

# Chapter 4

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## *Alkylation Of Arenes*

One important consequence for chemistry due to new environmental legislation and drive towards "Clean Technology" will be the use of "Environmentally Friendly Catalysis", typically involving the use of solid catalysts. The present chapter and the results therein show the great versatility of sulfated titania based catalysts in Friedel-Crafts reactions of aromatic compounds. The chapter is divided into two sections. The first section depicts the liquid phase benzylation of toluene and *o*-xylene using benzyl chloride over different sulfated titania systems and the effects of various operational parameters on the catalytic activity. The reaction is found to be very clean and produces the desired monoalkylated product with very high yield. The catalytic efficiency of the prepared systems in *tert*-butylation of phenol in the vapour phase is presented in the second section. Variation of catalytic activity over the systems is compared and discussed in terms of the strength of the acid sites.

### **SECTION 1**

#### **FRIEDEL - CRAFTS BENZYLATION OF ARENES**

##### **4.1 INTRODUCTION**

The Friedel-Crafts reactions are of great interest due to their importance and common use in synthetic and industrial chemistry. Strongly acidic reagents are normally employed as catalysts in Friedel-Crafts reactions. Traditional mineral acids such as HF and H<sub>2</sub>SO<sub>4</sub> or Lewis acids such as AlCl<sub>3</sub> and BF<sub>3</sub> are not environmentally benign<sup>1</sup>. The use of these substances involves technological

economic and environmental problems due to their corrosive nature, the difficulty of recycling and the formation of large amounts of harmful wastes. The high Lewis acidity of these homogeneous catalysts also results in several undesirable side reactions leading to secondary reaction products. Several solid acid catalysts relevant to Friedel-Crafts reactions have recently been developed to replace conventional homogeneous catalysts. A wide range of solid acid catalysts from clays<sup>2</sup> and zeolites<sup>3-5</sup> to heteropolyacids<sup>6</sup> have been tested for their applicability towards this reaction. These solid acid catalysts are more selective, safe, environmentally friendly, regenerable and reusable.

Benzylation of toluene using benzyl chloride over sol-gel derived titania and sulfated titania was reported<sup>7</sup>. Inversion of relative reactivities and selectivities of benzyl chloride and benzyl alcohol in Friedel-Crafts alkylation with toluene using different solid acid catalyst was also investigated<sup>8,9</sup>.  $\text{CuCr}_{2-x}\text{Fe}_x\text{O}_4$  spinel catalysts were used for benzylation of benzene with benzyl chloride<sup>10</sup>. Sebti *et al.*<sup>11</sup> compared the activities of  $\text{ZnCl}_2$ ,  $\text{NiCl}_2$  and  $\text{CuCl}_2$  supported on hydroxyapatite for Friedel-Crafts alkylation of benzene, toluene and *p*-xylene by benzyl chloride. Sulfated zirconia<sup>12</sup>, sol-gel derived silica<sup>13</sup> and rare earth oxides<sup>14</sup> were also used for Friedel-Crafts alkylation reactions. Benzylation of toluene over iron incorporated sulfated rutile was studied by Sugunan *et al.*<sup>15</sup>. The general scheme of benzylation reaction of a typical arene is represented as in figure 4.1.

It is well documented that sulfated metal oxides can be used as solid acid catalysts due to its high acid strength. More recently, these sulfated metal oxide catalysts have been found to have increasing applications and utility in Friedel-Crafts reactions. Catalytic activity of titania, sulfated by different agents for the gas phase alkylation of benzene and substituted benzenes using isopropanol was investigated by Samantaray *et al.*<sup>16</sup> By contrast, the utility of modified sulfated titania catalysts in the Friedel-Crafts alkylation of aromatic

compounds has not been explored in sufficient detail. Hence we report the benzylation of toluene and *o*-xylene by benzyl chloride over the sulfated titania systems. In the present investigation, structural stability, catalytic activity and reusability of transition metal-loaded sulfated titania systems have been investigated.

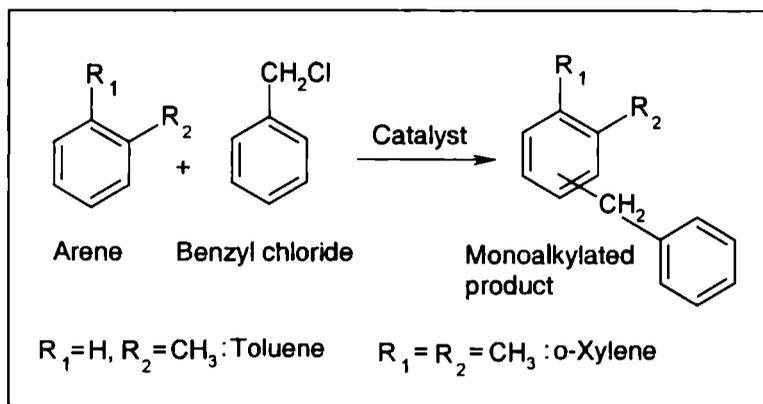


Figure 4.1 General scheme for Friedel-Crafts benzylation of arenas

## 4.2 PROCESS OPTIMIZATION

All the reactions were carried out in a round bottomed flask (50 mL) equipped with a reflux condenser, calcium chloride guard tube and magnetic stirrer. In a typical reaction procedure, the preactivated catalyst, the substrate (toluene or *o*-xylene) and benzyl chloride in a required molar ratio at a particular temperature were refluxed using an oil bath. The reaction mixture was withdrawn at specific time intervals and was filtered and analyzed using Gas Chromatograph equipped with SE-30 column and FID detector. The reaction always yielded a single major product, which is identified as the monoalkylated product (MAP). Due to the difficulty of identifying the product as *ortho* or *para*, we name as MAP.

### **I. Effect of the Catalyst**

We made the reaction run using benzyl chloride and toluene in the absence of a catalyst (blank run) and in the presence of the catalyst [0.1 g STCr(6)] at the refluxing temperature of the mixture. We observed a percentage conversion of 2.1 and 98.5 after 60 minutes of reaction in the absence and presence of the catalyst respectively. Low yield for the reaction in the absence of the catalyst is due to the higher activation energy of the uncatalyzed reaction. Addition of the catalyst significantly reduced the activation energy and the reaction proceeded through a different path with a lower activation energy, resulting in a higher percentage conversion.

### **II. Effect of Reaction Temperature**

The reaction temperature seems to play a major role in deciding the catalytic activity and selectivity. The influence of conversion of benzyl chloride (wt%) and product selectivity (%) on the reaction temperature is studied in the range of 70-110°C using STCr(6) catalyst over the two substrates (Table 4.1). At low temperatures, the percentage conversion is very low. An increase in the temperature results in enhanced activity. This is due to the speedy desorption of the alkylated product from the catalyst surface as the temperature increases, which facilitates the further adsorption of reactant molecules, resulting in the increased conversion of benzyl chloride. Maximum conversion is found to be at the refluxing temperature in the case of toluene with 100% selectivity to monoalkylated product (MAP). For *o*-xylene, at low temperatures, 100% selectivity to MAP is observed. At higher temperatures conversion of benzyl chloride increases, while selectivity to the MAP decreases. This may be due to the formation of consecutive products at higher temperatures. The results are in agreement with the literature report<sup>17</sup> that the higher reaction temperature favours the consecutive alkylation, disproportionation and decarboxylation.

Table 4.1 Influence of reaction temperature on benzylation of arenes

Temperature (°C)	Substrate			
	Toluene		o-xylene	
	Conversion of BC (wt%)	Selectivity (%) to MAP	Conversion of BC (wt%)	Selectivity (%) to MAP
70	19.50	100	49.54	100
80	39.25	100	76.85	100
90	62.20	100	93.82	100
100	90.50	100	98.59	98.74
110	98.54	100	100	94.23

Amount of catalyst: 0.1 g STCr (6), Substrate: benzyl chloride molar ratio: 10:1,  
Reaction time: 1 h.

### III. Effect of Substrate to Benzyl chloride molar ratio

The stoichiometric ratio between substrate and benzyl chloride influences the conversion and selectivity. To investigate the influence of molar ratio, we studied the benzylation of toluene and o-xylene at various molar ratios over STCr(6) keeping the amount of aromatic substrate constant. As shown in table 4.2, a continuous increase in the percentage conversion of benzyl chloride is registered with increase in substrate to benzyl chloride molar ratio. The product selectivity also depends on the molar ratio. At lower substrate to benzyl chloride ratios, the amount of polyalkylation is negligible while it considerably increases at higher molar ratios. The results show that the benzylation is favoured with a lower concentration of benzylating agent. Rohan *et al.*<sup>18</sup> reported that when the concentration of benzylating agent is high, there may be enhanced poisoning effect by the alkylated products, which is strongly adsorbed on the catalyst surface. This restricts further adsorption of the reactant molecules and thus reduces the conversion of benzyl chloride. At high arene to benzyl chloride molar ratio, this inhibition would be less

significant, which helps to desorb the products formed from the catalyst surface easily. Similar observation is also reported for benzylation of toluene over H-Y<sup>19</sup> and *o*-xylene over H- $\beta$  zeolites<sup>5</sup>.

