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Liquid phase benzylation of benzene and toluene with benzyl alcohol over modified zeolites ☆

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Abstract

Benzylation of benzene and toluene with benzyl alcohol has been investigated over a series of zeolites and metal modified zeolites. 5 wt% Ceβ, 5 wt% Feβ and 5 wt% Wβ were found to be good catalysts for the liquid phase benzylation of benzene and toluene. The catalysts were characterized using XRD, FTIR and NH_3-TPD.

Keywords: Benzylation; Benzene; Toluene; Benzyl alcohol; Modified zeolites

1. Introduction

Diphenylmethane and substituted diphenylmethanes are industrially important compounds used as pharmaceutical intermediates [1] and fine chemicals [2,3]. Liquid phase benzylation of aromatic compounds, using homogeneous acid catalysts, is a commercially practiced Friedel-Craft type reaction in organic synthesis [4]. The commonly used homogeneous acid catalysts (e.g. $AlCl_3$, BF_3 and H_2SO_4) having several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. The replacement of liquid acid catalysts by solid acids for the Friedel-Craft reaction of aromatic alkylation is a challenging task. In particular, microporous solids (zeolites), besides their natural acidity, and shape selective character can promote a specific selectivity owing to their molecular sieving character and ecofriendly nature. Catalysts based on various zeolites possess major importance both in petroleum and fine chemical industries.

This is mainly due to the large variability of their acid–base and redox properties while retaining shape selectivity. Friedel-Craft alkylation using Lewis acid catalyst in solution generally gives complex reaction. The increased tendency of alkylated products towards further alkylation and isomerization, coupled with the long contact of the reactant with the catalyst, result in complex mixture of products. Polyalkylation, isomerization, transalkylation, dealkylation and polymerization all occur under the normal reaction conditions. Therefore, there is substantial interest to carry out alkylation reactions with solid acid catalysts, which decrease these side reactions. Reports appeared on the alkylation of benzene and toluene by alkyl and benzyl halides, alcohols and alkenes, on montmorillonite dopped with transition metal cations [5,6], clays [7–9], sulfated zirconia [10], cation exchanged resins [11], niobium phosphate [12] and silica supported poly-tri-fluro methane sulfosiloxane catalysed benzylation of benzene and substituted benzene [13]. Recently, benzylation of aromatic compounds appeared on Ga–Mg–hydrotalcite [14], $AlCl_x$-grafted Si-MCM-41 [15], Fe-TUD-1 [16] and Al-SBA-15 [17] using benzyl chloride. The use of benzyl alcohol rather than benzyl chloride is an ecofriendly process. To explore the potential of zeolites as well as metal ion modified zeolites for this

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type of reaction we have carried out a study on the benzylation of benzene, toluene with benzyl alcohol over various zeolites and modified β-zeolites.

2. Experimental

2.1. Preparation of modified β-zeolite

All the catalysts were prepared by impregnation method, 4 g of the catalyst added to the 5 wt% aqueous solution of corresponding metal nitrates and stirred at 80 °C for 24 h. After impregnation, the catalyst was dried at 100 °C for overnight and calcined at 450 °C for 6 h. The catalysts were characterized by XRD, FTIR and NH_3-TPD.

2.2. Benzylation of benzene and toluene with benzyl alcohol

Benzyl alcohol (2 mmol) and 10 ml of benzene or toluene and 100 mg of catalyst were added to a 50 ml two neck round bottom flask having condenser and equipped with magnetic stirrer. The reaction mixture was stirred at 80 °C for the time reported in Tables 1–4. After the reaction, the mixture was then filtered and solid was washed with dichloromethane. The combined filtrates were concentrated under reduced pressure and column chromatography to give the products. The products were characterized by NMR, mass spectra and the selectivity was determined by GC. The overall reaction has been shown in Scheme 1.

3. Results and discussion

3.1. Benzylation of benzene and toluene over unmodified zeolites

The zeolite catalysed benzylation of benzene with benzyl alcohol gave diphenylmethane and benzyl ether in different proportions depending on the type of zeolite (Table 1).

