Friedel Craft alkylation is one of the most widely used synthetic tools for the introduction of alkyl groups in aromatics. Generally alkylation reaction is carried out by homogeneous Lewis acid catalysts such as aluminium chloride or Bronsted acid catalyst such as sulphuric acid which pose serious environmental issues. The corrosive nature of traditional liquid phase Friedel Craft catalysts directed major search for green eco-friendly heterogeneous catalysts with high catalytic efficiency. Natural aluminosilicates such as zeolites and clays are solid acids that are particularly promising candidates owing to their intrinsic acidity to substitute liquid acids in chemical transformations. Tertiary butylation of phenol is an industrially important reaction as the alkylated product found profound application in industry. Butylation of phenol reaction is regarded as a model test reaction in order to understand the behavior of solid acid catalysts. Furthermore, the mechanistic aspects developed by several researchers facilitate to understand the reaction pathways which will be helpful to choose the nature of catalysts depending on the kind of product one can look for. Vapour phase alkylation of phenol is done over transition metal impregnated pillared clays and porous clay heterostructures. Reaction parameters are optimized to get maximum conversion. Kinetics of the reaction was studied and kinetic parameters were evaluated.
4.1 Introduction

The alkylation of phenol and substituted phenols is one of the fundamental and industrially important reaction due to the usage of alkylated products in large amounts in the manufacture of antioxidants and phenolic resins [1-2]. Their derivatives found application ranging from pharmaceuticals to pesticides. Alkylation of phenol mainly yield mono alkylated products 2-tertiary butylphenol (2-TBP), 4-teriary butylphenol (4-TBP) and disubstituted product 2, 4 di tertiary butylphenol (2, 4 di-TBP). 4- tertiary butyl phenol is used as raw materials in the production of phenolic resins, synthetic lubricants, antioxidants, polymerization inhibitors, wire enamels, printing inks, lube additives, phosphate ester and fragrances. 2-TBP is an intermediate for pesticides, fragrances and other products. 2, 4-Di-TBP is an intermediate for antioxidants and pharmaceuticals. Numerous attempts have been made to prepare both homogeneous and heterogeneous catalysts for the alkylation of phenols and substituted phenols due to the numerous applications of alkylated phenols.

Alkylated phenols are commercially prepared by reacting phenol with pure isobutylene gas or C4 fraction of naphtha using a liquid acid catalyst, which gives wide product distribution. Both C- and O-alkylations are possible depending on reaction conditions such as temperature, source of isobutylene and type of catalyst. The direct alkylation of phenol with short-chain alcohols and olefins is widely reported for the preparation of these intermediates. In general, tert-butylation of phenols is carried out in a homogeneous medium using sulphuric acid, phosphoric acid, aluminium chloride, boric acid or boron trifluoride as the catalyst [3-5]. The uses of the homogeneous mineral acids are restricted owing to its hazardous nature in addition to the tedious work-up for
the separation of catalyst from the products. Therefore, considerable efforts have been made for the development of suitable heterogeneous solid acid catalysts. Various solid acid catalysts such as zeolite materials, modified mesoporous silica materials, ionic liquids, supported heteropolyacids, polymer resins have been reported for tertiary butylation of phenols in liquid phase as well as in vapour phase with alkyting agent tertiary butanol or methyl tertiary butyl ether (MTBE) [6-8]. Most of the solid acid catalysts reported are active and the most important problem is the selectivity for the desired product. Recently P Selvam et al. reviewed various solid acids used for this title reaction and their reaction conditions and their product selectivity [6].

Depending on the nature of catalyst, alkylation of phenol can take place at oxygen of phenol to produce phenyl ethers (O- alkylation) and /or at ring carbon atoms to produce alkylated phenols(C- alkylation ) (Scheme 8.1).

**Scheme 8.1- Products of Tertiary butylation of phenol**

In general, C- alkylation requires strong acid sites than those responsible for O-alkylation. The catalyst react with alkyling agent to form a carbocation which attack on phenol ring preferentially in ortho and /or para position of –OH group according to the rule of electrophilic substitution. Since the monoalkylated products are more reactive than phenol, they get further alkylated if there is no steric hindrance. Although the electrophilic aromatic
substitutions of phenol produce thermodynamically favorable m isomer (3-TBP) the o- and/or p-isomers are kinetically more favored. Though o-isomer is kinetically more favorable than the p-isomer, steric hindrance at o-position leads to easy isomerization of o-isomer to more stable p-isomer. However the selectivity of the products strongly depends on the nature of the acidic sites as well as the reaction temperatures [6].