Table 4.2 Effect of substrate to benzyl chloride molar ratio in benzylation of arenes

Substrate: benzyl chloride	Substrate			
	Toluene <sup>a</sup>		<i>o</i> -Xylene <sup>b</sup>	
	Conversion of BC (wt%)	Selectivity (%) to MAP	Conversion of BC (wt%)	Selectivity (%) to MAP
5:1	50.42	100	68.67	100
10:1	90.50	100	93.82	100
15:1	96.24	96.84	100	95.30
20:1	100	89.53	100	90.78

Amount of catalyst: 0.1 g STCr(6), Reaction time: 1 h, Temperature: <sup>a</sup>100°C, <sup>b</sup>90°C

#### IV. Effect of Catalyst Concentration

The catalyst concentration is varied by taking different amount of STCr(6) catalyst and keeping the amount of benzylating agent constant. Table 4.3 shows the influence of amount of catalyst on catalytic activity and selectivity. In the absence of catalyst the conversion is too low. Addition of 0.05 g catalyst changes the percentage conversion from 1.8 to 75.4% in the case of toluene. An initial steep increase in the conversion is observed when 0.1 g catalyst is used, and reaches 100% when the amount is 0.2 g. These results indicate that only a small amount of catalyst is needed for the reaction to take place. At high catalyst concentration, decrease in selectivity to MAP is observed. As the amount of catalyst is increased, there was a steady increase in conversion, because of the increase in the total number of acid sites available for the reaction<sup>4</sup>. The product yield is found to be proportional to the amount of the

catalyst taken establishing that the reaction proceeds through a pure heterogeneous mechanism. Singh *et al.*<sup>5</sup> studied the influence of catalyst concentration in the benzylation of *o*-xylene using zeolite catalysts and found similar results.

Table 4.3 Influence of the amount of catalyst in benzylation of arenes

Amount of the catalyst	Substrate			
	Toluene <sup>a</sup>		<i>o</i> -Xylene <sup>b</sup>	
	Conversion of BC (wt%)	Selectivity (%) to MAP	Conversion of BC (wt%)	Selectivity (%) to MAP
-	1.80	100	8.85	100
0.05	75.42	100	80.64	100
0.10	90.50	100	93.82	100
0.15	95.84	96.67	98.73	97.40
0.20	100	93.40	100	95.23

Catalyst: STCr(6), Substrate: benzyl chloride molar ratio: 10:1, Reaction time: 1 h, Temperature: <sup>a</sup>100°C, <sup>b</sup>90°C

### V. Effect of Substrate

Catalytic activity depends largely on the substrate used. Variation of reactivity with substrate was studied by carrying out the reaction using benzene, toluene and *o*-xylene over the same catalyst under the same reaction conditions. Table 4.4 gives the details of results for reactions conducted with different substrates. The reactivity is in the order *o*-xylene > toluene > benzene, which is in perfect agreement with the electron releasing nature of the alkyl groups. -CH<sub>3</sub> being an electron-donating group will increase the electron density on the benzene ring and makes it more favorable to the attack by an electrophile. Thus it is worth mentioning that the reactivity of aromatic nucleus increases with the number of electron donating groups attached to the aromatic ring. Hence *o*-xylene, which has two methyl groups, reacts more easily than

toluene with only one methyl group. Benzene, since it does not possess any substituent methyl groups, is much less reactive than *o*-xylene and toluene. Sebti *et al.*<sup>11</sup> reported similar results over different Lewis acid supported on hydroxyapatite for benzylation reaction.

Table 4.4 Influence of substrate on catalytic activity in benzylation of arenes

Substrate	Time (min)	Conversion of BC (wt%)	Selectivity (%) to MAP
Benzene	60	4.86	100
Toluene	60	39.25	100
<i>o</i> -xylene	60	76.85	100

Amount of Catalyst: 0.1 g STCr(6), Substrate: benzyl chloride molar ratio: 10:1, Reaction Temperature: 80°C

## VI. Effect of moisture

Normally used homogeneous Friedel-Crafts catalysts suffer an inherent drawback of high moisture sensitivity. This makes the handling of these systems very difficult<sup>20</sup>. Conventional catalysts also demand moisture free solvent and reactants, anhydrous catalyst and dry atmosphere for their handling. In order to test the effect of moisture on catalyst performance two parallel runs were carried out, one using the fresh activated catalyst and another with the catalyst adsorbed with moisture. To prepare the catalyst adsorbed with moisture, the catalyst was first activated and then kept in a dessicator containing water vapour for 48 h. The results are presented in figure 4.2.

In the case of fresh samples the reaction commenced quickly, but for the moisture adsorbed sample, conversion remained very low even after 45 minutes. After that, catalytic activity of moisture adsorbed samples showed an increase and as the time progressed the catalytic conversion of benzyl chloride over moisture adsorbed system increased and became the same as that given by the fresh catalyst. Thus it is evident that presence of moisture

developed an induction period for the reaction, but in no way influenced the catalytic activity of the system. There is a time period for which the catalyst is inactive towards the reaction, when it is adsorbed with moisture. The moisture gets adsorbed on the active sites on the catalyst surface and prevents the interaction of benzyl chloride molecule with these sites. Once these water molecules are removed, reaction proceeds at the same rate as that of the fresh catalyst. Thus, though moisture initially blocks the active sites, after the induction period, the reaction rate is same in the case of fresh catalyst itself.

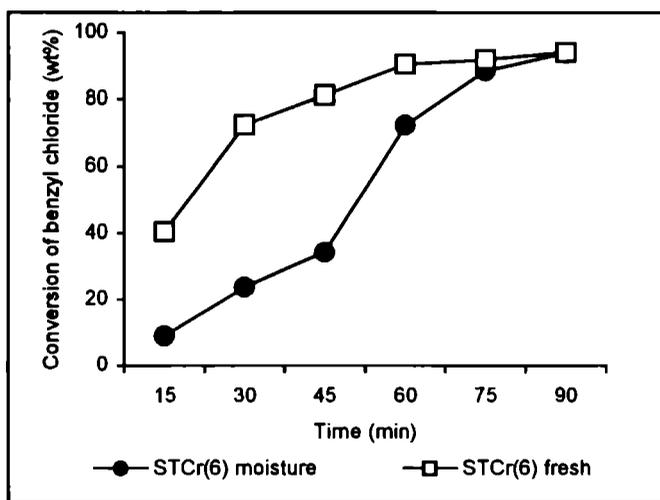


Figure 4.2 Influence of moisture on benzylation of toluene

Amount of catalyst: 0.1 g STCr(6), Toluene: benzyl chloride molar ratio: 10:1,  
Reaction Temperature: 100°C.

## VII. Effect of Metal Leaching

For any catalyst, chemical stability is an essential requirement, in addition to thermal stability. Leaching can occur during a catalyzed reaction without an induction period and the nature of reaction may gradually change from heterogeneous to homogeneous without any indications in the reaction profile<sup>21</sup>.

Table 4.5 Effect of metal leaching in benzylation of arenes

Systems	Toluene <sup>a</sup>		o-Xylene <sup>b</sup>	
	Conversion of benzyl chloride (wt%)			
	After 60 minutes	*After 90 minutes	After 60 minutes	*After 90 minutes
STCr(6)	90.50	91.00	93.82	94.15
STMn(6)	93.63	93.94	100.00	100.00
STFe(6)	100.00	100.00	100.00	100.00
STCo(6)	85.39	86.47	90.06	90.89
STNi(6)	75.50	76.14	80.62	81.47
STCu(6)	80.78	81.55	85.98	86.02
STZn(6)	90.00	90.57	100.00	100.00

Amount of catalyst: 0.1 g, Substrate: Benzyl chloride: 10:1, Reaction temperature: <sup>a</sup>100°C, <sup>b</sup>90°C (\*Reaction done after filtering the catalyst)

To prove the heterogeneous character of the reactions, the catalyst was removed from the reaction mixture after one hour and the filtrate was allowed to react under the same conditions for 30 minutes. The filtrate was further subjected to qualitative analysis for testing the presence of leached metal ions. No noticeable change in the conversion is obtained in any case after the removal of the catalyst (table 4.5). Qualitative analysis of the filtrate also confirmed the absence of any metal ion in the filtrate. Thus it is clear from the results that metal ions are not leaching from the metal oxide surface during benzylation reaction. These observations imply that the reaction is 100% heterogeneously catalyzed.

### VIII. Catalyst Regeneration

One of the major objectives guiding the development of solid acid catalysts includes the easy separation of final products from the reaction mixture and efficient catalyst recovery.

