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Benzoylation of toluene with benzoyl chloride over zeolite catalysts

Anand P. Singh *, D. Bhattacharya, S. Sharma

Catalysis Division, National Chemical Laboratory, Pune-411008, India

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Abstract

The liquid phase benzoylation of toluene with benzoyl chloride (BOC) has been studied over ZSM-12, beta, mordenite, Y and REY zeolites and $AlCl_3$ at 383 K. Zeolite H-beta is more active and selective than the other zeolites. H-ZSM-5, Na-Y and amorphous SiO_2–Al_2O_3 do not catalyze the reaction. The acidity of the zeolites was measured by temperature programmed desorption of ammonia. The activity and acidity of the Y zeolites correlate with the degree of RE^{3+}-exchange. The influence of various parameters such as duration of the run, SiO_2/Al_2O_3 ratio, catalyst concentration, reaction temperature, molar ratios of reactants and reuse of the zeolite H-beta in the benzoylation of toluene are also reported. The conversion of BOC over H-beta is significantly enhanced by increasing duration of the run, the reaction temperature, catalyst amount and molar ratios toluene/BOC. Increase in SiO_2/Al_2O_3 ratio decreases the BOC conversion. The HCl formed during the reaction deactivates the catalyst.

Keywords: Benzoylation; Toluene; Zeolites

1. Introduction

Selective benzoylation of toluene to 4-methylbenzophenone (4-MBP) is of considerable interest due to its commercial importance as additive (fixative) in the perfumery industry [1] (Scheme 1). Several homogeneous acidic catalysts ($AlCl_3$, $TiCl_4$, $FeCl_3$, $SnCl_4$, CF_3SO_3H, FSO_3H and H_2SO_4) have been widely used for the acylation reactions [2,3]. Recently the use of solid acid catalysts such as Nafion-H [4], clay [5], heteropoly acids [6] and metal oxides promoted by sulphate ions (SO_4^{2-}/Al_2O_3, SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, $FeSO_4$ and $Fe_2(SO_4)_3$) has been reported for the benzoylation of toluene with benzoyl chloride [6–8]. These catalysts tend to give either lower conversion of benzoyl chloride or lower yield of the para isomer (4-MBP). Zeolites are known for their shape selective properties and they have been used widely in a variety of acid and base catalyzed shape selective reactions. However, not much attention has been paid to the use of zeolites in acylation reactions [9–14]. The objective of the present work is to study the para-selective benzoylation of toluene over acidic zeolite catalysts. We report the results of the effect of different zeolite catalysts, various level of RE^{3+}- and Na^+-exchange in Y zeolite, acidity of the zeolite catalysts, duration of the run, silica-to-alumina ratio, catalyst concentration, reaction temperature, molar ratios of reactants and reuse of the zeolite catalyst (H-beta) on the conversion of benzoyl chloride and the formation of 4-MBP.

* Corresponding author. Fax: (+91-212)334761.

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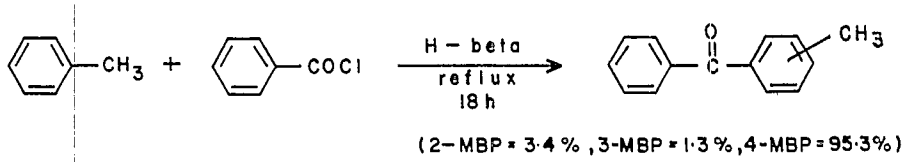

Scheme 1.

The results obtained over various zeolites are compared with those from conventional catalysts ($AlCl_3$, amorphous SiO_2–Al_2O_3). Benzoylation of toluene over beta type zeolite has not been reported so far in the open literature.