The use of solid catalysts came in practice as early as 1956 by Kolka et al. by the use of aluminium phenoxide for the liquid-phase alkylation of phenol which yielded 2-TBP is the major product [7]. Since the reaction is acid catalyzed, solid acids such as zeolite H Beta and zeolite Y with high intrinsic acidity and thermal stability were employed for the reaction [8-10]. Corma et al. have first employed zeolite H-Y as a potential catalyst for this reaction and showed that at low temperature, O-alkylated product tertiary butyl phenyl ether (TBPE) and at higher temperature, C-alkylated products were obtained as the major products [8]. However the selectivity of bulky 2, 4 di TBP was very poor due to the small pore diameter in the microporous region (<2 nm). However, the use of large pore zeolites such as H-Y and H-BEA provided more phenol conversion with appreciable 2, 4-di-TBP selectivity [11-14]. Recently hierarchical zeolites were also evaluated for the tertiary butylation of phenol [15-17]. Hierarchical H-ZSM-15 showed very high activity for phenol conversion (85%) with 40% 2, 4-di-TBP selectivity due the presence of hierarchical pore facilitating the formation of 2, 4-diTBP converting 2-TBP and 4-TBP in to 2, 4 di-TBP [17].

A huge volume of literature is devoted to the vapour phase butylation of phenol over mesoporous silica materials such as MCM-41[18-26], MCM-48 [27-29] and SBA-15 [30-32]. Sakthivel et al. for the first time, studied
vapor-phase tertiary butylation of phenol over H-AlMCM-41[18]. The conversion of phenol varied depending on the reaction conditions with greater than 80% 4-TBP selectivity. At higher reaction temperatures, an increase in thermodynamically favorable 2-TBP product was noticed. Various transition metal ions (Zn, Fe, Co) containing H-AlMCM-41 were also executed for this reaction [19-21]. The main products were found to be 2-TBP. The presence of cobalt in the extra framework of mesoporous materials brings both phenol and isobutyl cation in close proximity and favours the formation of 2-TBP. Studies were also conducted in various trivalent metal ions such as B, Al, Ga, Fe substituted MCM-41 catalysts for tertiary butylation of phenol [22-24]. Tertiary butylation of phenol is also used as model test reaction to understand the nature of acid sites as well acidic strength of various catalysts. A series of H-AlMCM-41 catalysts using various aluminium sources and different aluminium content were evaluated for the title reaction [25-26]. The reaction was executed over trivalent metal substituted Me-MCM-48 (where Me - B, Al, Ga, Fe) catalysts [27-29]. Me-MCM-48 catalysts were found to be superior in activity and selectivity for dialkylated products compared to the corresponding MCM-41 analogues due to three-dimensional pore openings which reduces the deactivation considerably. Recently T. Jiang et al. evaluated sulphated zirconium incorporated MCM-48 for the alkylation of phenol which showed more than 90% conversion [30].

Tertiary butylation of phenol was also reported over various metal modified SBA-15 by various researchers [31-33]. Phenol conversion and 2, 4-di-TBP selectivity is more in these catalysts compared to their MCM-41 analogues owing to their large three dimensional mesopores and strong Bronsted acidity. Various researchers studied vapor phase alkylation of phenol
and substituted phenols over AlSBA-15 [32-33]. They have reported a good phenol conversion with considerable amount of diTBP and 4-TBP selectivity. They also observed decreased conversion at very high temperature due to considerable dealkylation process. Several other mesostructured and disordered metallosilicates were also screened for the title reaction [34-37].

Tertiary butylation of phenol was also reported over sulphated zirconia and sulfated titania which showed good 4-TBP selectivity [38]. Various heteropoly acids loaded on various supports such as ZrO₂ [39-40], alumina [41], APO [42], SBA-15 [43] also were evaluated for the title reaction owing to their high Bronsted acidity. Devassy et al. have studied heteropolyacids silicotungstic acid (STA) and phosphomolybdic acid (PMA) supported on zirconia catalysts for tertiary butylation of phenol [39-40]. STA/ZrO₂ was found to be more reactive since STA stabilizes the tetragonal phase of ZrO₂. Tertiary butylation of phenol was carried out over MCM-41 supported PTA and rare earth metal triflates in supercritical carbon dioxide showed excellent conversion [45]. Their high reactivity was attributed to the very good solubility of reactants, products and minimal coke formation as coke gets dissolved in supercritical CO₂.