Table 4.6 Regeneration of catalyst

No. of cycles	1	2	3	4
Conversion of benzyl chloride (wt%)	78.10	75.54	72.28	61.48

Amount of Catalyst: 0.1 g STCr(3), Toluene: benzyl chloride molar ratio: 10:1,  
Reaction Temperature: 100°C

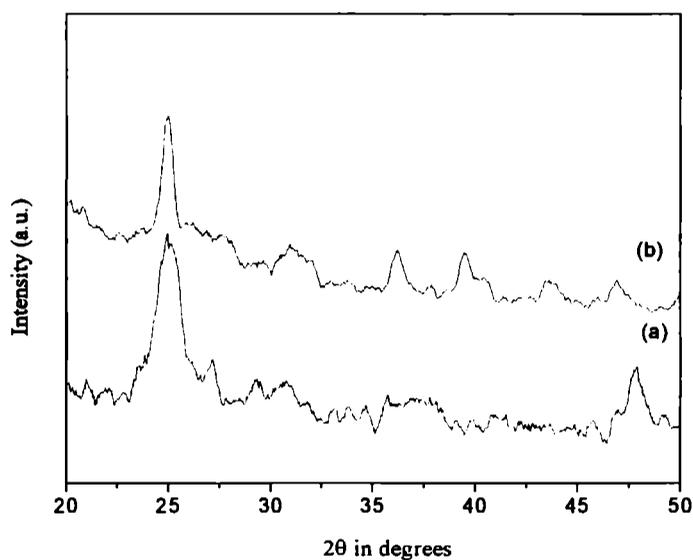


Figure 4.3 XRD patterns of STCr(3) catalyst (a) Before reaction  
(b) After reaction

Regeneration studies were done by removing the catalyst by filtration from the reaction solution, washed thoroughly with acetone and then dried and activated at 500°C for 5 h. The same catalyst was again used for carrying out subsequent runs under similar reaction conditions. To check the structural change during the reaction, the XRD spectrum of the used catalyst was taken. No pronounced change could be observed in the XRD pattern, except a slight lowering of intensity, symptomatic of the retention of the crystalline nature

(figure. 4.3). It was tested for catalytic activity and only a slight decrease was observed. This suggests the resistance to rapid deactivation in benzylation reactions. However, the decrease becomes more pronounced as the cycles are repeated. Table 4.6 displays the conversion of benzyl chloride obtained for toluene benzylation using regenerated STCr(3) catalyst during a four times recycling process. The hydrogen chloride produced in the electrophilic benzylation of toluene is responsible for the deactivation of the catalyst. These results are consistent with the earlier reports<sup>22,23</sup>.

### IX. Effect of Reaction Time

The reaction mixture is analyzed at various time intervals in order to study the effect of reaction time on conversion of benzyl chloride. The variation of product selectivity with time is also subjected to screening (table 4.7). These results show that the reaction time is also having a deciding effect on the catalytic activity and product selectivity.

Table 4.7 Effect of reaction time on benzylation of arenes

Time (minutes)	Substrate			
	Toluene <sup>a</sup>		o-Xylene <sup>b</sup>	
	Conversion of BC (wt%)	Selectivity (%) to MAP	Conversion of BC (wt%)	Selectivity (%) to MAP
30	72.48	100	83.40	100
60	90.50	100	93.82	100
90	94.12	100	97.43	100
120	98.66	100	100	98.64
150	100	100	100	95.74

Amount of catalyst: 0.1 g STCr(6), Reaction Temperature: <sup>a</sup>100°C, <sup>b</sup>90°C, Reaction time: 1 h

There is an increase in the conversion as time proceeds, but the selectivity remained constant throughout the course of the reaction, when the substrate as toluene. Conversion becomes 100% at 2.5 h of reaction time.

Only monoalkylated product is detected in the case of *o*-xylene upto 1.5 h. Prolonged reaction time is found to generate undesirable products in the case of *o*-xylene. After 1.5 h, secondary alkylation is observed, resulting in low selectivity towards MAP. Conversion reaches 100% at 2 h reaction time at the expense of selectivity to the monoalkylated product for *o*-xylene. The increase in conversion of benzyl chloride with time confirms the heterogeneity of the catalytic reaction.

#### 4.3 COMPARISON OF DIFFERENT SYSTEMS

After optimization studies, catalytic activity of all the systems were evaluated at a molar ratio of 10:1, using 0.1 g catalyst and at a reaction temperature of 100°C and 90°C for toluene and *o*-xylene respectively. Tables 4.8 and 4.9 present the results of benzylation of toluene and *o*-xylene using benzyl chloride over different metal loaded sulfated titania systems.

Table 4. 8 Influence of the type of metal loaded in the benzylation of arenes

Systems	Toluene <sup>a</sup>		<i>o</i> -Xylene <sup>b</sup>	
	Conversion (wt%)	Selectivity (%) to MAP	Conversion (wt%)	Selectivity (%) to MAP
T	20.20	100	38.60	100
ST	60.65	100	70.78	100
STCr(3)	78.10	100	80.82	100
STMn(3)	83.60	100	85.41	100
STFe(3)	100.00	100	100.00	100
STCo(3)	72.80	100	76.62	98.54
STNi(3)	65.29	100	71.51	98.20
STCu(3)	70.18	100	73.75	97.58
STZn(3)	96.98	100	100.00	100

Amount of catalyst: 0.1 g, Substrate: Benzyl chloride: 10:1, Reaction time: 1 h,  
Reaction temperature: <sup>a</sup>100°C, <sup>b</sup>90°C

Pure TiO<sub>2</sub> gave very low conversions under the specified reaction conditions. An interesting observation was that only monoalkylated product was obtained in all the cases when toluene is used as the substrate. An enhanced conversion at the expense of monoalkylated product is observed in the case of *o*-xylene. The sulfated system gives comparatively high conversion than the pure titania. Among the various metal loaded systems, a notable deviation was observed in the case of iron incorporated systems. Abnormally high conversions, which do not commensurate with the Lewis acidity values, may be attributed to the reducible character of the iron. The conversion becomes 100% within 15 minutes in the case of iron loaded systems. This may be an indication of the fact that the iron content or the Lewis acidity is not the only factor favouring the reaction.

Table 4. 9 Influence of amount of metal loading in benzylation of arenes

Systems	Toluene <sup>a</sup>		<i>o</i> -Xylene <sup>b</sup>	
	Conversion (wt%)	Selectivity (%) to MAP	Conversion (wt%)	Selectivity (%) to MAP
STCr(6)	90.50	100	93.82	100
STMn(6)	93.63	100	100.00	100
STFe(6)	100.00	100	100.00	100
STCo(6)	85.39	100	90.06	100
STNi(6)	75.50	100	80.62	98.20
STCu(6)	80.78	100	85.98	99.00
STZn(6)	90.00	100	100.00	100
STCr(9)	85.63	100	89.43	100
STMn(9)	90.39	100	96.78	97.34
STFe(9)	100.00	100	100.00	100
STCo(9)	80.02	100	87.05	97.04
STNi(9)	70.15	100	77.63	95.54
STCu(9)	73.79	100	80.78	96.80
STZn(9)	99.30	100	100.00	100

Amount of catalyst: 0.1 g, Molar ratio: 10:1, Reaction time: 1 h, temperature: <sup>a</sup>100°C, <sup>b</sup>90°C

It is reported that catalysts containing reducible cations like  $\text{Fe}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sb}^{3+}$ , etc. exhibit high alkylation activity regardless of their low Lewis acidities<sup>24-26</sup>. When the redox mechanism is operating there will be a homolytic rupture of the carbon-chlorine bond of the alkylating agent (benzyl chloride). The radicals so formed are powerful reductants, which would be readily oxidized to carbocations in the presence of reducible metallic ions such as  $\text{Fe}^{3+}$ . When *o*-xylene was used as the substrate, catalytic activity followed the same trend as in the case of toluene. Monoalkylated products were obtained in major proportion, with a small amount of polyalkylated product. The maximum conversion was shown by the systems with 6% metal loading and minimum by those with 3% metal loading i.e., as the percentage loading increases conversion increases and then decreases at high loadings.

