Chapter 4

FRIEDEL – CRAFTS BENZYLATION OF TOLUENE, O-XYLENE AND ANISOLE

Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings where alkyl chlorides, alcohols and alkenes being the commonly employed alkylating agents and hence is a key reaction in organic chemistry. The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride and benzyl alcohol is an important process for the production of diphenyl methane and substituted diphenyl methanes which are industrially important. Benzylation using benzyl alcohol requires Brönsted acidity while benzyl chloride requires Lewis acidity for the catalysts. The present chapter deals with the liquid phase benzylation of toluene, o-xylene and anisole using benzyl chloride as benzylating agent. Here in this chapter, conversion of the reactant in terms of benzyl chloride is correlated with the acidities of the prepared catalysts. The various reaction parameters like temperature, molar ratio of substrate to benzyl chloride, weight of catalyst and time of the reaction were optimized using iron loaded catalyst for toluene benzylation. o-Xylene and anisole were also benzylated in the same optimized condition.

4.1 Introduction

The development of sciences and technologies has resulted in a substantial improvement of our lifestyles. These almost unbelievable achievements have, however, led to some impacts on the global environment and public awareness. In particular, chemistry has been contributing to this evolution. Through the combination of knowledge on molecular reactivity, design and other sub disciplines of chemistry and chemical engineering, green chemistry has been looked upon as a sustainable science which accomplishes both economic and environmental goals, simultaneously. With this objective, we developed an alternative process to obtain the industrially important benzyl aromatics by benzylation of aromatics using benzyl chloride, catalysed by solid mesoporous acids. Friedel and Crafts first reported the alkylation of benzene with alkyl chlorides in the presence of aluminium chloride in 1877 [1]. Their historical discovery initiated an unimaginable flow of new synthetic processes. Over the past century, overwhelming number of compounds has been synthesized through the modification of the original approach, a field now commonly referred to as Friedel-Crafts chemistry. The Friedel-Crafts alkylation of aromatic substrates is an industrially important synthetic transformation. Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings where alkyl chlorides, alcohols and alkenes being the commonly employed alkylating agents and hence is a key reaction in organic chemistry. The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride and benzyl alcohol is an important process for the production of diphenyl methane and substituted diphenyl methanes. Benzyl aromatics are key intermediates in the multifaceted angle of industrial applications. They are industrially important compounds used

as pharmaceutical intermediates, heat transfer fluids, aromatic solvents, fragrances, monomers for polycarbonate resins and fine chemicals [2]. Dimethyl diphenyl methane is used as a synthetic intermediate for the production of dielectric fluids [3]. Despite more than 120 years of history, the Friedel–Crafts alkylation and acylation reactions are still in the forefront of organic synthesis research. The catalysts used in these reactions are often homogeneous catalyst such as HF, H_2SO_4, $AlCl_3$ and BF_3. Though readily available and inexpensive, these catalysts have numerous drawbacks, which include violent decomposition with water, liberating HCl, its corrosive nature and poor selectivity leading to undesired poly substituted and isomerized by-products. During the reaction workup, the catalyst is destroyed not only generating large volumes of gaseous effluent (HCl), but also generating Al-rich acidic effluents, which are difficult to deal with. These traditional catalysts have difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity etc. Moreover, these catalysts are highly moisture-sensitive and hence require moisture-free solvent and reactants and anhydrous conditions, and also dry atmosphere for their handling [4]. In addition, the catalysts are added in stoichiometric amounts which add the cost of the reaction. These catalysts also catalyse undesirable side reactions due to alkyl isomerizations, trans alkylation, and poly alkylation reactions. In order to reduce these reaction products the reactions are generally done at very low temperature (below -10°C) and in solvents like carbon disulphide and nitro methane. Unfortunately, they do not fulfill the current requirements of environmental protection and safety standards. The work up procedure for the reaction using traditional catalysts involve a water quench which prevents the acid from being reused and on subsequent neutralization leads to the formation of salt waste. These drawbacks become a major disadvantage in the times

of environmental concern emphasizing the need to develop an alternative to the conventional homogeneous Lewis acid catalyst. Replacing homogeneous catalytic systems with heterogeneous ones is advantageous mainly because of easy catalyst recovery, reusability and work-up of reaction products. During the past decade, much attention has been paid to the replacement of homogeneous catalysts by solid acid catalysts such as zeolites sulphated ZrO_2 or Fe_2O_3, sulphated $Al_2O_3–ZrO_2$ or TiO_2, clays, metal oxides and modified silica. Recently, ceaseless search for greener chemical process has become one of the most important tasks of today's chemical researchers [5]. There are lots of methods to achieve this goal such as alternative feed stocks, reagents, solvents, products, catalysts and so on. An important issue in these environmentally conscious days is the choice of suitable acid catalyst [6]. The environmental concern and the drive towards a 'clean technology' urge the replacement of the liquid acids by eco-friendly solid acid catalysts. In the past, benzylation of benzene has been carried over different iron containing mesoporous materials like Fe containing mesoporous silicate catalysts [7] and FeSBA-15 [8]. Introduction of iron into the mesoporous material by wet impregnation technique showed high redox property than tetrahedrally coordinated Fe^{3+} located in the skeleton of the materials [9] which would be highly beneficial for the title reaction as it follows redox mechanism as confirmed by earlier report [7]. Mesoporous materials as support [10] and iron loaded mesoporous materials [11] as catalysts have proved to be highly active and efficient in previous studies. The use of iron loaded mesoporous materials as catalyst can also eliminate the hurdles like pore size constraint, recyclability, thermal and hydrothermal stability etc. Benzylation of o-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over a homogeneous Lewis acid

catalyst AlCl₃ [12]. Catalytic behaviour of rare earth oxides has been explored for many reactions and a wide variety of catalytic properties have been known [13]. These oxides can be used in Friedel-Crafts reactions, too [14]. Benzylation of toluene with either benzyl alcohol or benzyl chloride (B-Cl) has extensively been studied previously. For example, alkylation of toluene with BC in presence of Al-SBA-15 as catalyst has been carried with 31% conversion and 88% para-selectivity [8]. A similar reaction catalyzed by Fe-SBA-15 afforded the corresponding para-alkylated product with 66% conversion and 100% selectivity [15]. Utilization of benzyl alcohol in the presence of Ga-Al-MCM-41 has converted 78% of toluene to a mixture of ortho and para during 6 hours [16]. Catalytic activities of niobium phosphate in the benzylation of toluene with benzyl alcohol have also been reported [17, 18]. In most cases, reactions either need long reaction times or are carried out at relatively high temperatures. More importantly, they mostly end up with a mixture of ortho and para-alkylated products [18, 19, 20]. After the induction period the toluene benzylation proceeds rapidly almost at the same rate in all these cases. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and due to this process, the catalyst activation is enhanced [21]. The fundamental concept is to identify new, stable and recyclable catalysts as replacements for the conventional liquid acids, and ultimately develop environmentally safe industrial processes. Herein we report a recyclable, easily separable, eco-friendly and highly effective catalytic system of mesoporous ceria modified with transition metals (Fe modification giving maximum activity) for the benzylation of toluene with benzyl chloride (B-Cl), a typical example of Friedel Crafts alkylation.