Ionic liquids [46-51] such as 1-butyl-3-methylimidazolium hexa fluorophosphate ([bmim]PF₆)₃ and 2-methyl pyridinium trifluoro acetate were appeared to be most promising for tertiary butylation of phenol with high conversion and dialkylated product selectivity. The observed high selectivity of 2, 4-diTBP is attributed to strong acidic nature (Hammett constant around 1.5) of the catalysts [51].

Various cation exchanged resins such as Amberlyst-15, Nafion NR-50, Engelhard F-24, monodispersed K-2661 and p- toluene sulfonic acid (p-TSA)
were used for liquid phase tertiary butylation using MTBE as alkylating agent [52-53]. Alkylation of phenol was done using various other alkylating agents such as mono tertiary butyl ether of mono ethyl glycol (MEG-MTBE), TBA and isobutylene (i-BT) over Amberlyst-15 catalysts [52]. It was found that the overall rate of the reactions depend on the different alkylating agent in the following order i-BT > MEG-MTBE > MTBE > TBA. Density functional theory (DFT) [53-54] studies on the phenol alkylation over Amberlyst-15 catalyst showed that the energy barrier for the C-alkylation is 5-10 kcal/mol higher than that of O-alkylation and it was reduced significantly by protonation. It was also demonstrated that the acidity of the catalyst can control the reaction pathway significantly and the ortho/para ratio could be well controlled by this way.

Clay based catalysts were also reported for the title reaction. G. D. Yadav et al. [55] have employed several phosphotungstic acid loaded montmorillonite (K-10) clay based catalysts for liquid phase tertiary butylation of phenol using MTBE and TBA as alkylating agents. Among them, 20% PTA/K-10 showed better phenol conversion with good 4-TBP selectivity than K-10 and unsupported PTA owing to easy availability of protons and its blocked pores which induce shape selectivity. Scinde et al. studied liquid phase alkylation of phenol with TBA with FeCl3/K-10 catalyst [56]. Sugunan et al. studied tertiary butylation of phenol over ion exchanged pillared clays and showed that incorporation of transition metal in pillared clays resulted improvements in conversion of the phenol [57].

From the above discussion it is clear that the conversion and selectivity of the reaction depends on nature of catalysts, its acidity, textural properties and reaction conditions. Tertiary butylation of phenol was done in vapour phase. The reactor tube was charged with active catalyst sandwiched between
silica beads. The liquid reactants were fed into the reactor by syringe pump and desired temperature is maintained. The products of the reaction were collected downstream from the reactor at specified intervals. The major products of reactions are 2-TBP, 4-TBP and 2, 4-DTBP. Phenyl ether was not detected at all since the reaction was done at high temperature. The reaction conditions are optimized to get maximum conversion.

4.2 Effect of Reaction Parameters

4.2.1 Effect of phenol to tertiary butanol ratio

Reactions were done at different phenol to tertiary butanol ratio and the result is shown in Figure 4.1. The phenol conversion increases with increase in phenol to TBA ratio and maximum conversion is obtained at 1:3 ratio. Further increases in mole ratio do not increase the conversion as it will only dilute phenol. Moreover there may be competitive adsorption of TBA over phenol.

Figure 4.1 Effect of phenol to TBA mole ratio, Temperature - 190°C, WHSV-10.08, Time - 2hour, Catalyst-CoZrSiPCH
and only few sites are available for phenol molecule to adsorb and hence conversion decreases [12]. The dialkylated product selectivity increases with increase in TBA ratio in the feed. This may be due to the higher availability of tertiary butanol which results further alkylation of monoalkylated products. Similar results have been found in mono and bimetal substituted MCM-41 molecular sieves [18-24].