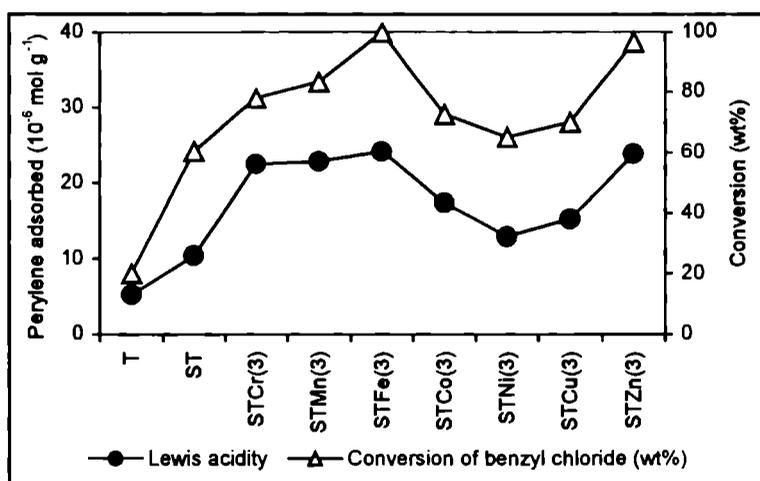


Figure 4.4 Catalytic activity correlated with Lewis acidity determined from perylene adsorption studies

The acid base properties of metal oxide carriers can significantly affect the final selectivity of heterogeneous catalysts<sup>19</sup>. So an attempt is made to correlate the catalytic activity with the acidic characteristics determined by different methods. Figures 4.4 and 4.5 show the correlation of benzylation

activity of the systems with the acidity in benzylation of toluene. From the figures it is clear that the percentage conversion for different systems are in agreement with the amount of Lewis acid sites measured from perylene adsorption studies.

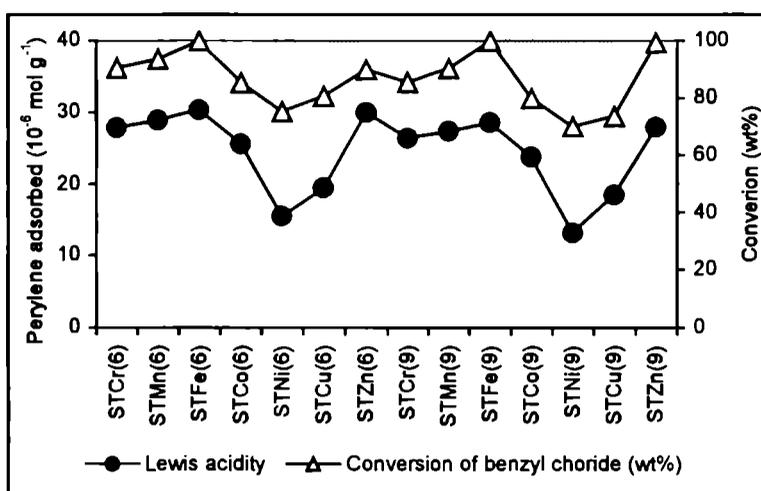


Figure 4.5 Catalytic activity correlated with Lewis acidity determined from perylene adsorption studies

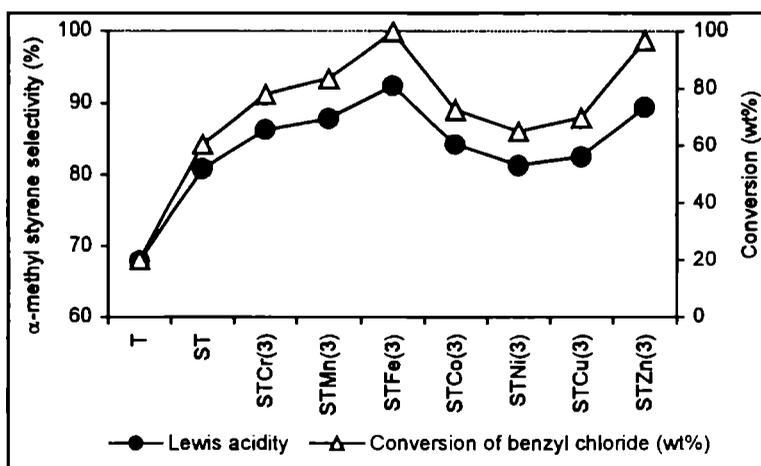


Figure 4.6 Catalytic activity correlated with  $\alpha$ -methyl styrene selectivity from cumene conversion reaction

The Lewis acidity trend predicted by  $\alpha$ -methyl styrene selectivity from cumene conversion reaction also parallels the reactivity observed with the increase in the percentage conversion (figures 4.6 and 4.7). Metal loading and sulfate modification provoke considerable synergistic effect leading to an enhanced activity. The metal oxide surface contains both Brønsted and Lewis acid sites and the above observations clearly indicate the dominating impact of Lewis acid sites for the benzylation reaction over the sulfated titania systems. Introduction of sulfate ions increases the surface acidity due to electron withdrawing nature of sulfate groups, which increases the number of Lewis sites.

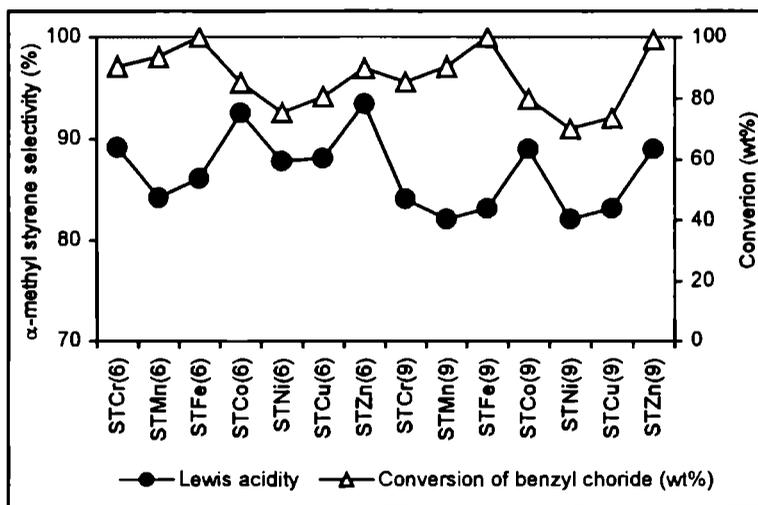


Figure 4.7 Catalytic activity correlated with  $\alpha$ -methyl styrene selectivity from cumene conversion reaction

#### 4.4 MECHANISM OF BENZYLATION REACTION

The catalytic activity studies on different transition metal loaded sulfated titania systems suggest the involvement of Lewis acid sites in the reaction. Barlow *et al.*<sup>27</sup> reported the benzylation of anisole over Clazic is catalyzed by

Brønsted sites, below 40°C. Rhodes *et al.*<sup>28</sup> found that the enhanced catalytic activity of adsorbed  $\text{ZnCl}_2$  (Clazic) was not due to increased Lewis acidity but may be due to the increased accessibility of Lewis sites to reactant molecules.

The reaction appears to proceed by an electrophile, which involves the reaction of benzyl chloride with the acidic titania catalyst. The acidic catalyst polarizes the benzylating agent and, in turn, produces an electrophile ( $\text{C}_6\text{H}_5\text{CH}_2^+$ ). Thus, the generated electrophilic species attack the benzene ring, resulting in the formation of the corresponding dimethyl diphenyl derivative<sup>29,30</sup>. Nonpolar nature of the substrate molecules also supports the formation of the electrophilic species by adsorption of benzyl chloride molecule on the catalyst surface. A plausible mechanism for the reaction can be represented schematically as shown in figure 4.8.

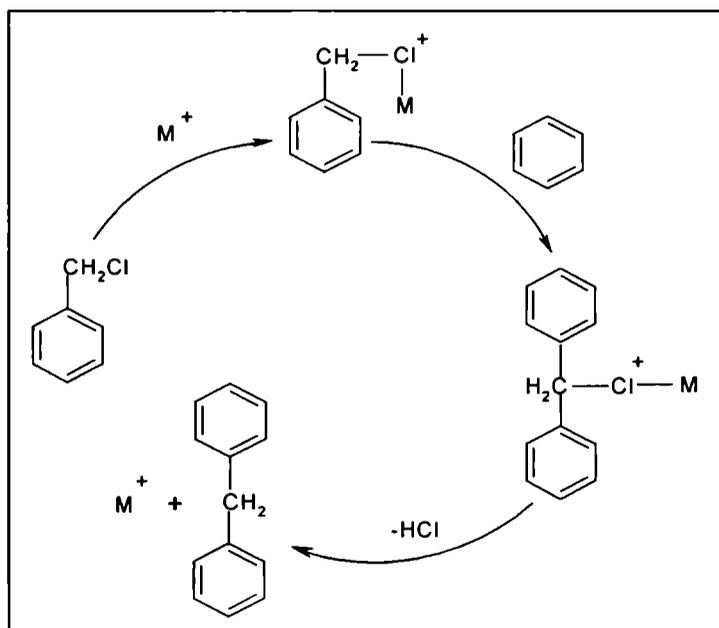


Figure 4.8 Mechanism of Friedel-Crafts benzylation using benzyl chloride showing the active involvement of Lewis acid sites.