Preliminary screening reactions were carried in order to compare the catalytic activity of the different zeolites,

Table 1
Benzylation of benzene with benzyl alcohol over zeolites[a]

S. No.	Catalyst	Conversion[b] (%)	Selectivity[c] (%)		Yield (%)	
			Diphenylmethane	Benzyl ether	Diphenylmethane	Benzyl ether
1	Hβ(Si/Al = 15)	100	92	8	92	8
2	Hβ[d](Si/Al = 15)	43	62	38	27	16
3	Hβ[e](Si/Al = 15)	18	66	34	12	6
4	HZSM-5 (Si/Al = 40)	14	68	32	10	4
5	H-Mordenite	89	96	4	85	4
6	HMCM-41 (Si/Al = 30)	33	32	68	11	22
7	SiO_2	–	–	–	–	–
8	SiO_2–Al_2O_3	–	–	–	–	–
9	No Catalyst	–	–	–	–	–

Reaction temperature = 80 °C, Time = 1 h.
[a] Benzyl alcohol (2 mmol), benzene (10 ml) and catalyst (100 mg).
[b] Conversion is based on benzyl alcohol.
[c] The products were characterized by NMR, mass spectra and quantified by GC.
[d] Catalyst (50 mg).
[e] Catalyst (25 mg).

Table 2
Benzylation of toluene with benzyl alcohol over zeolites[a]

S. No.	Catalyst	Conversion[b] (%)	Selectivity[c] (%)		Yield (%)	
			Monobenzylated toluene (*para*/*ortho*)	Benzyl ether	Monobenzylated toluene (*para*/*ortho*)	Benzyl ether
1	Hβ[d] (Si/Al = 15)	100	80(79/21)	20	80(79/21)	20
2	HZSM-5 (Si/Al = 40)	<5	–	–	–	–
3	H-Mordenite	72	89(58/42)	11	64(42/30)	8
4	HMCM-41 (Si/Al = 30)	31	77(59/41)	23	24(18/13)	7
5	SiO_2	<5	–	–	–	–
6	SiO_2-Al_2O_3	<5	–	–	–	–
7	No Catalyst	–	–	–	–	–

Reaction temperature = 80 °C, Time = 5 h.
[a] Benzyl alcohol (2 mmol), toluene (10 ml) and catalyst (100 mg).
[b] Conversion is based on benzyl alcohol.
[c] The products were characterized by NMR, mass spectra and quantified by GC.
[d] Reaction time = 2 h.

Table 3
Benzylation of benzene with benzyl alcohol over modified β-zeolite[a]

S. No.	Catalyst	Conversion[b] (%)	Selectivity[c] (%)		Yield (%)	
			Diphenylmethane	Benzyl ether	Diphenylmethane	Benzyl Ether
1	5%Coβ	32	79	21	25	7
2	5%Niβ	29	75	25	22	7
3	5%Pbβ	94	84	16	79	15
4	5%Laβ	69	78	22	54	15
5	5%Ceβ	99	97	3	96	3
6	5%Ceβ[d]	64	77	23	49	15
7	5%Ceβ[e]	21	67	33	14	7
8	5%Feβ	95	94	6	89	6
9	5%Wβ	99	97	3	96	3
10	5%Crβ	96	82	18	79	17
11	5%Cuβ	41	74	26	30	11
12	5%Znβ	11	79	21	9	2

Reaction temperature = 80 °C, Time = 30 min.
[a] Benzyl alcohol (2 mmol), Benzene (10 ml) and catalyst (100 mg).
[b] Conversion is based on benzyl alcohol.
[c] The products were characterized by NMR, mass spectra and quantified by GC.
[d] Catalyst (50 mg).
[e] Catalyst (25 mg).

Table 4
Benzylation of toluene with benzyl alcohol over modified β-zeolite[a]

S. No.	Catalyst	Conversion[b] (%)	Selectivity[c] (%)		Yield (%)	
			Monobenzylated toluene (*para*/*ortho*)	Benzyl ether	Monobenzylated toluene (*para*/*ortho*)	Benzyl ether
1	5%Coβ	11	56(67/33)	44	6(7/4)	5
2	5%Niβ	21	79(75/25)	21	17(16/5)	4
3	5%Pbβ	36	63(78/22)	37	23(28/8)	13
4	5%Laβ	35	68(75/25)	32	24(26/9)	11
5	5%Ceβ	75	70(77/23)	30	53(58/17)	22
6	5%Feβ	98	77(78/22)	23	75(76/22)	23
7	5%Wβ	98	78(78/22)	22	76(76/22)	22
8	5%Wβ[d]	75	71(77/23)	29	53(58/17)	22
9	5%Wβ[e]	36	60(80/20)	40	22(29/7)	14
10	5%Znβ	<5	–	–	–	–
11	5%Crβ	59	63(76/24)	37	37(44/14)	22
12	5%Cuβ	15	66(80/20)	34	10(12/3)	5

Reaction temperature = 80 °C, time = 1 h.
[a] Benzyl alcohol (2 mmol), toluene (10 ml) and catalyst (100 mg).
[b] Conversion is based on benzyl alcohol.
[c] The products were characterized by NMR, mass spectra and quantified by GC.
[d] Catalyst (50 mg).
[e] Catalyst (25 mg).