4.2.2 Effect of temperature

Reactions were done at different temperature from 160 °C to 200 °C and results are shown in Figure 4.2. Reaction temperature has profound influence on conversion and product selectivity. A steady increase in conversion is noted with increase in temperature and conversion reaches maximum at 190°C and then falls. The decrease in conversion at higher temperature may be due to the predominant dealkylation over alkylation and the diminishing availability of TBA. At higher reaction temperatures the formation of undesired products are prominent and they consumes reactants (TBA) without producing the desired products leading to lower phenol conversion. The 4-TBP selectivity increases with temperature. The observed selectivity of 4-TBP is due to the different diffusion kinetics as compared to other products and the absence of secondary alkylation products. Similar trends have been reported for other catalysts also [22-24, 58]. Song et al. explained the preferential formation of 4-TBP as due to different diffusion kinetics with the help of computational modeling [59]. The selectivity of 2.4 di- TBP is maximum at lower temperature which may be due to the higher availability and stability of tertiary butyl cation. The 2, 4-di-TBP selectivity decreases with increase in temperature. For further studies 190 °C is taken as the optimum temperature.
4.2.3 Effect of flow rate (WHSV)

The flow rate of the reactants greatly influences the reaction rate. Very low contact time (high flow rate) may result in poor reaction as little time is available for the adsorption of the reactants on the catalysts surface, whereas high contact time mostly results in undesired products. Hence in order to get maximum conversion and selectivity an optimum flow rate is essential. The reactions were done at various WHSV (Weight Hourly Space Velocity) and result is shown in Figure 8.3. As expected, phenol conversion decreases with increase in WHSV due to shorter contact time with catalysts. Maximum conversion is obtained for WHSV, 10.08. The selectivity of 2-TBP increases with increase in WHSV. The increase of the 2-TBP yield with increasing space velocity has been ascribed to the elimination of inter particle diffusional resistances at higher space velocities [21]. The dialkylated product selectivity decreases with increase in WHSV.
4.2.4 Effect of time on stream

Maximum conversion is obtained after 2nd hour and the catalysts retain its appreciable activity after several hours. The selectivity of di substituted products increases with progress of the reaction time and then a slight decrease is noted.
This may be due to the following reasons. Dialkylated product selectivity is usually correlated with Lewis acidity. The water molecules formed during the reaction convert some of Lewis acid sites into Bronsted sites. Pore blocking due to the formation of coke may also result in reduction in dialkylated product selectivity. From the above experiments it is clear that reaction conditions play a crucial role for obtaining good conversion and selectivity for the products. Vapour phase tertiary butylation of phenol was done over all the prepared catalysts with optimized conditions given in the Table 4.1. The results are given in Table 4.2.

### Table 4.1. Optimized reaction conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>190°C</td>
</tr>
<tr>
<td>WHSV</td>
<td>10.08</td>
</tr>
<tr>
<td>Phenol to TBA ratio</td>
<td>1: 3</td>
</tr>
<tr>
<td>Time on stream</td>
<td>2 hour</td>
</tr>
</tbody>
</table>