A Friedel – Crafts reaction mixture involves many components:

- The substance to be substituted

- A reagent that supplies the substituent

- A catalyst which may be a Lewis acid type or a proton acid as in Brönsted –Lowry concept

- A solvent which are generally non-ionizing type like CS_2, CCl_4 etc. or with high dielectric constant like nitrobenzene, nitro methane etc.

- The product formed in the reaction

- The by-product and conjugate acid formed in the reaction.

The combinations of these components give rise to complexity to the result of the reaction.
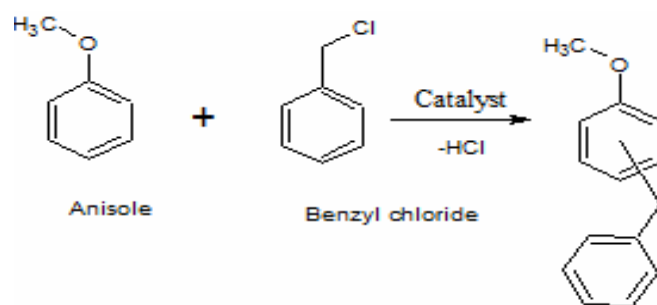
The Friedel-Crafts benzylation of aromatics using benzyl chloride catalysed by solid mesoporous acids is of significant interest in the field of organic chemistry. Acidic mesoporous heterogeneous catalysts, having Brönsted or Lewis acid centres are capable of replacing traditional homogeneous acids. Here we studied the liquid phase benzylation of toluene using benzyl chloride as benzylating agent over transition metal (Fe, Mn, Cr, Co, Cu & Ni) modified mesoporous ceria. The general scheme of Friedel-Crafts benzylation of toluene, o-xylene & anisole are shown in Figure 4.1.
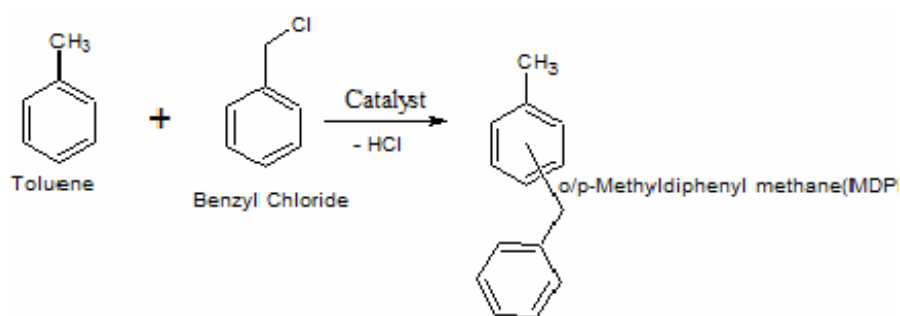
Benzylation of Toluene
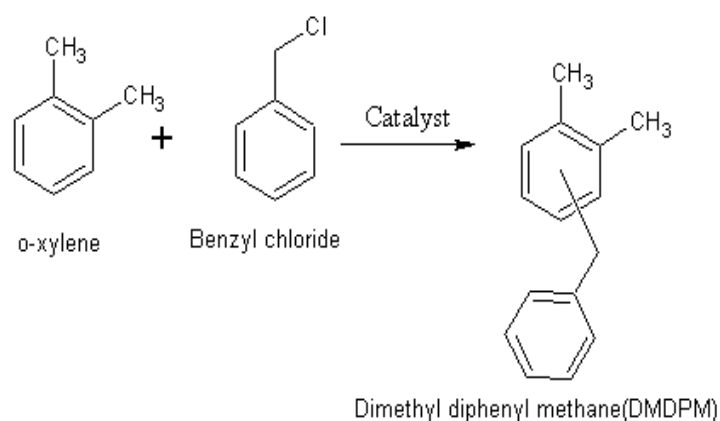
Benzylation of o-xylene

Benzylation of Anisole

Fig.4.1 The general scheme of Friedel-Crafts benzylation of Toluene, o-Xylene & Anisole

The reactions were carried out in a double necked round bottom flask fitted with are flux condenser. In a typical run, appropriate amounts of toluene /o-xylene / anisole, benzyl chloride and the catalyst were allowed to react at specified temperatures under magnetic stirring. The reaction mixtures were analysed periodically using 8610 GC equipped with SE-30 column and FID detector. As toluene /o-xylene /anisole taken in excess, the yield of the reaction was expressed as the total percentage of benzyl chloride transformed. The product formed was identified as o/p methyl diphenyl methane /dimethyl diphenyl methane/ methoxy diphenyl methane for toluene, o-xylene & anisole respectively.

4.2 Influence of reaction conditions

Generally for any reaction, the conversion and selectivity to a desired product depends on various reaction parameters such as temperature, mole ratio of the reactants, catalyst weight, and time of the reaction. Before testing the catalytic activities of different catalytic systems prepared, it is necessary to optimize the reaction parameters.

4.2.1 Effect of temperature

In a typical reaction, to a definite amount of toluene taken in the RB flask, required amount of catalyst was added and heated for 25 minutes with stirring. Then required amount of benzyl chloride was added at a particular temperature. The influence of temperature on benzylation of toluene was tested in a temperature range from $60^{o}C$ to $90^{o}C$. The observations are represented in Fig. 4.2.