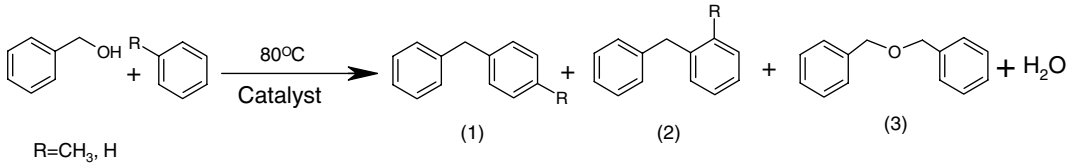
SiO_2–$Al_2O_3$and SiO_2. It was found that Hβ was good catalyst for benzylation of both benzene and toluene with 100% conversion of benzyl alcohol compared to other catalysts due to its higher acidity and large pore size. Selectivity of mono benzylated products diphenylmethane, in the case of benzylation of benzene and substituted diphenylmethane, in the case of benzylation of toluene, have been found to be 92% and 80% (Tables 1 and 2), respectively. It is observed that reaction does not proceed in the absence of a catalyst (Table 1, S. No. 9; Table 2, S. No. 7). Catalyst (100 mg) gave better results compared to 50 mg and 25 mg (Table 1, S. No. 1, 2, 3).

3.2. Benzylation of benzene and toluene over modified β-zeolite

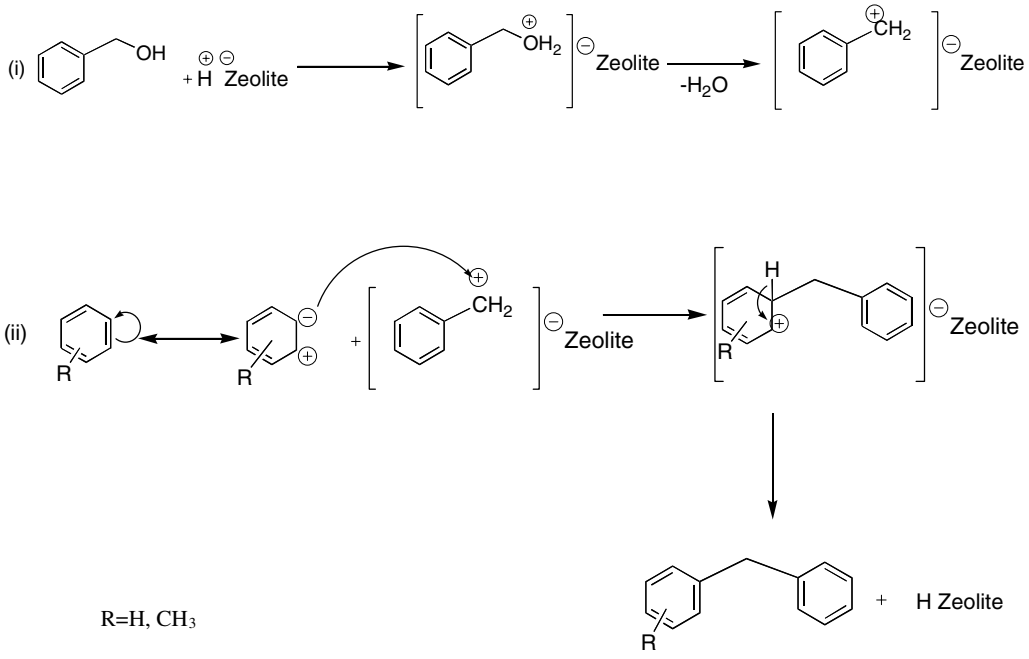
Benzylation reactions of benzene and toluene with benzyl alcohol have also been carried out using β-zeolite modified with various transition metal cations. Results of reaction time, conversion and selectivity percentages of products in respect of different metal ion modified zeolites are listed in Tables 3 and 4. The metal ion modified zeolites decreased the reaction time to half of that observed in the case of unmodified β-zeolite. The conversion percentage of benzyl alcohol has been drastically changed over different