The percentage conversions obtained in the case of iron loaded systems were much higher than that expected from its Lewis acidity. The high activity of iron systems, which does not commensurate with the acidity values, can be attributed to the redox or free radical mechanism (figure 4.9). Recently Choudary *et al.*<sup>18</sup> suggested the possibility of a redox mechanism for reducible cations when benzyl chloride was the alkylating agent. Considering all the aspects, we propose the existence of a redox or a free radical mechanism in the case of Fe loaded samples side by side with the involvement of Lewis acid sites. Radicals are powerful reductants, which can readily be oxidized to cations in presence of reducible metal cations. Thus the high activity associated with these reducible cations involves the initiation of the reaction by the homolytic cleavage of the carbon-chlorine bond followed by the oxidation of the radical to the corresponding ion.

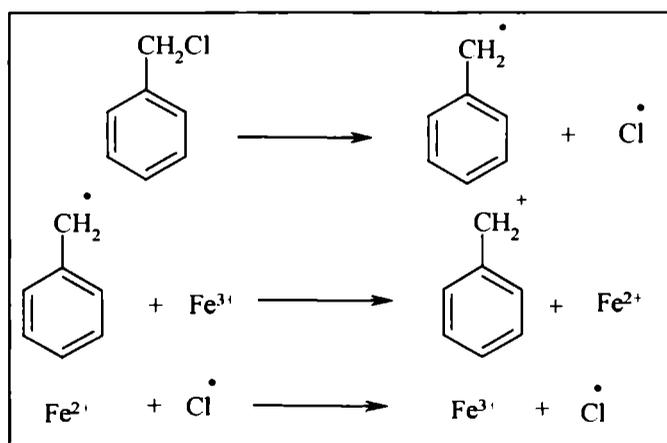


Figure 4.9 Free radical mechanism for benzylation of arenes

#### 4.5 CONCLUSIONS

The following conclusions can be drawn from the present study.

- ∅ Sulfated titania catalysts can be used for the benzylation of toluene and *o*-xylene, leading to the formation of monoalkylated products. The

conventional catalyst,  $\text{AlCl}_3$  does not possess shape selectivity and favours the formation of large amount of polyalkylated products.

- ∅ The conversion of benzyl chloride and product distribution largely depends on the experimental condition. The conversion of benzyl chloride increases with increasing reaction time, catalyst concentration, reaction temperature and substrate to benzyl chloride molar ratio.
- ∅ The reaction is found to be clean with negligible formation of polyalkylated products. The activity of the systems is found to be increasing with the number of electron donor methyl groups present in the aromatic substrates. Catalysts are reusable and resistant to rapid deactivation in benzylation reaction even in the presence of moisture.
- ∅ The Lewis acid sites in the catalysts appears to be very important for the polarization of benzyl chloride into an electrophile ( $\text{C}_6\text{H}_5\text{CH}_2^+$ ) which then attacks the benzene ring resulting in the formation of products.
- ∅ Free-radical mechanism explains the exceptionally high activity of iron loaded samples for the benzylation reaction.

## SECTION 2

### TERT-BUTYLATION OF PHENOL

Phenol alkylation with *tert*-butyl alcohol (TBA) has been studied extensively owing to industrial interest in the production as antioxidants, ultraviolet adsorbers and heat stabilizers of polymeric materials. The catalytic efficiency of the prepared titania systems in the *tert*-butylation of phenol in vapour phase has been studied and is presented in this section. Influence of various reaction parameters such as temperature, flow rate and molar ratio of the reactants on phenol conversion and selectivity of the product is discussed in detail. Variation of catalytic activity among the systems are compared and discussed in terms of the strength of the acid sites. Medium acid sites on the catalysts are advantageous in producing 4-*tert*-butylphenol, whereas strong acid sites are helpful for the formation of 2,4-di-*tert*-butylphenol.

## 4.6 INTRODUCTION

Short chain alkyl phenols are important intermediates for the production of resins, antioxidants, drugs, dyes, polymer additives, agrochemicals and antiseptic substances<sup>1</sup>. The direct alkylation of phenol with short-chain alcohols and olefins is widely used for the preparation of these intermediates. The catalytic reactions of phenol with *tert*-butyl alcohol or isobutene as well as with methyl-*tert*-butyl ether are important, because C-alkylation products such as 4-*tert*-butylphenol (4-TBP), 2-*tert*-butylphenol (2-TBP) and 2,4-*di-tert*-butylphenol (2,4-DTBP) have great commercial significance. Some commonly used catalysts for alkylation of phenol are H<sub>2</sub>SO<sub>4</sub>, BF<sub>3</sub>, aluminum phenoxide, etc<sup>2</sup>. Catalytic alkylation of phenol using solid acid catalysts is a very promising way for their synthesis considering the increasing demand for eco-friendly routes in the chemical industry. Reports and patents concerning this catalytic reaction, which has been carried out both in the liquid and gas phase, are available<sup>3-14</sup>.

Generally, in the alkylation of aromatics over zeolites, catalytic activity is controlled by acidity where as selectivity is controlled by pore structure and acid strength of the catalyst<sup>15-19</sup>. The catalyst reacts with the alkylating agent to form a carbocation or a carbanion, which further rearranges to one which is as branched as possible. The carbanion attacks the phenol ring preferentially in the *ortho* and/or *para* position to the –OH group according to the rules of electrophilic substitution<sup>20</sup>. In addition to alkylation, etherification of the –OH group can also occur under mild reaction conditions. Since the monoalkylated products are more reactive than phenol, they get further alkylated provided there is no steric hindrance. The ratio of mono to di and tri alkyl phenol is proportional to the ratio of phenol to alkylating agent.

## SYNTHESIS OF BUTYL PHENOLS

Depending on the nature of the catalyst, alkylation of phenol can take place at the oxygen (O-alkylation) and/or at ring carbon atoms (C-alkylation). Reports<sup>21-23</sup> indicate that the selectivity largely depends on the acid strength of the catalyst. In general, C-alkylation requires stronger acid sites than those responsible for O-alkylation<sup>11,24,25</sup>. C-alkylation of phenol can give rise to 2-,3- and 4-alkylphenols as well as multi substituted products. *Tert*-butyl phenols (TBP's) are formed by the reaction of phenol with isobutene or *tert*-butanol. 2-*tert*-butyl phenol is produced as the main product if phenol is reacted with isobutene in presence of an acidic ion-exchange resin catalyst. *Tert*-butyl phenyl ether (TBPE), which is the O-alkylated product, can also be formed as a byproduct but its amount decreases with increasing the temperature. Zhang *et al.*<sup>26</sup> have shown that 2-TBP selectivity can be enhanced by the use of beta zeolites under specific conditions. Padmasri *et al.*<sup>27</sup> have shown that the production of 2-TBP can be performed with good selectivity over aluminum hydrotalcites. In the US patent by Chang and Hellring<sup>12</sup>, they have demonstrated that *tert*-butanol can be used as the butylating agent. On catalysts namely MCM-22 and beta zeolite, they obtained high selectivity for 4-TBP.

### 4.7 PROCESS OPTIMIZATION

The vapour phase *tert*-butylation of phenol was carried out in a conventional fixed bed reactor under atmospheric pressure. The reaction is found to be extremely sensitive to reaction conditions. The most important concern with respect to catalytic alkylation of phenol is the catalytic activity and catalytic selectivity towards the desired C-alkylated product, with regard to the structural and acid properties of the catalysts.

In the present study, the major products obtained were 2-TBP, 4-TBP and 2,4-DTBP. The last one mentioned is the product of further alkylation of

2- or 4-*tert* butyl phenol. 2-*tert* butyl phenol easily isomerises to 4-*tert* butyl phenol whereas the reverse reaction is not significant. 3-TBP and 2,6-DTBP are not formed on any of the catalysts, while a trace amount of *tert*-butyl phenyl ether (TBPE) is detected. A detailed investigation on the optimization of the process is discussed below.

### I. Effect of Phenol to TBA Molar ratio

In order to understand the optimum feed mix ratio, a series of experiments were performed at 180°C with various molar ratios of phenol to TBA over STFe(6). The formation of 2-TBP, 4-TBP and 2,4-DTBP is observed at different reactant ratios. From Table 4.10, we can find that at high phenol content, the production of 4-TBP is dominant and at lower content the selectivity of 2,4-DTBP is enhanced.

Table 4.10 Influence of molar ratio on the conversion and product selectivity in *tert*-butylation of phenol

Phenol: TBA	Conversion of Phenol (wt%)	Selectivity (%)			<i>p/o</i> ratio
		2-TBP	4-TBP	2,4-DTBP	
1:1	21.02	18.49	70.48	5.93	3.81
1:2	29.25	21.93	68.75	7.47	3.13
1:4	31.04	23.51	66.22	9.49	2.82
1:6	35.60	26.15	58.53	14.24	2.24

Amount of catalyst: 0.5 g STFe(6), Flow rate: 4 mL h<sup>-1</sup>, Reaction temperature: 180°C, Reaction time: 2 h.