At low temperatures below $80^{o}C$ there was no reaction taking place. The reaction was found to be 100% selective towards methyl diphenyl

methane (MDPM) at 80°C with 100% conversion of benzyl chloride. Hence for the benzylation temperature is an important factor.
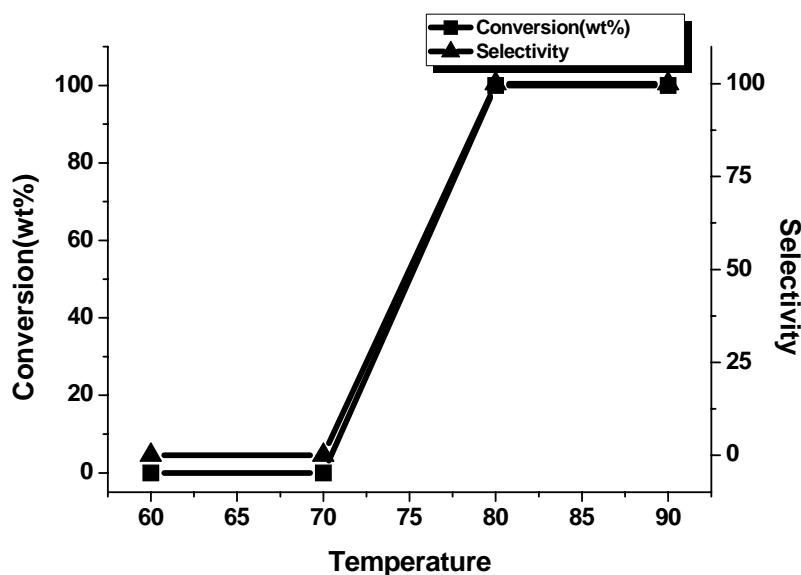

Fig.4.2 Effect of temperature on benzylation of toluene.

Reaction conditions: catalyst CeFe (10%), Time-4hrs, Toluene: benzyl chloride (mole) – 13:1, Weight of catalyst-0.1g

4.2.2 Effect of catalyst weight

To study the effect of catalyst weight on reaction, the weight was varied from zero (absence of catalyst) to 100mg. The reaction was conducted with CeFe (2%). In the run 13 moles of toluene with definite weight of the catalyst was heated for 25 minutes to activate the catalyst. Then 1 mole of benzyl chloride was added and the reaction was allowed to proceed for 2 hours. The results obtained with different weights of catalyst are given below in Fig.4.3.
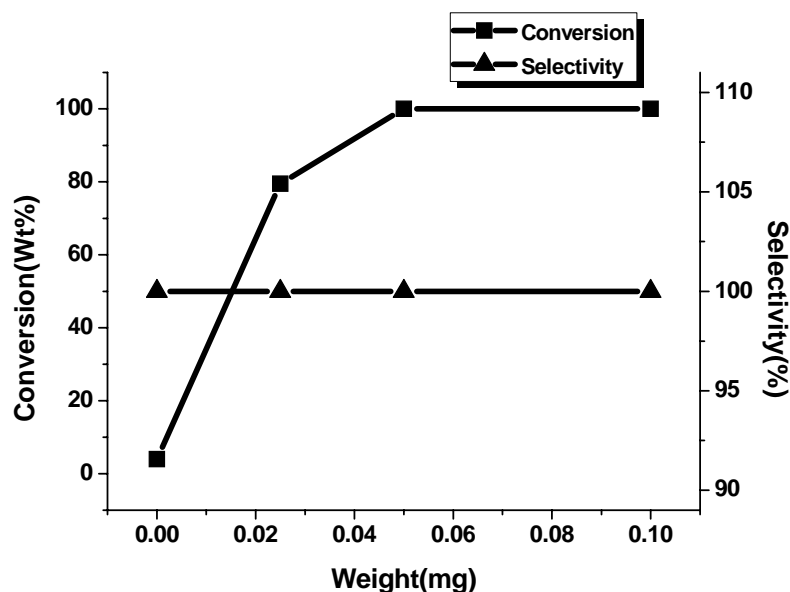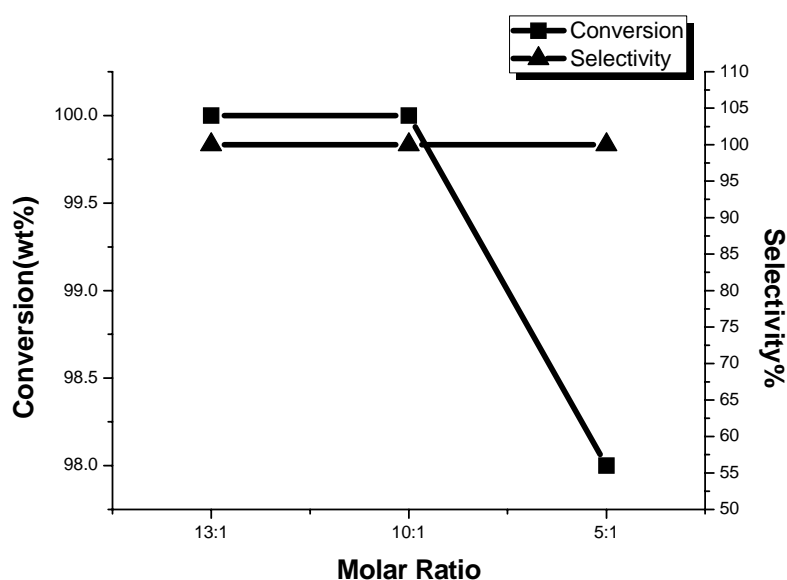
Fig.4.3 Effect of catalyst weight on benzylation of toluene.

Reaction conditions: catalyst CeFe (2%), Time-2hrs, Toluene: benzyl chloride – 13:1

The presence of catalyst has pronounced effect on the benzylation reaction. In the absence of any catalyst there was no reaction taking place. This shows that the reaction proceeds through the formation of benzyl carbonium ion in the presence of the catalyst. As the catalyst weight is increased the conversion of benzyl chloride increases and reaches 100% at a catalyst weight of 50mg. The selectivity is also 100% at all conversions producing only mono alkylated product. The increase in the conversion with increase in the catalyst weight shows that the reaction is truly heterogeneous in nature. On increasing the catalyst concentration the number active sites on the surface increases which in turn increases the catalyst activity.