metal modified β-zeolite and the selectivity towards diphenylmethane has been increased from Cuβ to Ceβ. Remarkable conversion and selectivity percentages were observed when Ceβ, Feβ and Wβ were used as catalysts (Table 3, S. No. 5, 8 and 9). Whereas Znβ is shown less conversion of benzyl alcohol (11%) and 79% selectivity of diphenylmethane (Table 3, S. No. 12).

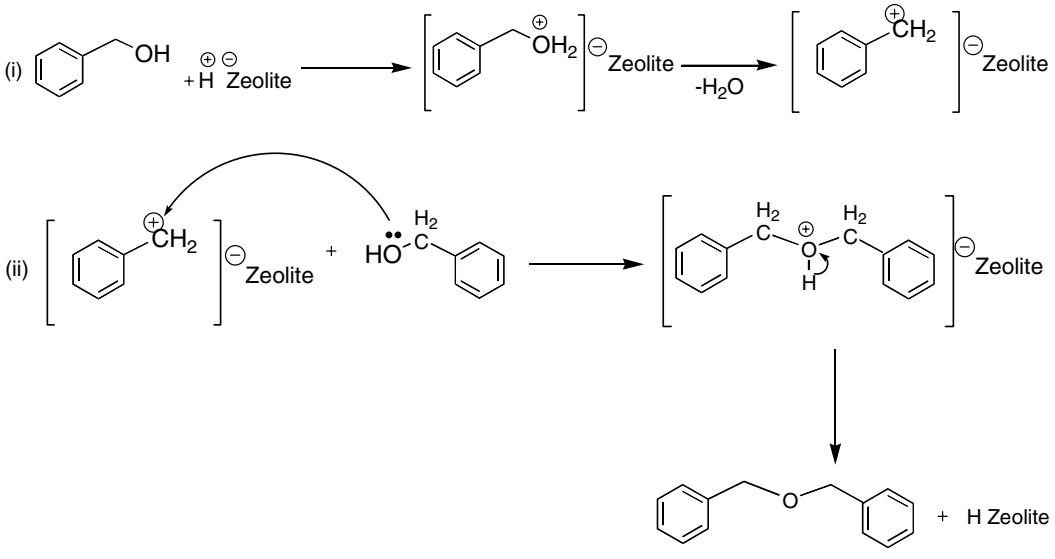
In order to optimize the amount of catalyst required for better conversion, studies using varying amounts of Ceβ were carried out. The conversion percentage is found to



Scheme 1.



Scheme 2.



Scheme 3.

be 21, 64 and 99 using 25 mg, 50 mg and 100 mg of Ceβ, respectively (Table 3, S. No. 5, 6 and 7). Since 100 mg of catalyst gave best conversion, studies on all the other modified catalysts were carried out using this optimum amount.

In the case of benzylation of toluene, Wβ and Feβ gave better results compared to other metal ion modified β-zeolites, Wβ and Feβ showed 98% conversion of benzyl alcohol and selectivity of 78% (*para* 78%, *ortho* 22%), 77% (*para* 78, *ortho* 22) mono benzylated product and 22%, 23% benzyl ether (Table 4, S. No. 6, 7). The reaction time has been decreased from 2 h to 1 h. Studies on the effect of amount of the catalyst using varying amount of Wβ revealed that increases in the amount of catalyst increase the conversion (Table 4, S. No. 7, 8 and 9). The catalyst (zeolite) was easily separated from the reaction mixture by simple filtration. Further, catalyst was reused in the benzylation of benzene and toluene. The recovered catalyst showed consistent activity. The high catalytic activity and selectivity were maintained even after third reuse. The catalyst was highly crystalline before and after the reaction, which was confirmed by XRD. The Bronsted acidic centers presented at the channel intersection of the zeolites are assumed to be the active centers in this reaction (Schemes 2 and 3).