2. Experimental

Zeolites ZSM-5, ZSM-12 and beta were synthesized by known procedures [15–17]. Organic templates of the zeolites were removed by calcining in air at 823 K for 16 h. The resulting zeolites were converted into their protonic form by repeated exchanges with a solution of NH_4NO_3 (1 M; 10 ml/g zeolite, 353 K; 6 h; pH = 7–8, three exchanges) followed by calcination at 823 K for 8 h. H-Mordenite and Na-Y were obtained from Laporte Inorganics, Cheshire, UK. H-Y and Na-REY were prepared from the Na-Y by exchanges with NH_4NO_3 (three times) and 5% RE-chloride (one exchange) solutions, respectively, maintaining the above conditions. The H-REY (42.2) and H-REY (70.6) were prepared by treating NH_4-Y with 5% rare earth chloride solution by following the above exchange conditions. The washed zeolites were dried at 383 K for 2 h and calcined at 823 K for 8 h. The chemical analysis of the zeolites were carried out by a combination of wet and atomic absorption (Hitachi 800) methods. The average particle sizes of the zeolites were determined using a Shimadzu (Model UV-2101 PC) scanning electron microscope. The surface areas of the zeolite were determined by sorption of nitrogen at liquid nitrogen temperature using Omnisorb 100CX apparatus.

In addition, temperature programmed desorption (TPD) of NH_3 was carried out to evaluate the acidic properties of the zeolites [18,19]. The zeolite sample (1 g, particle size 20–30 mesh) was packed in a quartz reactor (i.d. 1.5 cm, length 30 cm) and activated at 773 K for 4 h under flow-

Table 1
Physico-chemical properties of catalysts

Catalyst	SiO_2/Al_2O_3	Cation composition (%) [a]			Surface area	Micropore volume [b,c]	Mesopore volume [b]	Total acid sites [d]	Crystal size
	(molar ratio)	H^+	Na^+	RE^+	(m^2/g) [b]				(microns)
H-ZSM-5	41.0	98.1	1.9	–	413	0.151	0.009	1.2	0.5
H-ZSM-12	100.0	98.5	1.5	–	456	0.169	0.051	0.26	0.6
H-Beta	26.0	98.7	1.3	–	745	0.265	0.074	0.74	0.5
H-Mordenite	22.0	98.0	2.0	–	552	0.126	0.035	0.71	1.0
H-Y	4.1	98.2	1.8	–	615	0.209	0.018	1.43	1.0
Na-Y	4.1	0.7	99.3	–	632	0.211	0.021	1.15	1.0
Na-REY	4.1	2.5	66.0	31.5	651	0.214	0.036	0.63	1.0
H-REY (42.2)	4.1	56.0	1.8	42.2	712	0.236	0.072	0.90	1.0
H-REY (70.6)	4.1	28.1	1.3	70.6	659	0.216	0.051	0.78	1.0
SiO_2–Al_2O_3 (amorphous)	30.0	–	–	–	–	–	–	–	–

[a] H^+ was obtained by the difference between the Al content and the sum of the Na^+ and RE^{3+} metal values. Values are reported as percent of the total cation sites, taken as the aluminum content 100%.
[b] N_2 adsorption.
[c] Obtained from De Boer *t*-plots.
[d] NH_3 chemisorbed at 303 K (mmol/g).

Table 2
Benzoylation of toluene [a]

Catalyst	Reaction time [b]	Conversion of benzoyl chloride	Activity	Product distribution (wt%) [c]		
	(h)	(wt%)	(mmol/g/h)	2-MBP	3-MBP	4-MBP
H-ZSM-5	1	2.8	0.6	13.5	4.8	81.7
	18	4.2		14.6	5.1	80.3
H-ZSM-12	1	30.9	6.7	2.3	2.7	95.0
	18	41.0		2.4	2.9	94.7
H-Beta	1	45.9	9.9	2.2	2.7	95.1
	18	83.4		3.4	1.3	95.3
H-Mordenite	1	9.1	2.0	14.7	4.1	81.2
	18	19.5		14.9	4.4	80.7
H-Y	1	8.7	1.9	16.1	6.8	77.1
	18	18.8		22.9	6.1	71.0
Na-Y	1	1.9	0.4	20.5	2.6	77.3
	18	3.8		27.5	2.3	70.0
Na-REY	1	17.6	3.8	15.1	5.6	79.3
	18	31.6		16.2	5.7	78.1
H-REY (42.2) [d]	1	23.6	5.1	15.7	4.4	79.9
	18	42.3		16.0	5.1	78.9
H-REY (70.6) [d]	1	43.8	9.4	14.8	4.7	80.5
	18	61.7		15.1	5.4	79.5
$AlCl_3$	1	67.3	14.5	22.0	3.9	74.1
SiO_2-Al_2O_3	1	1.8	0.4	24.1	3.5	72.4
(amorphous)	18	3.2		25.4	3.4	71.2