4.2.3 Effect of substrate to benzyl chloride ratio

The influence of substrate to benzyl chloride molar ratio was investigated by changing the molar concentration of the substrate, keeping the amount of benzyl chloride constant. The reaction was done at a temperature of 80°C, by adding 50 mg of CeFe (2%) for 2hours. The result is shown in the Fig. 4.4.
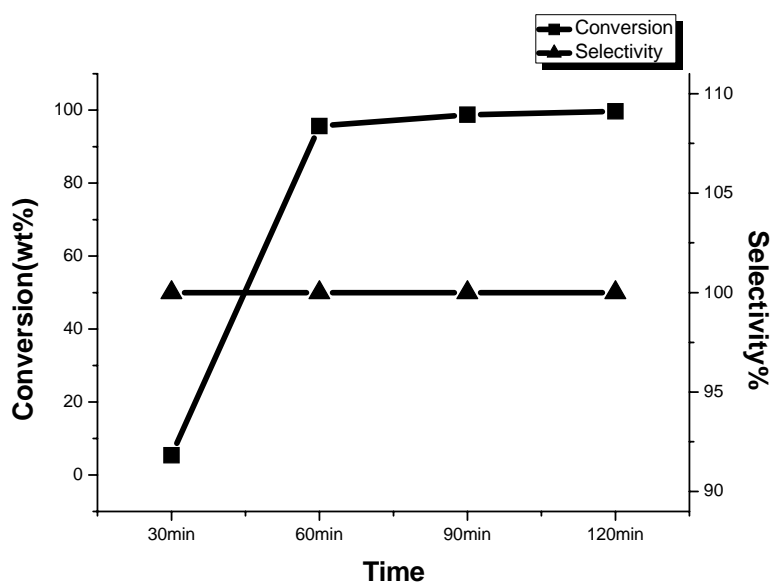

Fig.4.4 Effect of molar ratio of substrate to benzyl chloride on benzylation of toluene.

Reaction conditions: catalyst CeFe (2%), catalyst weight 50mg, Time-2hrs, Temperature: $80^{o}C$

As depicted from the figure, the ratio of the substrate to benzyl chloride is optimised to be 5:1 considering the conversion of benzyl chloride and also atom economy of the reactants. When ratio changes from 5:1 to 10: 1 the change in conversion is only 2%. Selectivity is always 100% to mono alkylated product.

4.2.4 Effect of Time

The reaction was carried out for 2 hrs to study the effect of time on conversion and selectivity. Results are shown in the Fig.4.5. The reaction was done with 50 mg of CeFe (2%) at a temperature of 80°C with toluene to benzyl chloride molar ratio of 5. When the reaction was conducted for 30 minutes the conversion was only 5.4 indicating an induction period essential for the reaction to proceed. After the induction period the conversion increases steadily to above 95%. Then it changes slowly. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and this process of the catalyst activation is enhanced [21]. The temperature effect and the existence of an induction period indicate the possibility of redox or free radical mechanism.

Fig.4.5 Effect of Time on benzyl chloride conversion in benzylation of toluene
Reaction conditions: catalyst CeFe (2%), Catalyst weight 50mg, Temperature80^{o}C, Ratio 5:1

4.2.5 Optimised conditions

From the results of the studies on various parameters on benzylation of toluene by benzyl chloride, the optimized parameters are given in Table 4.1

Table 4.1 Optimized Reaction conditions

Parameters	Optimized conditions
Weight of the catalyst	50mg
Temperature	80^oC
Time	2hrs
Substrate to B-Cl ratio	5:1

4.3   Comparison of Catalysts

After the optimization studies, under the optimized conditions the catalytic activities of all the prepared systems were studied for the benzylation of toluene using benzyl chloride as the reagent. Under the same optimized conditions o-xylene and anisole are also benzylated using benzyl chloride. The results are given in the Table 4.2.

Table 4.2. Benzylation over transition metal modified ceria systems.

Catalyst	Toluene		o-Xylene		Anisole		
	Benzyl chloride conversion (Wt%)	% Selectivity	Benzyl chloride conversion (Wt%)	% Selectivity	B-Cl Conversion (Wt%)	%Selectivity o-pdt	p-pdt
Without catalyst	4		nil		nil	-	
Ce	4.3	100	21	100	22	45	55
CeFe(2%)	99.7	100	100	100	93.9	46.8	53.2
CeFe(4%)	100	100	100	100	100	47.3	52.7
CeFe(10%)	100	100	100	100	100	47.3	52.7
CeCr(2%)	38.4	100	21.1	100	26.9	41.8	58.2
CeCr(4%)	45.2	100	15.9	100	47.5	43.5	56.5
CeCr(10%)	68.3	100	19	100	61.7	49.5	50.5
CeMn(2%)	42.3	100	18.1	100	38.1	51.2	48.7
CeMn(4%)	24	100	23.3	100	19.4	-	100
CeMn(10%)	27.5	100	16	100	28.7	47.5	52.5
CeNi(2%)	23.4	100	30.2	100	29.5	42.8	57.2
CeNi(4%)	39.8	100	25.8	100	27.7	44.3	55.7
CeNi(10%)	27.3	100	21	100	35.6	48.1	51.9
CeCo(2%)	32	100	15.7	100	39.1	29.8	70.2
CeCo(4%)	24	100	21	100	35.8	46.3	53.7
CeCo(10%)	24.5	100	33	100	23.4	43.7	56.3
CeCu(2%)	14.6	100	21	100	27.7	41	59
CeCu(4%)	28.3	100	26	100	35.6	43.4	56.6
CeCu(10%)	35.7	100	28.5	100	38.6	46.9	53.1

To determine the role of catalyst, the same reaction was carried in the absence of the catalyst. The desired product was not observed even after 40-45 minutes, which indicates that the catalysts exhibit a high catalytic activity in this transformation. Pure ceria gave low conversions than various metal modified samples. The metal modification improves the %conversion to a great extent. The increase in % conversion and activity may be attributed to the increase in the acid sites up on metal modification. The catalytic activities of the samples vary with variation in the metal percentages. In the case of each metal, as the metal percentage increases, the benzyl chloride conversion and the catalytic activity also changes. The same trend is observed for all the metals. This trend is illustrated in the Fig.4.6.1 to 4.6.3.
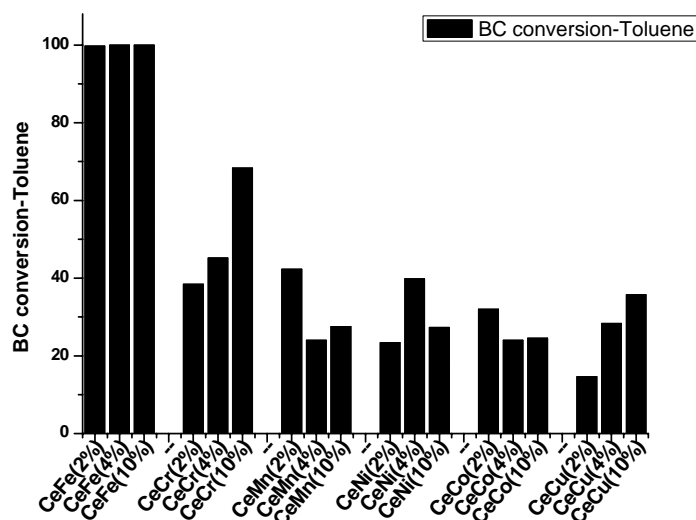