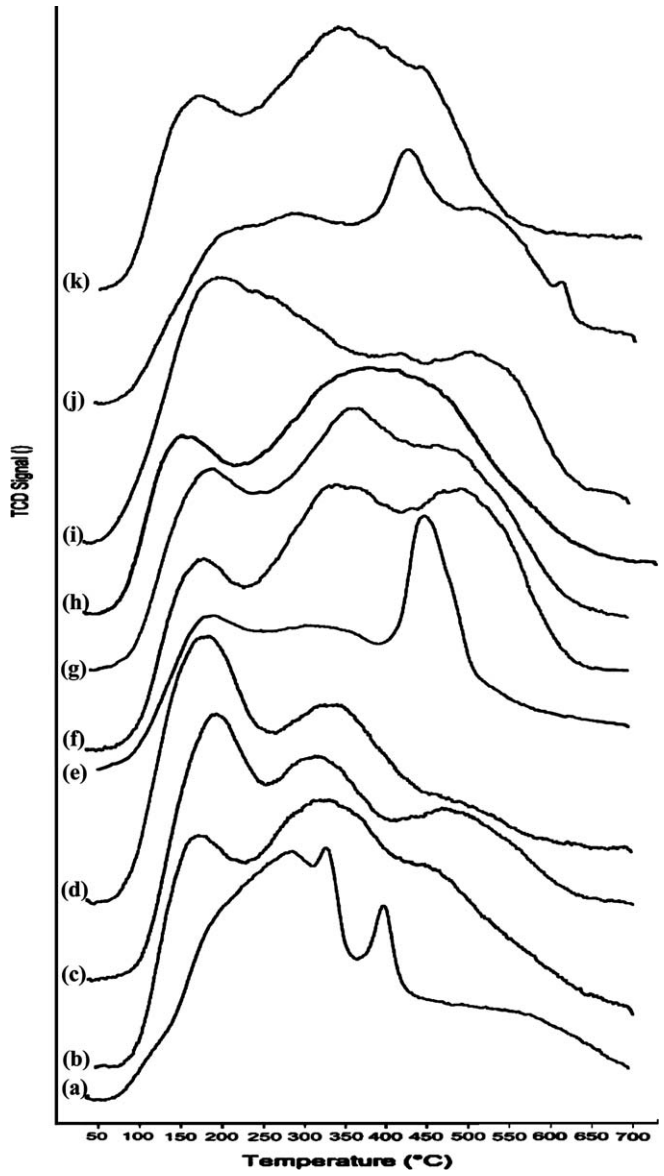


Fig. 1. NH_3-TPD profiles of: (a) Cuβ, (b) Laβ, (c) Pbβ, (d) Hβ, (e) Niβ, (f) Feβ, (g) Crβ, (h) Ceβ, (i) Znβ, (j) Coβ, and (k) Wβ.

3.3. Temperature programmed desorption of ammonia (NH_3-TPD)

The temperature programmed desorption (TPD) is one of the efficient methods of determining the nature and level of acidity and basicity in a catalyst. The amount and strength of acid sites are determined by temperature programmed desorption (TPD) of ammonia. The NH_3-TPD profiles of some typical catalysts are given in Fig. 1.

NH_3-TPD profile of 5 wt% Wβ showed temperature maxima at 174 °C and 363 °C (Fig. 1k). NH_3-TPD profile of 5 wt% Feβ showed temperature maxima at 179 °C, 340 °C and 492 °C (Fig. 1f) and NH_3-TPD profile of 5 wt% Ceβ showed temperature maxima at 166 and 374 °C (Fig. 1h). The NH_3desorption peaks of 5 wt% Feβ, 5 wt% Cuβ, and 5 wt% Pbβ at 340 °C, 322 °C, and 307 °C temperature maxima are considered as β-state sites, which can be assigned as medium strength sites.

The results of ammonia desorption of modified β-zeolite in weak, medium and strong regions are depicted in Table 5.