Phenol conversion increases on increasing TBA concentration in the feed. Higher amount of TBA in the feed helps in promoting the alkylation, provided the alkylating agent is not consumed in non-selective parallel reactions. The *p/o* ratio is decreasing as the amount of TBA in the feed increases. Higher amount of TBA on the catalyst surface, result in the

formation of 2,4-DTBP. An optimum feed mixture of phenol to TBA in 1:2 molar ratio is chosen for further investigations, considering the phenol conversion and selectivity to 4-TBP.

## II. Effect of Reaction Temperature

The reaction temperature has a profound influence on the catalytic activity as well as the product selectivity. The reaction is carried out at various reaction temperatures in the range of 160-220°C, close to the boiling point of phenol (180°C). Table 4.11 clearly shows the product distribution and selectivity of desired products at various temperatures. The general trend for the alkylation reaction is that the conversion increases with increase in temperature and reaches a steady state at high temperature. The selectivity of 4-TBP was enhanced, while that of 2-TBP and 2,4-DTBP decreased with increase in reaction temperature. There is a clear cut relation between the concentration of 2-TBP and 2,4-DTBP in the products as the latter falls along with 2-TBP.

Table 4.11 Influence of reaction temperature on the conversion and product selectivity in *tert*-butylation of phenol

Temperature (°C)	Conversion of Phenol (wt%)	Selectivity (%)			<i>p/o</i> ratio
		2-TBP	4-TBP	2,4-DTBP	
160	29.05	23.04	65.43	7.58	2.84
180	29.25	21.93	68.75	7.47	3.13
200	32.20	20.91	70.48	7.25	3.37
220	25.30	20.05	73.42	5.34	3.66

Amount of catalyst: 0.5 g STFe(6), Flow rate: 4 mL h<sup>-1</sup>, Phenol:TBA: 1:2 Reaction time: 2 h.

It is reported in literature<sup>28</sup> that the formation of 2,4-DTBP takes place in a consecutive step by alkylation of mono alkylated product. It was also observed<sup>28</sup> that when a mixture of 4-TBP and 2-TBP were reacted, the latter

preferably react to form 2,4-DTBP. Our results also demonstrate a similar trend. The fall in 2-TBP selectivity also lead to a fall in 2,4-DTBP selectivity. A moderate reaction temperature is helpful in enhancing the selectivity of 2,4-DTBP. At higher reaction temperatures the formation of undesired products are enhanced and they consume reactants (TBA) without producing the desired products, which may lead to lower phenol conversion and 2,4-DTBP selectivity. The conversion of phenol increases up to 200°C, and after that it decreases. Considering the phenol conversion and product distribution, the proper reaction temperature chosen is 200°C. At this temperature the conversion of phenol is higher compared to the other investigated temperatures.

### III. Effect of Flow Rate

The contact time between the catalyst and the reactants greatly influence the reaction rate. Very low contact time (high flow rate) may lead to poor reaction on account of the fact that little time is available for the adsorption of the reactants on the catalyst surface. At the same time, very high contact time (low flow rate) mostly results in undesired side reactions. Thus each reaction requires an optimum contact time with which maximum conversion and desired product yield is achieved.

The reaction is carried out at various flow rates at a reaction temperature of 200°C and with phenol to TBA molar ratio of 1:2 and the trend is presented in figure 4.10. There is an increase in phenol conversion when we change the flow rate from 3 mL h<sup>-1</sup> to 4 mL h<sup>-1</sup>. After that phenol conversion decreases with increasing flow rate, due to the shorter contact time values at higher flow rate. 2,4-DTBP selectivity is low for higher contact time values whereas it improves and remains almost steady at lower contact time values. There is an optimum contact time for the reaction to take place and 4 mL h<sup>-1</sup> is chosen as the flow rate for further studies.

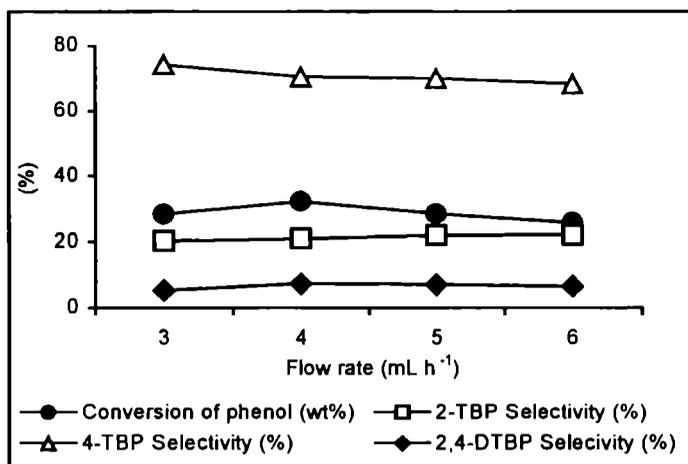


Figure 4.10 Influence of flow rate on phenol conversion and product selectivity  
 Amount of catalyst: 0.5 g STFe(6), Phenol:TBA: 1:2, Reaction time: 2 h,  
 Reaction temperature: 200°C.

#### IV. Effect of Time on Stream-Deactivation study

The effect of time on stream is expected to throw light on deactivation of a particular catalyst and its influence on product selectivities. The performance of the reaction for a continuous 7 h run tests the susceptibility of deactivation of the catalyst. The products were collected and analyzed after every one hour. Figure 4.11 represent the phenol conversion of representative systems towards time on stream. In the initial hours the catalyst may adsorb phenol strongly and after 2 h, the catalyst activity established an equilibrium level. The conversion of phenol gradually increased with time on stream in the initial reaction period for 2 h, and then the conversion level attained a steady value at 5 h and after that it decreases for T and ST. In the case of metal incorporated systems, the deactivation starts slowly from 3 h onwards. At 7 h, conversion decreases to a greater extent. This can be explained by the fact that the catalytic activity progressively decreases with time having a reduction in conversion.

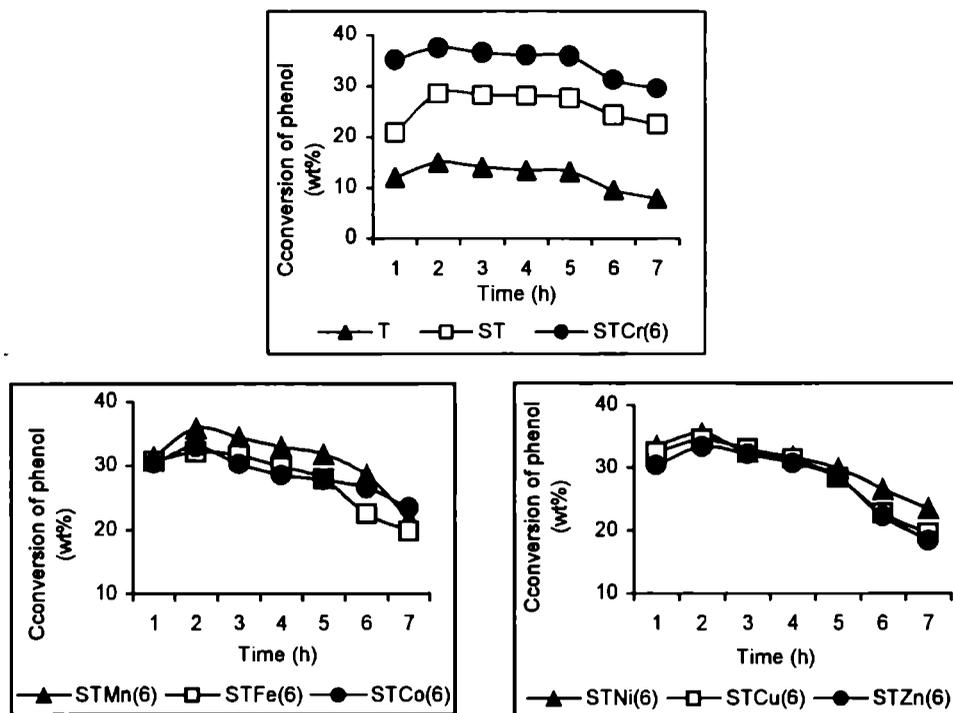


Figure 4.11 Deactivation studies on the conversion of phenol over different systems

Amount of catalyst: 0.5 g, Phenol: TBA: 1:2, Flow rate:  $4 \text{ mL h}^{-1}$ , temperature:  $200^\circ\text{C}$

#### 4.8 COMPARISON OF DIFFERENT SYSTEMS

A comparative account of the catalytic activity of various sulfated titania systems in the butylation reaction is given in this section. All the prepared systems were tested for activity over a reaction time of 2 h under the optimized reaction conditions, temperature of  $200^\circ\text{C}$ , flow rate of  $4 \text{ mL h}^{-1}$  and a reactant ratio of 1:2. An attempt to correlate the surface acidity with the product selectivity is carried out. Pure titania exhibited poor activity towards *tert*-butylation of phenol under the specified reaction conditions. The reaction proceeds very efficiently over different sulfated titania systems. In comparison with simple sulfated system, metal incorporated samples are more efficient for

the butylation reaction (Tables 4.12 and 4.13). Chromium loaded samples show the highest activity when compared with the other systems. In all cases *ortho* and *para* isomers were obtained with a high selectivity for the *para* isomer. The *p/o* ratio was maximum for chromium and minimum for iron.