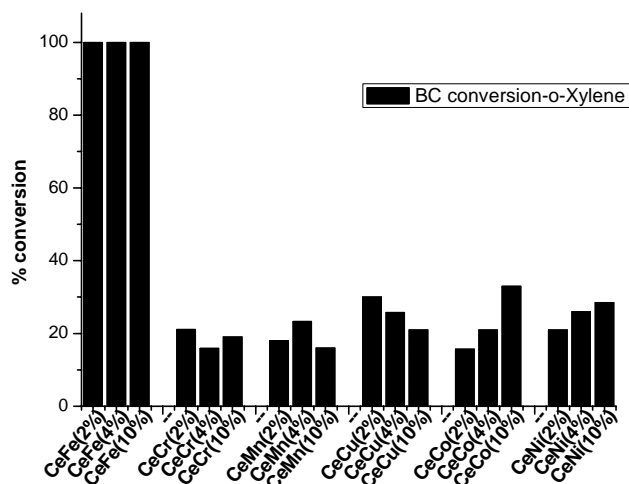**Fig.4.6.1 B-Cl Conversion in benzylation of Toluene by different systems**

Fig.4.6.2 B-Cl Conversion in benzylation of o-xylene by different systems
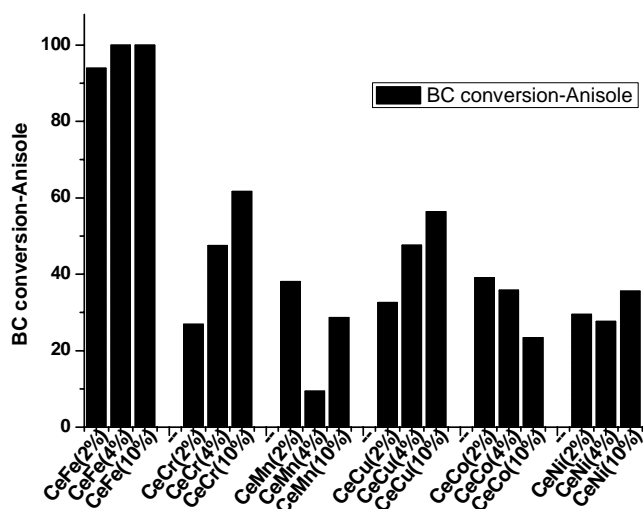

Fig.4.6.3 B-Cl Conversion in benzylation of Anisole by different systems

From Table 4.2, it is understood that among the various transition metals studied, Fe modified samples gave maximum conversion for toluene, o-xylene and anisole. This catalytic activity of Fe samples are greater than other metals like Cr, Ni, Cu etc. which have total acidity and α-methyl styrene selectivity (which is an indication of Lewis acidity) greater than that of Fe. Hence the

high activity of Fe systems cannot not be explained on the basis of their Lewis acidity alone. This hike in the conversion points to the fact that benzylation activity of iron loaded systems cannot be explained on the basis of usual carbocation mechanism for alkylation reaction. It is reported that catalysts containing reducible cations like Fe^{3+}, Cu^{2+} etc. exhibit high alkylation activity regardless their Lewis acidity [22]. When a redox mechanism is operating there will be homolytic fission of carbon- chlorine bond of the alkylating agent (benzyl chloride). The radicals so formed are powerful reductants, which would be readily oxidised to carbocations in the presence of reducible metallic Fe^{3+}. The mechanism is depicted in Fig.4.13. It may be assumed that the below $80^{o}C$, the energy for the homolytic rupture of carbon-chlorine bond may not be attained and therefore no reaction occurs below this temperature [23]. This may be the reason for no conversion at temperatures below $80^{o}C$.

Good correlation is obtained for benzyl chloride conversion and total acidity obtained from TPD of ammonia for benzylation of toluene, o-xylene & anisole. The results are illustrated in Fig4.7.1 to 4.9.2
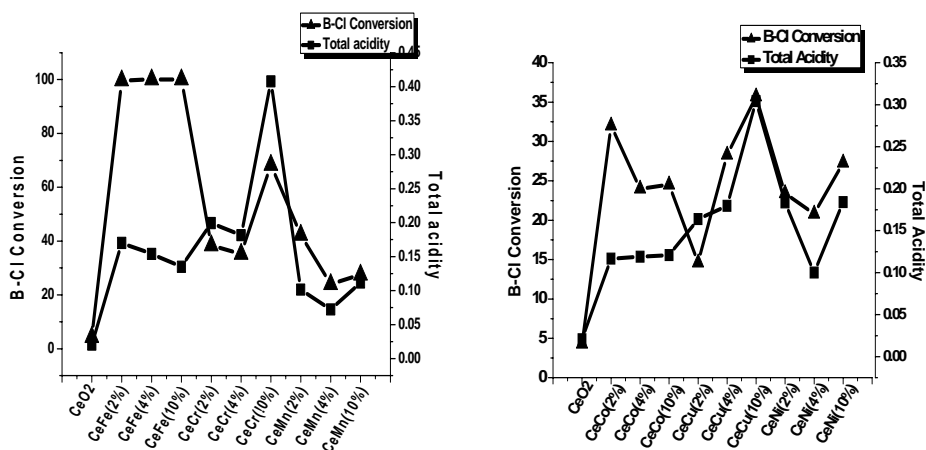