[a] Reaction conditions: catalyst/C_6H_5COCl (wt/wt) = 0.33; reaction temperature = 388 K; toluene/C_6H_5COCl (molar ratio) = 5; toluene = 0.11 mol.
[b] Reaction times (18 h) indicated are the ones after which conversion of C_6H_5COCl remains roughly unchanged.
[c] 2-MBP = 2-methylbenzophenone; 3-MBP = 3-methylbenzophenone; 4-MBP = 4-methylbenzophenone.
[d] Percentage of RE^{3+}-exchange is given in brackets.

ing nitrogen (50 ml/min). After the pretreatment, the reactor temperature was decreased to 303 K and the zeolite was saturated with NH_3 for 30 min. The physically adsorbed ammonia was desorbed in the flow of nitrogen (50 ml/min) for a period of 15 h. The ammonia chemisorbed at 303 K was desorbed in a flow of nitrogen (10 ml/min) at temperatures from 303 to 773 K in a number of steps. After the temperature of each step was reached it was maintained for a period of 30 min to desorb the reversibly adsorbed ammonia. The ammonia evolved in each step was trapped in a HCl solution (30 ml; 0.1 N) that was continuously titrated by a standard NaOH solution (0.1 N). The main properties of the zeolites are summarised in Table 1. Before reaction, the zeolite samples were dehydrated at 473 K under N_2 for 6 h.

Toluene and benzoyl chloride were high purity (Analar R) grade. The catalytic benzoylation was performed in a 50 ml glass flask fitted with a condenser, N_2 gas supply tube and a septum. The temperature of the reaction vessel was maintained using an oil bath. A typical procedure of the reaction is as follows: A mixture of toluene (0.11 mol), benzoyl chloride (0.02 mol) and powdered catalyst (1.0 g) was stirred under reflux for 18 h in a nitrogen atmosphere. The course of the reaction was followed by GC analysis using a Blue star Model 421 apparatus equipped with a flame ionisation detector and a 50 m × 0.2 mm capillary column with methyl silicone gum. GC/MS spectral analysis and authentic samples were used for product identification.

3. Results and discussion

3.1. Activity of various catalysts

The catalytic results are presented in Table 2. In all cases, the major products are 2-, 3- and 4-methylbenzophenones (MBP), the 4-isomer being favoured. Similar products have been reported in the benzoylation of toluene using benzoyl chloride as benzoylating agent and $FeSO_4$ or $Fe_2(SO_4)_3$ as catalyst [8]. The activity of the catalyst is defined as:

$$\text{Activity} = \frac{\text{Mass of benzoyl chloride reacted}}{(\text{Mass of catalyst used}) * (\text{reaction time})} \ (h^{-1})$$

In benzoylation of toluene, H-beta is found to be most active and selective compared to the other zeolites. H-ZSM-12 was also found to be selective but less active, which may be attributed to its higher $SiO_2/Al_2O_3 = 100$ ratio and hence the lower number of acid sites. The catalytic activities of H-mordenite and H-Y were found to be almost identical. However, the former was more selective. When Na-Y is exchanged to H-Y, Na-REY, H-REY (42.2) and H-REY (70.6), the catalytic activities are enhanced considerably which may be due to the higher amount (Table 1) and strength of acid sites (Fig. 1), generated by H^+ and RE-cations. It is observed from the temperature programmed desorption of ammonia over zeolites that all acidic zeolites have a wide range of acid strength distribution (Fig. 1). $AlCl_3$ produces 22% 2-MBP, 3.9% 3-MBP, and 74.1% 4-MBP at 67.3% conversion level of BOC while H-beta gave 3.4% 2-MBP, 1.3% 3-MBP, and 95.3% 4-MBP products at 83.4% BOC conversion. The formation of 4-MBP (95.3%) in the present study over H-beta is even higher than the earlier reported over $AlCl_3$ (89.3%) [3]. Among the zeolites studied, H-beta revealed the highest activity which may be attributed to its stronger acid sites (Fig. 1) and mesoporous system (Table 1).