### Table 4.2 Performance of different catalysts for tertiary butylation of phenol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of phenol (%)</th>
<th>Rate constant (mol⁻¹ l⁻¹ min⁻¹ m⁻²)x 10⁵</th>
<th>2-TBP</th>
<th>4-TBP</th>
<th>2, 4-di-TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaM</td>
<td>11</td>
<td>0.291</td>
<td>21</td>
<td>78</td>
<td>1</td>
</tr>
<tr>
<td>ZrPC</td>
<td>46</td>
<td>0.852</td>
<td>31</td>
<td>59</td>
<td>10</td>
</tr>
<tr>
<td>Cu(3)ZrPC</td>
<td>39</td>
<td>0.905</td>
<td>31</td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td>Ni(3)ZrPC</td>
<td>56</td>
<td>1.48</td>
<td>32</td>
<td>57</td>
<td>11</td>
</tr>
<tr>
<td>Co(3)ZrPC</td>
<td>55</td>
<td>1.40</td>
<td>28</td>
<td>57</td>
<td>15</td>
</tr>
<tr>
<td>V(3)ZrPC</td>
<td>50</td>
<td>1.24</td>
<td>25</td>
<td>65</td>
<td>10</td>
</tr>
<tr>
<td>FeAlPC</td>
<td>42</td>
<td>1.21</td>
<td>11</td>
<td>85</td>
<td>4</td>
</tr>
<tr>
<td>SiPCH</td>
<td>59</td>
<td>0.452</td>
<td>32</td>
<td>53</td>
<td>15</td>
</tr>
<tr>
<td>ZrSiPCH</td>
<td>68</td>
<td>0.628</td>
<td>25</td>
<td>59</td>
<td>16</td>
</tr>
<tr>
<td>CuZrPCH</td>
<td>66</td>
<td>0.757</td>
<td>20</td>
<td>63</td>
<td>17</td>
</tr>
<tr>
<td>NiZrSiPCH</td>
<td>74</td>
<td>1.22</td>
<td>26</td>
<td>55</td>
<td>19</td>
</tr>
<tr>
<td>CoZrSiPCH</td>
<td>80</td>
<td>0.99</td>
<td>22</td>
<td>57</td>
<td>21</td>
</tr>
<tr>
<td>VZrSiPCH</td>
<td>72</td>
<td>0.89</td>
<td>24</td>
<td>59</td>
<td>17</td>
</tr>
</tbody>
</table>
From the results it can be seen that negligible conversion is obtained for unmodified clay with very small dialkylated product selectivity. This lower conversion may be due to lower surface area and pore volume of parent clay. Reasonable conversion of phenol is observed for zirconium pillared clays and its transition metal impregnated analogues. In nickel, vanadium and cobalt loaded zirconium pillared clays conversion of phenol is greater than that of bare zirconium pillared clay probably due to the higher acidity of those catalysts than that of zirconium pillared clay.

In copper impregnated samples conversion of phenol and selectivity of dialkylated product is lower than that of zirconium pillared clay due to its lower surface area and lower acidity than that of zirconium pillared clay. Almost similar dialkylated product selectivity is observed for transition metal loaded zirconium pillared clays with the exception of copper.

The conversion of phenol for the porous clay heterostructures and its transition metal loaded analogues are greater than that of pillared clays and its transition metal loaded analogues. This may be due to the higher total acidity, higher surface area and larger pore size of PCHs than that of pillared clays. The dialkyalted product selectivity is also greater than that of pillared clays. The maximum conversion is obtained for CoZrSPCH catalyst by virtue of its higher total acidity. For the conversion of phenol, PCHs follows the same trend of the conversion of cumene in cumene cracking reaction. The dialkyalted product selectivity usually depends on the strong acid sites (Lewis sites). In PCHs the dialkyalted product selectivity can be correlated with strong acidity obtained from TPD of ammonia. Such correlation cannot be made in PILCs as pore size limitation play a crucial role for the production of dialkyalted products even though PILCs contain sufficient amount of strong acid sites.
4.2.5 Effect of substrates

Alkylation of phenol was done with different alkylating agents and the result is given in Table 4.3. Tertiary butyl bromide shows greater conversion than tertiary butanol probably due to greater polarizing and leaving power of bromide ions compared to -OH. In alcohols tertiary butanol showed higher conversion due to higher stability of its carbocation intermediate.

**Figure 4.3 Effect of substrate, phenol to alkylating agent mole ratio-3:1, Temperature -190°C, Flow rate -4ml/hr, Time -2hour**

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Conversion/ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Conversion of phenol 83</td>
</tr>
<tr>
<td>T- butyl bromide</td>
<td>2- TBP 33</td>
</tr>
<tr>
<td></td>
<td>4- TBP 43</td>
</tr>
<tr>
<td></td>
<td>2, 4- di-TBP 24</td>
</tr>
<tr>
<td></td>
<td>Conversion of phenol 64</td>
</tr>
<tr>
<td>Phenol</td>
<td>2, 4 Di Isopropyl phenol 34</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>Isopropyl phenols 66</td>
</tr>
<tr>
<td>Phenol</td>
<td>Conversion of phenol 58</td>
</tr>
<tr>
<td>Methanol</td>
<td>Cresols 97</td>
</tr>
<tr>
<td></td>
<td>Anisole 3</td>
</tr>
</tbody>
</table>

4.2.6 Correlation between activity and acidity

Corma et al. found in zeolites that strong acid sites are required for the selectivity of 2, 4 di-TBP and medium sites are helpful in 4-TBP selectivity [8]. In both pillared clays and porous clay heterostructures, the phenol conversion can be correlated with total acidity due to medium and strong acid sites obtained from TPD of ammonia. The dialkylated product selectivity in PCHs can be correlated with strong acid sites obtained from the TPD of ammonia. The conversion of phenol in PCHs can be correlated with the conversion of cumene cracking reaction.
Tertiary butylation of phenol