Fig. 4.7.1 and 4.7.2 Correlation between total acidity from TPD of ammonia & B-Cl conversion in toluene benzylation
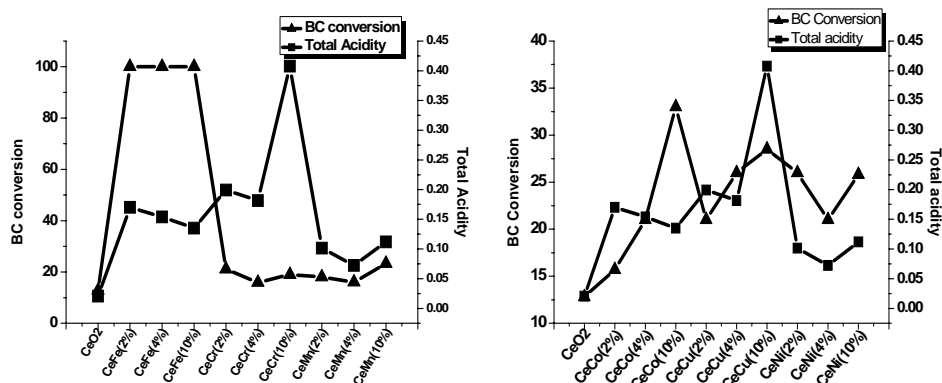
Fig. 4.8.1 and 4.8.2 Correlation between total acidity from TPD of ammonia & B-Cl conversion in o-xylene benzylation
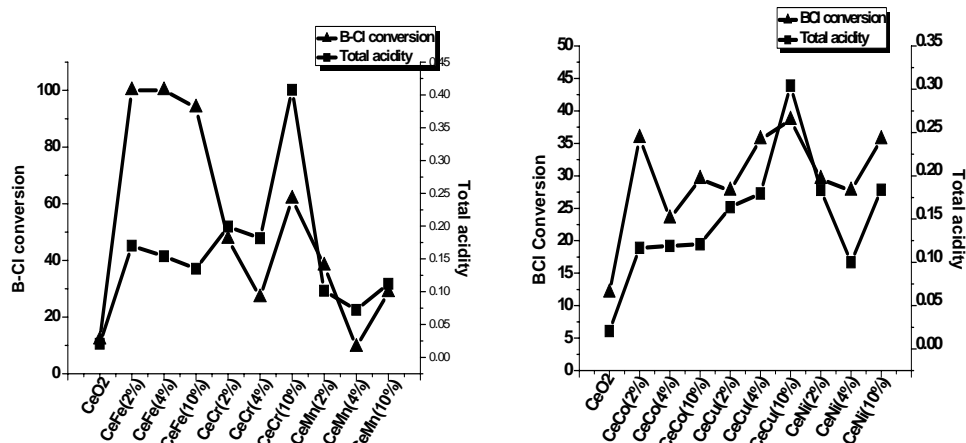

Fig. 4.9.1 and 4.9.2 Correlation between total acidity from TPD of ammonia & B-Cl conversion in anisole benzylation

All prepared samples show high selectivity towards α-methyl styrene in vapour phase cumene cracking test reaction on acidity which is an indication of Lewis acid site availability on the catalyst surface. The involvement of Lewis acid sites in carbocation generation is well established. The correlation between the benzyl chloride (B-Cl) conversion in benzylation of toluene, o-xylene, and anisole with α-methyl styrene selectivity in vapour phase cumene cracking reaction are given in Fig.4.10.1 to 4.12.2

Fig. 4.10.1 and 4.10.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction & B-Cl Conversion in Toluene benzylation
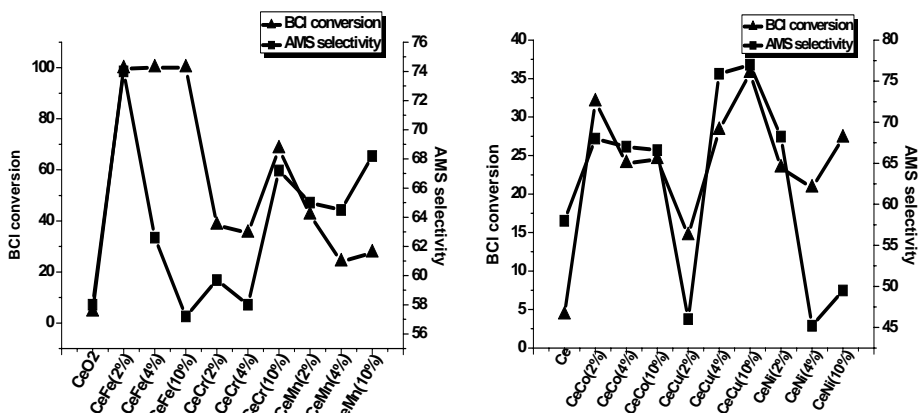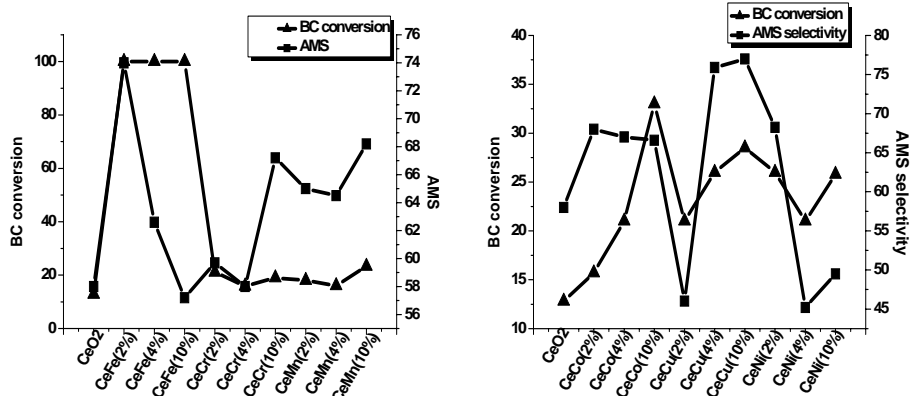

Fig.4.11.1 and 4.11.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction & B-Cl conversion in o-xylene benzylation
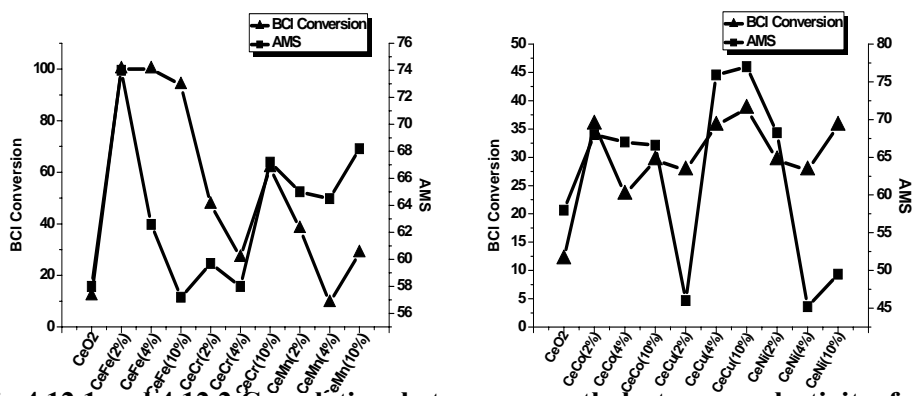

Fig.4.12.1 and 4.12.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction& B-Cl conversion in anisole benzylation

The productivity of a catalyst can be described by the turn over number (or TON) and the catalytic activity by the turn over frequency (TOF), which is the TON per time unit. Catalyst activity = mmoles of reactant reacted/ Surface area of catalyst/time. The TON, TOF and catalyst activities of the prepared samples in liquid phase benzylation of toluene, o-xylene and anisole are given in the Tables 4.3 to 4.5.