In Hβ zeolite, weak acidic sites and few medium acidic sites are observed while strong acidic sites are not found (Fig. 1d). Upon modification of Hβ with different metal ions, the medium and strong acidic sites are enhanced (Fig. 1). The medium and strong acidic sites are found to be more in the case of 5 wt% Feβ (Fig. 1f), 5 wt% Wβ (Fig. 1k) and 5 wt% Ceβ (Fig. 1h). In the case of 5 wt%

Table 5
Desorption of ammonia of modified zeolites at different acidic regions

S. No.	Catalyst	Desorption of ammonia (ml/g STP)		
		Weak acidic site (150–300 °C)	Medium acidic site (300–400 °C)	Strong acidic site (400–500 °C)
1	Hβ	10.88	8.60	–
2	Niβ	10.97	5.70	8.41
3	Cuβ	20.38	6.06	15.42
4	Pbβ	8.49	8.99	4.00
5	Laβ	7.27	14.28	6.01
6	Ceβ	6.31	26.62 (medium + strong)	
7	Crβ	8.57	15.50	7.97
8	Feβ	6.41	15.12	8.73
9	Wβ	6.23	23.75 (medium + strong)	
10	Znβ	20.56	6.62	–
11	Coβ	15.95	11.52	5.37

Niβ, there are more number of stronger acidic sites than medium and weak acidic sites (Fig. 1e).

3.4. Correlation of selectivity with acidity

The variation of acidity of various metal ion modified β-zeolites measured by TPD technique is shown graphically in Fig. 2a. The selectivity percentage of diphenylmethane formed in the benzylation of benzene is plotted against different metal ion modified β-zeolites (arranged in increasing order of acidity) is also shown in Fig. 2b.

These results revealed that the combination of medium and strong acidic sites are responsible for high selectivity towards diphenylmethane.

From Fig. 2, it is evident that increase in the acidity of the zeolite increases the selectivity of the diphenylmethane. The small deviations from the trend may be due to the distribution of acidic sites in medium and strong regions.

Fig. 3 gives graphical representation of variation of acidity of modified zeolites (a) and also selectivity % of 1-benzyl-4-methylbenzene (*para* isomer) formed in the benzylation of toluene over modified zeolites (b). Increase in the acidity from Znβ to Ceβ has increased the selectivity similar to the case of selectivity of diphenylmethane.

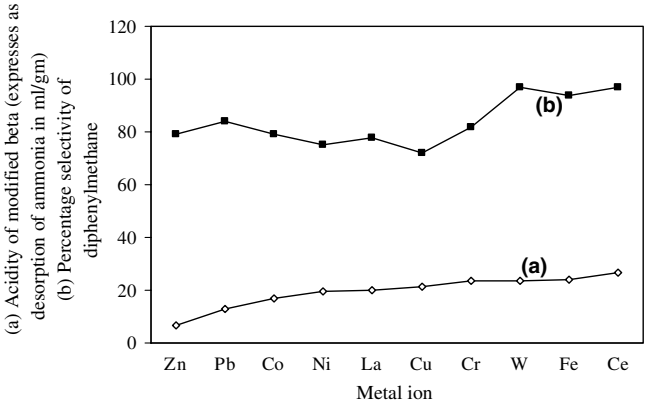


Fig. 2. Variation of acidity of modified zeolites and selectivity of diphenylmethane.

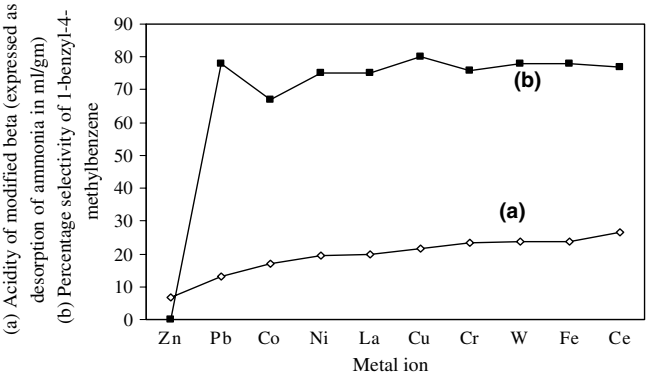


Fig. 3. Variation of acidity of modified zeolites and selectivity of 1-benzyl-4-methylbenzene.

3.5. Reaction mechanism

The proposed reaction mechanisms for formation of diphenylmethane and formation of benzyl ether are shown in Schemes 2 and 3, respectively. Benzyl ether formation from benzyl alcohol can be explained on the basis of the intermolecular reaction pathway involving Bronsted acid sites of the zeolite.

4. Conclusions

The benzylation of benzene and toluene with benzyl alcohol in liquid phase can be carried out in the presence of metal ion modified β-zeolites to get high selectivity and conversion within shorter reaction time. Use of Benzyl alcohol instead of benzyl chloride is advantageous due to the formation of side product is only water, which is environmentally friendly. The catalyst (zeolite) is reusable.

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