields the observed reaction products.

7.2 Influence of reaction parameters

Generally in any reaction, the yield and selectivity to a desired product depends on various reaction parameters such as temperature, mole ratio of the reactants, flow rate etc. Before testing the catalytic activity of various systems prepared, it is essential to optimize the reaction parameters.

7.2.1 Effect of Temperature

The vapour phase reaction of benzene with isopropanol was studied at 423, 473 and 523 K over SBW3 catalyst.

![Conversion and Product Distribution vs Temperature](image)

**Figure 7.1** Reaction conditions: SBW3-0.2g, mole ratio-7:1, WHSV-21.6, Time-2h
The reaction was investigated by co-feeding benzene and isopropanol in the ratio 7:1, WHSV 21.6 and the results are presented in Figure 7.1. The major products were found to be cumene and di/tri isopropyl benzene.

The isopropyl conversion decreased slightly with increase in temperature. The selectivity to cumene was high at low temperatures but decreases gradually with the increase in temperature to 523 K. This may be due to subsequent alkylation to di/tri isopropyl benzene, which takes place at high temperature. It was observed that the selectivity to di/tri isopropyl benzene increases with increase in temperature in this study. Maximum cumene selectivity with good conversion of isopropanol is obtained at a temperature 423 K. The selected temperature for further reaction is 423 K.

### 7.2.2 Effect of Mole ratio of Benzene/isopropanol

![Distribution of products](chart.png)

**Figure 7.2** Reaction conditions: SBW3-0.2g, WHSV-21.6, Temp-423K, Time-2h

The effect of feed ratio on conversion and product selectivity were studied at a temperature 423 K and WHSV 21.6 over SBW3. The feed ratios employed were (B: IPA) 5:1, 7:1, and 10:1. The results are shown in Figure 7.2. It was
observed that the conversion of isopropanol increases with increasing mole ratio in the feed up to 7:1. Further increase causes reduction in conversion. The selectivity to product cumene also increases from 62 to 74 % with increase in the mole ratio from 5:1 to 7:1 and then decreases to 55% with further increase of mole ratio to 10:1. The selectivity of di/trisopropyl benzene decreases with the change in feed ratio from 5:1 to 10:1 and the decrease in the selectivity of di/tri isopropyl benzene is due to the fact that trans alkylation of these products is more favoured with increased benzene. Mole ratio 7:1 was selected for further studies.

7.2.3 Effect of WHSV

Contact time is an important parameter, as it not only influences the conversion of a reactant; it also leads to change in selectivity of various products. Desired selectivity to a particular product can be achieved by choosing right space velocity. The effect of WHSV on isopropanol conversion and product selectivity was studied over SBW3; feed ratio 7:1 (B: IPA) at 423 K. The WHSV was varied as 12.9, 21.6, and 30.3 h⁻¹ and the results are shown in Figure 7.3.

![Diagram showing conversion and distribution of products with changing WHSV](image)

**Figure 7.3** Reaction conditions: SBW3-0.2g, Mole Ratio-7:1, Temp-423K, Time-2h
The conversion increased with increase in WHSV up to 21.6 and then decreases to 63%. The reduction in the conversion may simply be due to high diffusion when the WHSV is increased from 21.6 to 30.3. It was observed that the selectivity of di/tri isopropyl benzene increases with increase in WHSV. The selectivity to cumene increases with an increase if WHSV 12.9 to 21.6 and the increase is only about 6%. Further increase in WHSV to 30.3 causes a decrease in selectivity to cumene and it could be suggested that with increase in the WHSV there might be less concentration of isopropyl cation on the catalyst surface.

7.3 Comparison of different catalytic systems

The catalytic activity of all the prepared catalysts on isopropylation of benzene was evaluated under the optimized reaction condition.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized condition</th>
</tr>
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<tbody>
<tr>
<td>Temperature</td>
<td>423K</td>
</tr>
<tr>
<td>WHSV</td>
<td>21.6</td>
</tr>
<tr>
<td>Time</td>
<td>2h</td>
</tr>
<tr>
<td>Mole ratio</td>
<td>7:1</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.2g</td>
</tr>
</tbody>
</table>

Very low conversion with comparatively poor cumene selectivity was obtained for the isopropylation of benzene over parent SBA-15. Among the different transition metal incorporated SBA-15 materials SBCo1 gives maximum conversion. Cumene is the major product over all the catalytic systems. The conversion was found to be very low in chromia incorporated systems which may be due to their low Bronsted acidity values. It was found that most of the prepared catalysts effectively catalyze the isopropylation of benzene at relatively low temperature and catalyst weight.
**Table 7.2.** Catalytic activity of the prepared systems

Reaction conditions: Mole ratio-7:1, WHSV-21.6, Temp-423K, Time-2h, Catalyst weight-0.2g