Table 4.3 Turn overs of different samples in the benzylation of toluene

Catalysts	Toluene		
	TON[a]	TOF[b] (h^{-1})	Catalyst Activity $(mmol/m^2/h)$
CeFe (2%)	47800	23900	0.043
CeFe (4%)	24000	12000	0.043
CeFe (10%)	9600	4800	0.077
CeCr (2%)	17100	8550	0.013
CeCr (4%)	10100	5050	0.016
CeCr (10%)	12100	5150	0.03
CeMn (2%)	20000	10000	0.015
CeMn (4%)	5500	2750	0.008
CeMn (10%)	2500	1250	0.010
CeCu (2%)	12500	6250	0.007
CeCu (4%)	4020	2010	0.015
CeCu (10%)	3010	1505	0.0215
CeCo (2%)	16200	8100	0.010
CeCo (4%)	6078	3039	0.008
CeCo (10%)	2480	1240	0.0098
CeNi (2%)	7380	3690	0.011
CeNi (4%)	7160	3580	0.019
CeNi (10%)	3610	2305	0.014

TON   =   (mmoles of reagent reacted/ mmoles of metal added) x 100

TOF   =   TON /hour

Catalyst activity   =   mmoles of reactant reacted/ Surface area of Catalyst / time

The catalyst activities of the samples in benzylation of various aromatics are correlated with total acidity and are shown in the Fig. 4.13. The catalyst activities have good correlation with the total acidities of the samples calculated by temperature programmed desorption of ammonia. There is change in the catalyst activity and TON of the samples with change in metal concentration.

Table 4.4 Turn overs of different samples in the benzylation of o-xylene

catalyst	o-Xylene		
	TON[a]	TOF[b] (h^{-1})	Catalyst Activity $(mmol/m^2/h)$
CeFe (2%)	50588	25294	0.043
CeFe (4%)	24571	12285.5	0.043
CeFe (10%)	9662	4831	0.082
CeCr (2%)	9550	4775	0.0074
CeCr (4%)	3707	1853.5	0.0057
CeCr (10%)	1729	864.5	0.0088
CeMn (2%)	8600	4300	0.006
CeMn (4%)	5566	2783	0.0085
CeMn (10%)	1528	764	0.006
CeCu (2%)	17200	8600	0.01
CeCu (4%)	7396	3698	0.014
CeCu (10%)	2408	1204	0.017
CeCo (2%)	7942	3971	0.0050
CeCo (4%)	5311	2655.5	0.0073
CeCo (10%)	3338	1669	0.0013
CeNi (2%)	10623	5311.5	0.013
CeNi (4%)	6526	3263	0.012
CeNi (10%)	3770	1885	0.01

Table 4.5 Turn overs of different samples in the benzylation of anisole

| catalyst	Anisole		
	TON[a]	TOF[b] (h^{-1})	Catalyst Activity $(mmol/m^2/h)$
CeFe (2%)	47500	23750	0.04
CeFe (4%)	25290	12645	0.043
CeFe (10%)	10120	5060	0.032
CeCr (2%)	12180	6090	0.0095
CeCr (4%)	10750	5375	0.017
CeCr (10%)	5585	2792.5	0.028
CeMn (2%)	18200	9100	0.014
CeMn (4%)	4630	2315	0.007
CeMn (10%)	2740	1370	0.011
CeCu (2%)	15880	7940	0.015
CeCu (4%)	10200	5100	0.02
CeCu (10%)	4426	2213	0.023
CeCo (2%)	19780	9890	0.0125
CeCo (4%)	9055	4527.5	0.0125
CeCo (10%)	2367	1183.5	0.0093
CeNi (2%)	14920	634.5	0.013
CeNi (4%)	7006	3503	0.014
CeN i(10%)	3601	1800.5	0.018
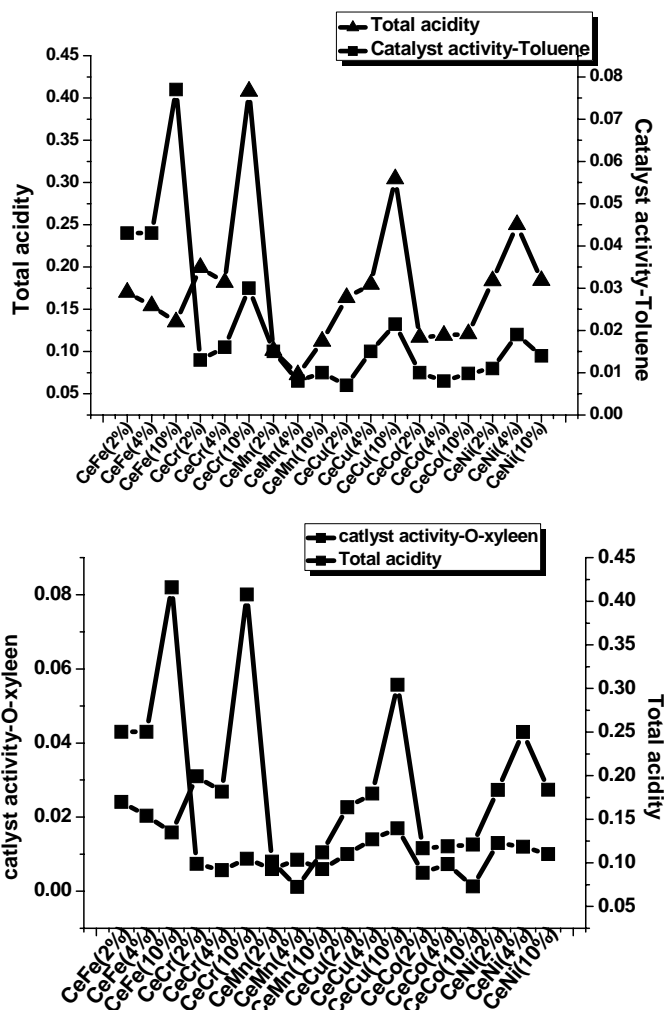
Fig. 4.13 Correlation between catalyst activity and total acidity

4.4 Mechanism of benzylation reaction

The reaction appears to proceed by an electrophile, which involves the reaction of benzyl chloride with the acidic oxide catalyst. The oxide catalyst polarizes the benzylating agent and in turn, produces an electrophile ($C_6H_5–CH_2^+$) [24, 25, 26)]. Thus the generated electrophilic species attacks the xylene ring, resulting in the formation of 3, 4-dimethyl diphenyl methane. Even though the catalysts have very low surface area

and pore volume, the presence of strong as well as weak acid sites on the catalyst surface appears to be very important for the polarization of benzyl chloride into an electrophile (C_6H_5-CH_2^+) which then attacks the benzene ring resulting in the formation of dimethyl diphenyl methane [27]. Non-polar nature of the substrate molecules also supports the formation of the electrophilic species by adsorption of B-Cl molecule on the catalyst surface. A plausible mechanism for the reaction can be represented schematically as shown in Fig.4. 13.