Figure 4.5 Correlation between activity and acidity in pillared clays

Figure 4.6 Correlation between activity and acidity in porous clay heterostructures

Figure 4.7 Correlation between activity and acidity in porous clay heterostructures
4.2.7 Discussion

Generally for alkylation reaction by solid acids, the catalytic activity is controlled by acidity where as the selectivity of the products are controlled by pore structure and acid strength of catalyst. In the present reaction, alkylation of phenol predominantly give para substituted product, 4-TBP. The accepted mechanism for the aromatic alkylation is that both phenol and tertiary carbocation adsorb on acidic sites of catalysts. Then tertiary carbocation interact with adsorbed phenol forming a π- complex by electrophilic substitution which rearranges to give σ –complex. The complex on proton elimination gives tertiary butyl phenol. It has been suggested that the phenol is adsorbed in such a manner that π-electron cloud of aromatic ring is parallel to surface of acid sites. It allows the alkylation at the para position easier compared to ortho positions. In a kinetically controlled heterogeneous catalyzed reactions, both electronic and steric factor play major roles. It is also reported that there is steric hindrance in transition state by the introduction of bulkier tertiary group at ortho positions and isomerization take place to give para selective product.
By carefully choosing reaction conditions one can manipulate the selectivity of the particular product over others. High temperature and low phenol to TBA ratio favor monoalkylated product selectively where as low reaction temperature and high TBA ratio favours dialkyl product. Pore structures of catalyst also have tremendous influence on selectivity. The selectivity of 2, 4 diTBP is high in porous clay heterostructures due to their large pore size.

The activities of catalysts were compared with other catalysts reported in literature and data are given in Table 4.4.

Table 4.4. Tertiary Butylation of Phenol over different reported catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temp (°C)</th>
<th>Alkylating agent and ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%PTA/K10</td>
<td>150</td>
<td>2:1(MTBE)</td>
<td>68</td>
<td>38</td>
</tr>
<tr>
<td>K10</td>
<td>150</td>
<td>2:1 (MTBE)</td>
<td>52</td>
<td>33</td>
</tr>
<tr>
<td>FeCl₃/K10</td>
<td>150</td>
<td>2:1(TBA)</td>
<td>10</td>
<td>30.5</td>
</tr>
<tr>
<td>Zn/FeAlPC</td>
<td>200</td>
<td>3:1(TBA)</td>
<td>51</td>
<td>70.1</td>
</tr>
<tr>
<td>H-AlMCM-41</td>
<td>175</td>
<td>1:4(TBA)</td>
<td>47.5</td>
<td>12.8</td>
</tr>
<tr>
<td>AlMCM-41</td>
<td>175</td>
<td>1:2(TBA)</td>
<td>35.9</td>
<td>8.1</td>
</tr>
<tr>
<td>FeAlMCM-41</td>
<td>200</td>
<td>1:3(TBA)</td>
<td>50.1</td>
<td>10.4</td>
</tr>
<tr>
<td>HAlSBA-15</td>
<td>150</td>
<td>4:1(TBA)</td>
<td>86.3</td>
<td>7.0</td>
</tr>
<tr>
<td>HGaFSM</td>
<td>160</td>
<td>2:1(TBA)</td>
<td>80.3</td>
<td>3.8</td>
</tr>
<tr>
<td>DTP/SBA-15</td>
<td>150</td>
<td>1:3(TBA)</td>
<td>70.1</td>
<td>6.6</td>
</tr>
<tr>
<td>CoZrSiPCH</td>
<td>190</td>
<td>1:3(TBA)</td>
<td>80</td>
<td>22</td>
</tr>
</tbody>
</table>

As far as phenol conversion is concerned, the catalyst CoZrSiPCH is best among clay based catalysts with appreciable dialkylated product selectivity. Its conversion is reasonable and promising. Its activity and
selectivity for dialkylated products is comparable or even better than that of metal modified MCM systems. Comparing with modified SBA-15 systems its selectivity for dialkylated products is inferior to them.