Table 4.12 Influence of the type of metal loaded in the *tert*-butylation of phenol

Systems	Conversion of Phenol (wt%)	Selectivity (%)			<i>p/o</i> ratio
		2-TBP	4-TBP	2,4-DTBP	
T	14.90	23.53	50.64	2.54	2.15
ST	28.45	19.81	65.64	5.44	3.31
STCr(3)	35.54	14.71	73.82	6.97	5.02
STMn(3)	33.55	16.18	69.88	6.04	4.32
STFe(3)	28.95	19.95	66.63	6.82	3.34
STCo(3)	29.10	19.99	67.05	5.94	3.35
STNi(3)	33.01	16.27	69.14	3.47	4.25
STCu(3)	32.54	17.20	68.97	4.14	4.01
STZn(3)	30.08	17.60	67.22	6.52	3.82

Amount of catalyst: 0.5 g, Flow rate: 4 mL h<sup>-1</sup>, Phenol: TBA: 1:2, Reaction time: 2 h,  
Reaction temperature: 200°C

An attempt to investigate the influence of the metal loading on catalytic activity is quite reasonable. As expected, variation in metal loading had a significant impact on the catalytic activity. An increase in metal content resulted in enhanced catalytic activity. As the metal loading was increased from 0 to 6% the conversion gradually increased, thereafter the conversion declined. In all the cases *para* isomer is the major product. Selectivity to 4-TBP and 2,4-DTBP also changed with respect to the metal loading. Selectivity to 4-TBP is maximum for 6% loading and minimum for 3% loading.

Table 4.13 Influence of the amount of metal loading in the *tert*-butylation of phenol

Systems	Conversion of Phenol (wt%)	Selectivity (%)			<i>p/o</i> ratio
		2-TBP	4-TBP	2,4-DTBP	
STCr(6)	37.48	14.54	76.87	7.89	5.29
STMn(6)	35.89	15.07	75.05	6.51	4.98
STFe(6)	32.20	20.91	70.48	7.25	3.37
STCo(6)	33.06	20.06	70.74	6.09	3.53
STNi(6)	35.47	17.00	73.07	3.85	4.30
STCu(6)	34.46	17.33	72.11	4.51	4.16
STZn(6)	33.42	18.13	71.61	6.85	3.95
STCr(9)	34.12	14.47	70.95	4.98	4.83
STMn(9)	33.85	14.94	70.02	3.47	4.68
STFe(9)	29.47	20.04	67.32	4.62	3.36
STCo(9)	32.94	19.79	69.05	4.25	3.49
STNi(9)	32.54	16.72	68.89	2.45	4.12
STCu(9)	31.25	17.17	68.01	2.92	3.96
STZn(9)	31.09	17.63	67.98	4.09	3.85

Amount of catalyst: 0.5 g, Flow rate: 4 mL h<sup>-1</sup>, Phenol: TBA: 1:2, Reaction time: 2 h,  
Reaction temperature: 200°C

The acid base properties of the catalysts affect the final selectivity of heterogeneous catalysts<sup>29</sup>. Figures 4.12 to 4.15 gives the correlation between the product selectivity and the acidity assessed by ammonia TPD. It was observed that the *p/o* ratio was very low in the case of pure titania and sulfated titania. Metal incorporation increased the selectivity to *para* isomer. Considering the acid site distribution from the TPD measurements, the increase in the medium acid sites with increase in the metal content is in agreement with the enhanced activity of the systems.

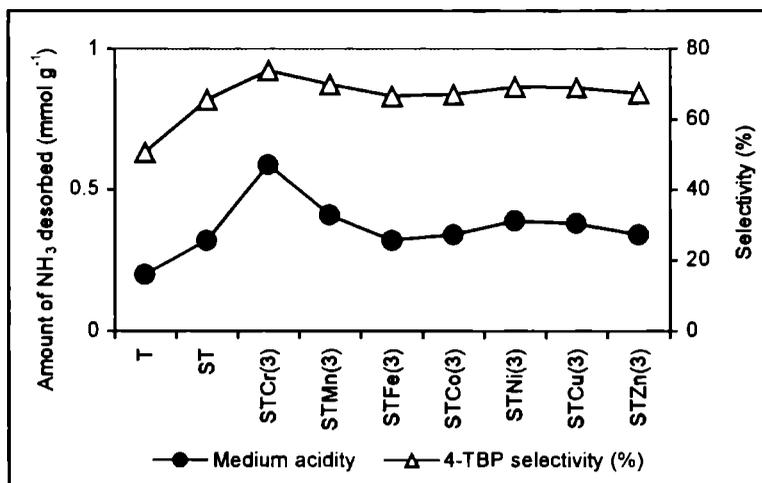


Figure 4.12 4-TBP selectivity correlated with the medium acidity from NH<sub>3</sub> TPD

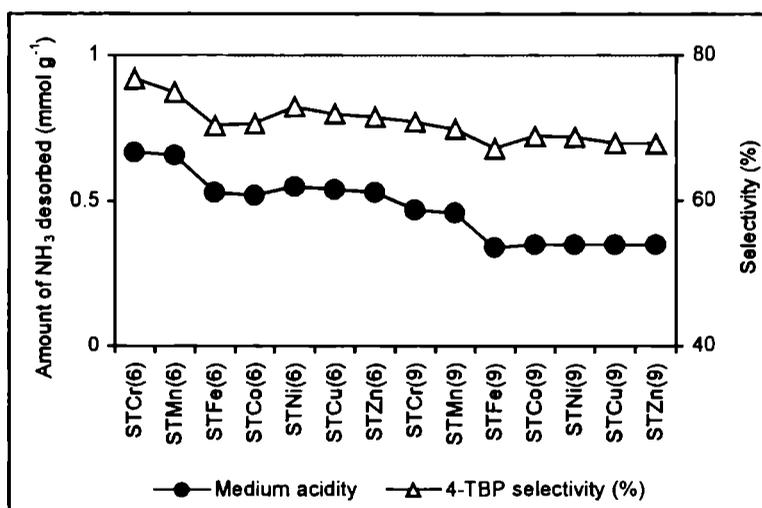


Figure 4.13 4-TBP selectivity correlated with the medium acidity from NH<sub>3</sub> TPD

In the present study the reaction was promoted by medium and strong acid sites. Strong acid sites are necessary to get higher selectivity of 2,4-DTBP while medium acid sites are helpful in enhancing the selectivity of 4-TBP. Corma *et al.*<sup>11</sup> reported the same observation in zeolites Y. Medium

acid sites may promote the isomerization or transalkylation reaction of *o*-TBP to *p*-TBP, while strong acid sites are helpful in forming 2,4-DTBP.

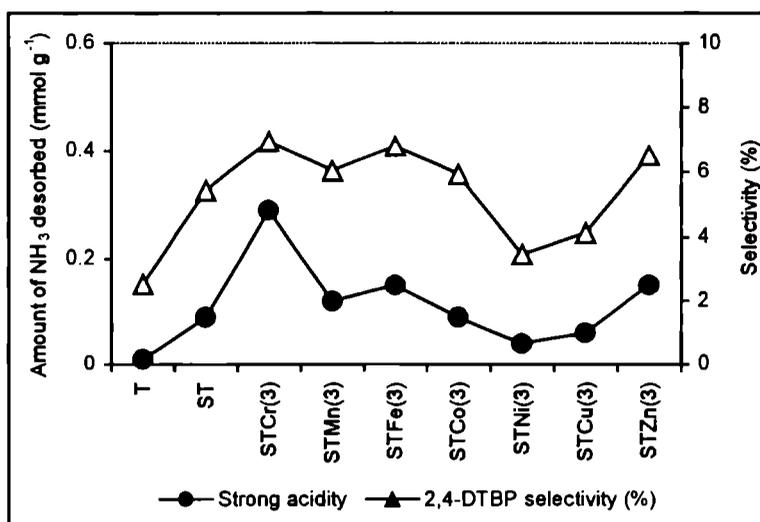


Figure 4.14 2,4-DTBP selectivity correlated with strong acidity from NH<sub>3</sub> TPD

The catalytic alkylation of phenol with alcohols gives rise to two distinct classes of products depending on the site where the alkyl group alkylates phenol. The formation of O-alkylated products depends both on the intrinsic properties of the alcohol and on the structural and acid-base properties of the catalysts. Corma *et al.*<sup>11</sup> found that the alkylation of phenol by TBA over the solid acid HNa-Y zeolites at 303 K occurs both at O- atoms and C-atoms, but the O-alkylation had a higher selectivity, whereas ring alkylation alone occurred at higher temperatures. Zhang *et al.*<sup>26</sup> already reported that the strong acidity was required for the formation 2,4-DTBP and acid sites of medium strength were responsible for the formation of 4-TBP. But it differs from our result as they speculate that weak acid sites are effective in producing 2-TBP. We do not get any correlation between weak acid sites and 2-TBP selectivity. Figures 4.16 to 4.17 indicate that the selectivity to 4-TBP and 2,4-DTBP lies nicely with the

medium and strong acid sites from the TPD of ammonia of the prepared systems.