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 (Fig.4.14). Choudary et al. [28] suggested the possibility of a redox mechanism for reducible cations when B-Cl 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 the 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 [29].
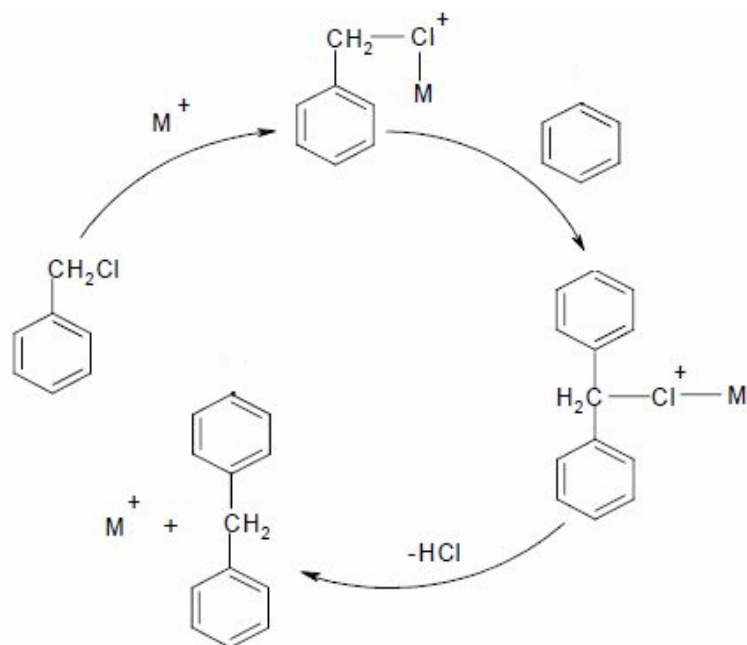
Fig. 4.14 Mechanism of Friedel-Crafts benzylation using benzyl chloride showing the active involvement of Lewis acid site.
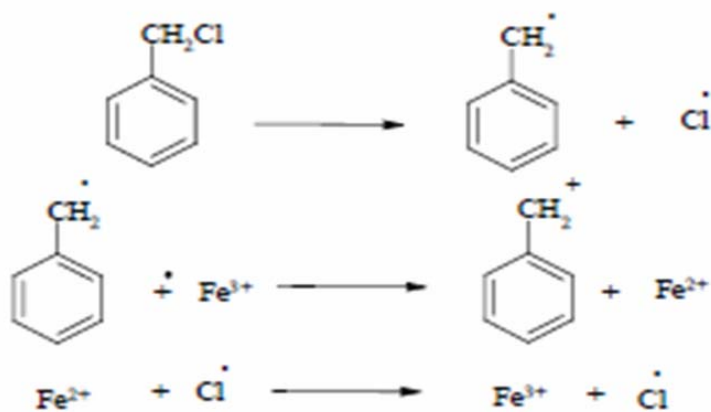

Fig. 4.15 Free radical mechanism for benzylation of arenes.

4.5 Metal Leaching studies

In the case of heterogeneous catalyst systems, metal leaching studies are essential because in some systems some metal ions will leach out from crystal lattice of catalyst and will homogeneously catalyse the reaction. For the leaching studies, the reaction was carried for a particular time and after that the catalyst was hot filtered off and the reaction was continued for another period without catalyst. Under optimized condition, in the presence of the catalyst (CeFe10%) the reaction was allowed to proceed for 30 minutes. Then the catalyst is filtered off and the reaction was allowed to proceed for 2 hours. The result of leaching studies is given in Table 4.3.

Table 4.6 Results of leaching study

Catalyst	Time	% Conversion
CeFe (10%)	30Min	25.3
	2Hrs	28

Reaction conditions: catalyst CeFe (10%), catalyst weight 50mg, Temperature80^{o}C, Ratio 5:1

Not much increase in the conversion was noticed after the removal of the catalyst confirming that there is no leaching of the metal ions during the reaction to the reactant system. This suggests that reaction proceed in a true heterogeneous manner.

4.6 Reusability

To study the reusability, the catalyst was removed from the reaction mixture after the reaction by filtration. It was thoroughly washed with

acetone and dried in an air oven and activated for 3 hours. The same catalyst was used again for carrying out another reaction under the same reaction condition. The reaction was repeated up to 3 cycles. Fe catalyst was tested for the reusability and the results are given in Table 4.7.

Table 4.7 Results of reusability study

Catalyst	No.of Cycle	% Conversion
CeFe (10%),	I	100
	II	100
	III	98

Reaction conditions: Catalyst CeFe (10%), Catalyst weight 50mg, Temperature 80°C, Ratio 5:1

From the results it is obvious that the catalyst is reusable. The catalyst can be regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make this heterogeneous reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds used as pharmaceutical intermediates, heat transfer fluids, aromatic solvents, fragrances, monomers for polycarbonate resins and fine chemicals. Thus this Fe modified ceria catalyst gives a solution for the ceaseless search for greener chemical process which has become one of the most important tasks of today's chemical researchers.

4.7 Conclusions

From the present study it can be concluded that

- On modification of mesoporous ceria with transition metals, the catalyst activity is very much improved. The catalyst activity& Turn over numbers which indicate the catalytic activity and productivity have good correlation with the total acidities of the samples.

- They are suitable solid acid catalysts for the liquid phase benzylation reaction. The most efficient catalysts among the prepared samples are iron modified ones. Exceptionally high activity in the case of iron systems proposed a free radical mechanism, which was confirmed by the effect temperature as well as the presence of an induction period for the reaction.

- The catalysts are regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make these catalyst to use in a truly heterogeneous manner and makes the benzylation reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds.

4.8 References

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