4.3 Kinetic studies

Computational studies reveal that both phenol and tertiary butanol adsorb weakly on acid sites of catalyst [61]. Since both reactants are weakly adsorbed on the catalyst surface a second order power law may be formulated [56]. The rate of the reaction can be written as,

$$\frac{-dC_P}{dt} = k_2 \cdot C_P \cdot C_m \cdot W,$$

where $C_P$ is the concentration of phenol, $W$- weight of the catalyst, $C_m$- concentration of alkylation agent.

This is a typical second order equation which on integration gives

$$\ln \left( \frac{(M_R - X_P)}{M_R(1 - X_P)} \right) = C_{P0}(M_R - 1)k_2 \cdot t \cdot W$$

where $C_{P0}$ - initial concentration of phenol, $M_R$- the molar ratio of alkylation agent, $X_P$- conversion of phenol, $W$- weight of the catalyst, $t$- time of reaction in minutes.

Thus a plot of LHS against time or $1/WHSV$ gives a straight line which pass through the origin. The validity of this equation can be checked by plotting $\ln \left( \frac{(M_R - X_P)}{M_R(1 - X_P)} \right) \cdot \frac{1}{WHSV}$ against $\frac{1}{WHSV}$ which gives stright line passing through the origin.

The apparent rate constant of the reaction is calculated by the equation and is given in the Table 8.4
Tertiary butylation of phenol

Figure 4.9 Validation of second order kinetics for tertiary butylation of phenol over CoZrSiPCH catalyst

Apparent rate constant \( k_2 = \frac{2.303}{Cp_0(M_R - 1)t.S.A.W \log \frac{(M_R - X_P)}{M_R(1 - X_P)}} \)

Figure 4.10 Arrhenius plot for tertiary butylation of phenol over CoZrSiPCH catalyst

Arrhenius plot was made as shown Figure 4.10. Kinetic parameters \( E_a \) and \( A \) were evaluated in the temperature range assuming the diffusion and
mass transfer effects were insignificant. The Enthalpy of activation and Entropy of activation were calculated by the equation.

\[ \Delta H^\ddagger = E_a - nRT \]

\[ \Delta S^\ddagger = R \left[ \ln A - \ln(kT/h) - n \right] \]

The kinetic parameters were calculated and are given in Table 8.5.

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy, $E_a$</td>
<td>66.67 kJ/mol</td>
</tr>
<tr>
<td>Frequency factor, $A$</td>
<td>$3.06 \times 10^8$ (kg of catalyst)$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td>Enthalpy of activation, $\Delta H^\ddagger$</td>
<td>61.72 kJ/mol</td>
</tr>
<tr>
<td>Entropy of activation, $\Delta S^\ddagger$</td>
<td>$-175.57$ J/Mol /K</td>
</tr>
</tbody>
</table>

The high value of activation energy indicates that reaction is intrinsically kinetically controlled. The activation energy is within the limit (30-130 kJ/mol) of phenol alkylation reactions reported in literature. The negative value of entropy implies that the reactant molecules are more ordered on the catalyst surface than in vapour phase.

### 4.5 Conclusions

- Zirconium pillared clays and zirconium silicon porous clay heterostructures effectively catalyze the tertiary butylation of phenol reaction.
- Incorporation of transition metals improves the catalytic efficiency of both pillared clays and porous clay heterostructures except in the case of copper.
- Conversion increases with increase in temperature and maximum conversion is obtained at 190°C. The dialkylated product selectivity decrease with increase in temperature.
Conversion and dialkylated product selectivity increases with increase in phenol to TBA ratio.

Conversion decreases with increase in flow rate and maximum conversion is obtained at WHSV 10.08.

Porous clay heterostructures and its transition metal loaded analogues show higher conversion and dialkylated product selectivity than pillared clays and its transition metal loaded analogues by virtue of their higher surface area, pore size and acidity.

CoZrSiPCH shows highest conversion with appreciable dialkylated product selectivity. This result is comparable to that of metal modified mesoporous silica materials.

A good correlation is obtained between conversion of phenol and acidity due to medium and strong acid sites obtained from TPD of ammonia.

Kinetics studies show that the reaction follows second order kinetics. The high value of activation energy implies that reaction is intrinsically kinetically controlled.

References


Chapter 4


Tertiary butylation of phenol


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