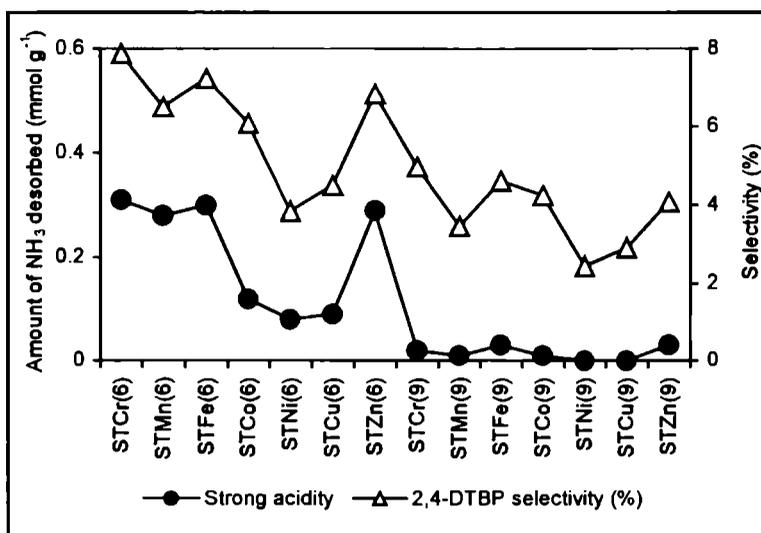


Figure 4.15 2,4-DTBP selectivity correlated with strong acidity from NH<sub>3</sub> TPD

#### 4.9 MECHANISM OF *TERT*- BUTYLATION OF PHENOL

The interesting aspect of this reaction is the high selectivity of alkylation at the *para* position. The generally accepted mechanism for aromatic alkylation is that the tertiary carbenium ion interacts with adsorbed phenol forming a  $\pi$ -complex, which then rearranges to  $\sigma$ -complex by the electrophile attacking a ring carbon atom. The complex on proton elimination gives *tert*-butyl phenol. General scheme for the reaction can be represented schematically as shown in figure 4.16. Alkylation reactions carried out in the gas-phase system at high reaction temperature in the presence of catalysts with weak<sup>30</sup>, medium<sup>12,28,31</sup> or strong acid sites<sup>32</sup> are suitable for the formation of *para*-C-alkylated isomer. Generally, the electrophilic substitution takes place in the *ortho* and *para* positions of the phenyl ring. The presence of phenolic group kinetically favors *ortho* alkylation<sup>33</sup>. It is accepted that when the product is not thermodynamically

controlled, both the electronic and the steric factors are very important for the alkylation reactions in heterogeneous catalysis<sup>20</sup>.

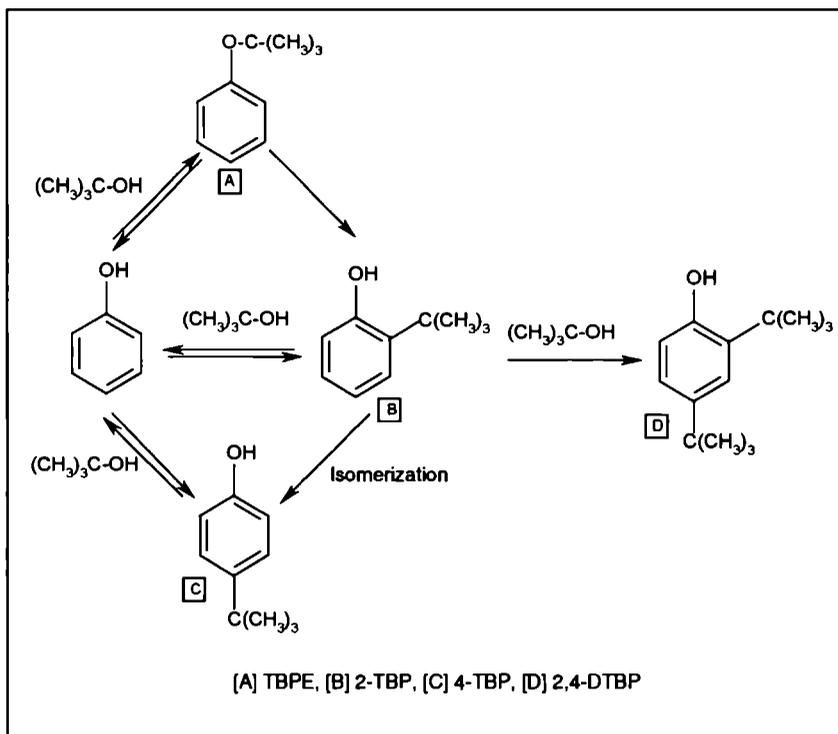


Figure 4.16 General scheme for *tert*-butylation of phenol

It is noticed that the presence of strong acid sites and higher reaction temperatures promoted the formation of 4-TBP. Another observation is that as the amount of 2-TBP increases, the amount of 2,4-DTBP also increases. This proves that 2-TBP is a precursor to the formation of 2,4-DTBP. 4-TBP can be formed either directly from phenol or from 2-TBP *via* rearrangement. The 3-TBP is formed only at higher temperatures (so also 3,5-DTBP) due to thermodynamic constraints. The formation of 2,6-DTBP can also take place from 2-TBP. These are competing reactions for 2,4-DTBP. The 2,6 product has, however, not been detected as its formation is promoted on basic sites

It has been suggested<sup>25,34,35</sup> that Brønsted acid sites interact with the  $\pi$ -cloud of aromatic ring bringing the molecule parallel to the surface. This will allow alkylation at the *para* position easier as compared to the *ortho* positions. The *para* selectivity of the catalysts can be attributed to the nature of adsorption of phenol over the catalyst surface. According to Tanabe<sup>36</sup>, the phenolate ion is adsorbed such that the *ortho* position is very near to the catalyst surface in the case of basic catalysts such as MgO, hence the *ortho* position can be alkylated. However the interaction of acidic catalysts are different which influence the electron current around the benzene ring such that the aromatic ring lie parallel to the catalyst surface (figure 4.17) favouring *para* alkylation. Also it has been reported that the steric hindrance in the transition state due to the substitution of bulkier *tert*-butyl group at the *ortho* positions, enhances the *para* selectivity<sup>37</sup>.

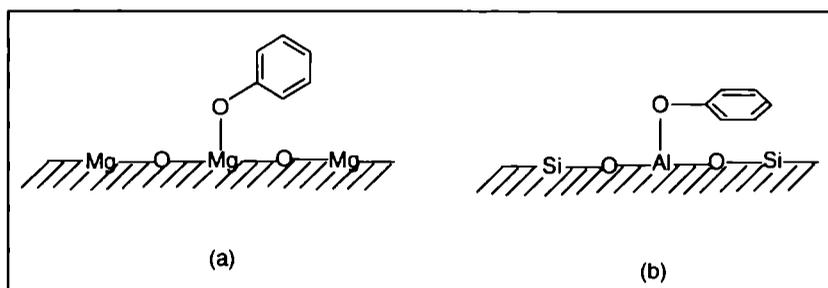


Figure 4.17 Adsorption of phenol on (a) MgO and (b) Al<sub>2</sub>O<sub>3</sub>

#### 4.10 CONCLUSIONS

The conclusions from the present results can be summarized as given below:

- ✂ Alkylation of phenol with *tert*-butyl alcohol over sulfated titania based catalysts shows good catalytic activity. The interesting aspect of this reaction is the high selectivity of alkylation at the *para* position.
- ✂ Reaction variables such as temperature, flow rate, molar ratio and reaction time have strong influence on the conversion and product selectivity.

- ✂ Higher flow rate is helpful in producing 4-TBP. The suitable reaction temperature range is from 180 to 200°C. Lower molar ratios are beneficial to 4-TBP. All the systems showed good resistance to catalytic deactivation.
- ✂ The acidity plays an important role in the butylation reaction. Medium acid sites are helpful to produce 4-TBP and strong acid sites govern the formation of 2,4-DTBP.
- ✂ In order to promote the formation of 4-TBP at higher conversions of phenol, a proper reaction temperature, lower reactant ratio and medium acidity on the sulfated titania based catalysts are recommended.



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