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of Isopropanol (%)</th>
<th>Distribution of Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cumene</td>
</tr>
<tr>
<td>SBA-15</td>
<td>7</td>
<td>64</td>
</tr>
<tr>
<td>SBW1</td>
<td>68</td>
<td>84</td>
</tr>
<tr>
<td>SBW2</td>
<td>51</td>
<td>66</td>
</tr>
<tr>
<td>SBW3</td>
<td>88</td>
<td>74</td>
</tr>
<tr>
<td>SBTi1</td>
<td>78</td>
<td>84</td>
</tr>
<tr>
<td>SBTi2</td>
<td>69</td>
<td>65</td>
</tr>
<tr>
<td>SBTi3</td>
<td>88</td>
<td>51</td>
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<tr>
<td>SBZr1</td>
<td>66</td>
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<td>SBZr2</td>
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<td>SBZr3</td>
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<td>30</td>
</tr>
<tr>
<td>SBV1</td>
<td>98</td>
<td>86</td>
</tr>
<tr>
<td>SBV2</td>
<td>89</td>
<td>88</td>
</tr>
<tr>
<td>SBV3</td>
<td>83</td>
<td>89</td>
</tr>
<tr>
<td>SBMo1</td>
<td>82</td>
<td>71</td>
</tr>
<tr>
<td>SBMo2</td>
<td>60</td>
<td>55</td>
</tr>
<tr>
<td>SBMo3</td>
<td>62</td>
<td>99.5</td>
</tr>
<tr>
<td>SBCo1</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
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<td>78</td>
</tr>
<tr>
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<td>69</td>
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<td>63</td>
</tr>
<tr>
<td>SBCr2</td>
<td>15</td>
<td>67</td>
</tr>
<tr>
<td>SBCr3</td>
<td>11</td>
<td>72</td>
</tr>
</tbody>
</table>
7.4 Conversion of Isopropanol and Acidity of Catalysts

Since isopropylation of benzene occurs over Bronsted acid sites, an attempt is made to correlate the catalytic activity with acidic characteristics of the prepared catalysts. Figure 7.6 shows the correlation of isopropanol conversion with the Bronsted (weak + medium) acid sites.

7.5 Recycling studies

One of the major objectives guiding the development of heterogeneous solid acid catalysts includes the easy separation of reaction products from the final reaction mixture and efficient catalyst regeneration. Remarkable results were obtained when SBW3 was reused for the 2nd run directly after filtration, subsequent drying and calcination. The results given in Figure 7.5 shows that highest selectivity is to cumene. The same catalyst was used for carrying out subsequent runs under similar conditions. Recycling studies (four times) of the catalyst confirmed that the catalyst retained its activity and impart higher product selectivity with respect to the fresh catalyst.
7.6 Effect of Substrates

**Figure 7.5** Reaction conditions: SBW3-0.2g, mole ratio-7:1, WHSV-21.6, Temp-423K, Time-2h

**Figure 7.6** Reaction conditions: SBW3-0.2g, mole ratio-7:1, WHSV-21.6, Temp-423K for benzene and Temp-473K for others, Time-2h

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion of Isopropanol (%)</th>
<th>Distribution of Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>88</td>
<td>Cumene 74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Di/Tri Substituted benzene 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Others 6</td>
</tr>
<tr>
<td>Toluene</td>
<td>83</td>
<td>Para isomer 67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ortho isomer 18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>others 15</td>
</tr>
<tr>
<td>Anisole</td>
<td>95</td>
<td>Para isomer 90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ortho isomer 10</td>
</tr>
<tr>
<td>Isobutyl Benzene</td>
<td>94</td>
<td>Para isomer 74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ortho/meta isomer 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>others 15</td>
</tr>
</tbody>
</table>
Catalytic activity of the prepared systems is largely dependent on the substrate used. Variation of reactivity with substrate was studied by carrying out the reaction using benzene, toluene, anisole, and isobutyl benzene over the same catalyst. Table 7.3 illustrates the influence of substrate on the catalytic activity for isopropylation reaction. The isopropylation of toluene and anisole with lower catalyst concentrations under mild conditions shows predominant ortho/para directing effect. When the substrate is isobutyl benzene, 74% para isomer is produced in the isopropylation reaction. A slight amount of meta isomer is also present in the reaction mixture. An electron donating group will increase the electron density on the aromatic ring and make it more flexible to the attack by an electrophile. Thus it is worth mentioning that the reactivity of aromatic nucleus increases with the number and strength of electron donating groups attached to the aromatic ring.

7.7 Discussion

The isopropylation of aromatics with isopropanol involve a complex reaction network. Alkylation of benzene with propene is the major reaction that occurs under the reaction scheme of isopropylation of benzene. This reaction is sometimes associated with several side reactions which results in the formation of various products through transalkylation, disproportionation, dealkylation etc. The formation of n-propylbenzene is always accompanied with the production of cumene, which is formed either by the isomerisation reaction of cumene or from the primary n-propyl cation formation before isopropylation of benzene. According to Kaeding and Holland the formation of n-propylbenzene is not a favourable reaction at low temperatures due to the wide variation in thermodynamic equilibrium ratios. Similar observations are also made by some other researchers [28, 29]. From the mechanism suggested it is clear that the isopropylation reaction takeplace over Bronsted acid sites. The isopropanol is converted into propene by dehydration followed by the
proton abstraction from Bronsted acid sites which results in the formation of carbocation. Isopropyl substitution on aromatic ring is possible by the attack of the carbocation after the removal of H⁺ back to the catalyst.

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{O} \quad \text{H}^+ \\
& \quad \text{H} \\
& \quad \text{H}^+ \\
& \quad \text{-H}^+ \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
\end{align*}
\]

**Scheme 7.2.** Benzene isopropylation over Bronsted acid sites

From the results obtained it is clear that the prepared catalysts are highly adequate for the reaction and producing better results.

### 7.8 Conclusions

- All the transition metal incorporated mesoporous SBA-15 catalysts prepared in the present work effectively catalyze the isopropylation reaction of benzene.
- Comparatively low activity was observed in the case of chromia incorporated systems.
- The present method offers an alternative method for the selective cumene preparation with low temperature and low catalyst weight.
- The critical role played by various reaction parameters on the catalytic activity and percentage distribution of products is well established.
- Bronsted acidity of the catalysts plays an important role in the present reaction.
- The reaction is found to be clean with negligible formation of polyalkylated products in comparison with monoalkylated product.
- The prepared catalytic systems are found to be reusable and resistant to rapid deactivation in the present isopropylation reaction.
References


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