The catalysts used in the study, show the following decreasing order of activity. $AlCl_3$ > H-beta > H-REY (70.6) > H-ZSM-12 > H-REY (42.2) > Na-REY > H-Mordenite > H-Y > H-ZSM-5 > Na-Y, SiO_2–Al_2O_3 (amorphous).

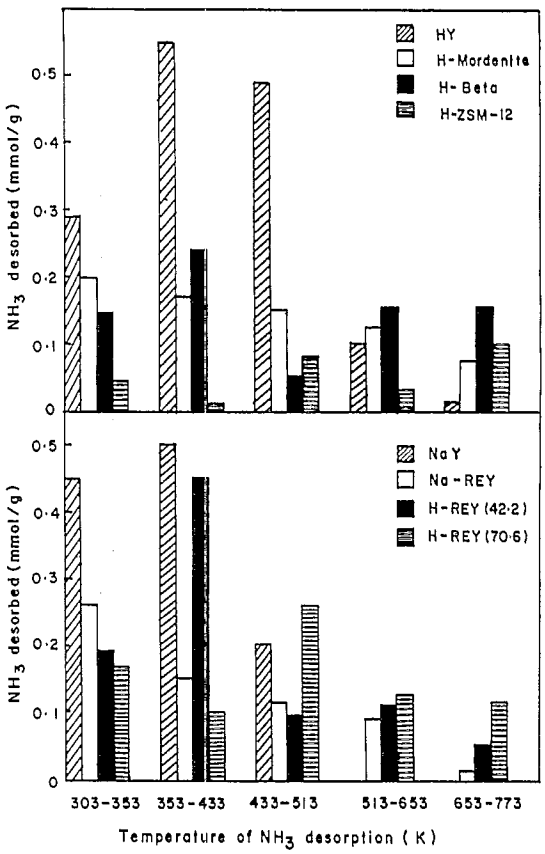

Fig. 1. Acid strength distribution on various zeolites.

The results indicate that mainly ortho and para substitutions take place over most of the zeolite catalysts which is expected for an electrophilic aromatic substitution pathway [4]. However, the selective formation of para-isomer over zeolite H-beta and H-ZSM-12 may be interpreted in terms of their narrow pore sizes compared to the other zeolites [10,20,21]. Acidic zeolites polarise the benzoyl chloride into an electrophile ($C_6H_5CO^+$) which attacks on the aromatic ring resulting in the formation of methylbenzophenones [4,7,10].

3.2. Acidity of zeolites

The results of the stepwise thermal desorption of ammonia from the zeolites are presented in Fig. 1. The total amount of NH_3 desorbed at 303 K is also given in Table 1. The results reveal that the total acid sites and the site energy distribution

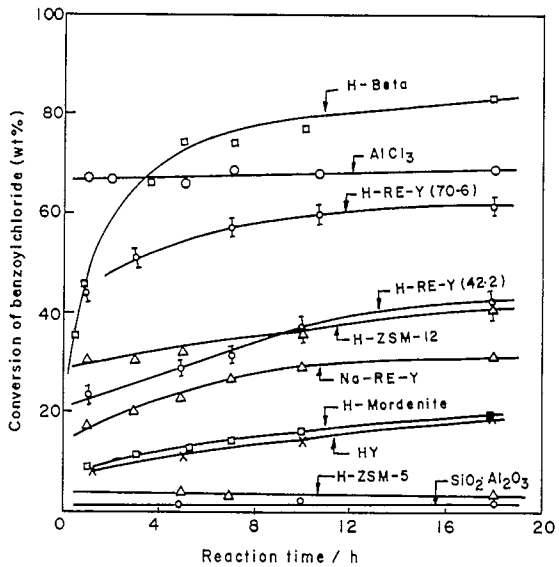

Fig. 2. Benzoyl chloride conversion over various catalysts as a function of reaction time. Reaction conditions: reaction temperature = 388 K; catalyst/benzoyl chloride (wt/wt) = 0.33; toluene/benzoyl chloride (molar ratio) = 5; toluene = 0.11 mol.

are dependent on the type of zeolite and are strongly influenced by the nature of the cation and degree of exchange in the zeolite. The number of sites of higher strength increase with the increase in the degree of RE^{3+}-exchange in HY and NaY. It is also clear from the Fig. 1 that NH_3 interacts strongly with Na^+ ions in the zeolite below 623 K [18]. One of the reasons of higher catalytic activities of H-beta and H-REY (70.6) may be their strong acid sites [7] however, no linear correlation was observed between the total acidity and catalytic activities of zeolites in the benzoylation of toluene [10].

3.3. Duration of the reaction

The conversion of benzoyl chloride as a function of reaction time for the benzoylation of toluene over various catalysts is displayed in Fig. 2. It is noted that H-beta exhibited the highest conversion of BOC (83.4%) compared to the other catalysts. Initially H-ZSM-12 performed better than H-REY (42.2), but after about 10 h, H-REY (42.2) showed a slightly better performance than H-ZSM-12.

3.4. Effect of SiO_2/Al_2O_3 ratio

The results obtained for the benzoylation of toluene over different SiO_2/Al_2O_3 ratios of H-beta are presented in Table 3. It can be seen (Table 3) that the conversion of benzoyl chloride decreases as the silica to alumina ratio increases from 26 to 60.

3.5. Effect of catalyst concentration

When the catalyst/BOC ratio was increased from 0.1 to 0.44, the conversion of benzoyl chloride increased from 37.0 to 90.1% (Table 4). Product distribution was not influenced due to the change in the catalyst concentration and para isomer was the major product in all experiments.

3.6. Effect of reaction temperature

The effect of reaction temperature on the rate of benzoylation of toluene with benzoyl chloride was studied over zeolite H-beta in the temperature range 333 to 393 K using a toluene/BOC (molar ratio) = 5 reactant mixture. A pronounced increase in the initial reaction rate was observed when the reaction temperature was increased from 333 to 393 K. However, the product distribution is not significantly influenced (Table 5). The apparent activation energy over H-beta was found to be 48.5 kJ/mol.

Table 3
Effect of SiO_2/Al_2O_3 molar ratio of zeolite H-Beta in the benzoylation of toluene at 388 K [a]

	SiO_2/Al_2O_3 molar ratio		
	26	42	60
Reaction time (h)	1	1	1
Conversion of benzoyl chloride (wt%)	45.9	34.3	9.9
Product distribution [c] (wt%)			
2-MBC	2.2	4.2	5.1
3-MBC	2.7	2.3	4.3
4-MBC	95.1	93.5	90.6

[a] Reaction conditions as in Table 2.
[c] See footnotes to Table 2.

Table 4
Influence of the amounts of zeolite H-Beta on the benzoyl chloride conversion in the benzoylation of toluene at 388 K [a]

Catalyst/C_6H_5COCl [d] (wt/wt)	Final conversion [b] of benzoyl chloride (wt%)	Product distribution [c] (wt%)		
		2-MBP	3-MBP	4-MBP
No catalyst	–	–	–	–
0.03	20.6	2.0	0.7	97.3
0.10	37.0	2.5	2.7	94.8
0.14	61.0	2.4	2.9	94.7
0.22	73.3	2.4	2.7	94.9
0.32	83.4	3.4	1.3	95.3
0.44	90.1	3.4	2.3	94.3

[a] Reaction conditions as in Table 2.
[b+c] See footnotes b and c to Table 2.
[d] Weight ratio of catalyst H-beta/C_6H_5COCl.

Table 5
Catalytic benzoylation of toluene with benzoyl chloride at various temperatures over H-beta [a]

Reaction temperature (K)	Initial reaction rate [b] (mmol/g/h)	Product distribution (wt%) [c]		
		2-MBP	3-MBP	4-MBP
333	1.0	2.2	3.4	94.4
353	4.6	3.6	2.1	94.3
373	7.7	2.3	2.1	95.6
393	9.9	2.2	2.7	95.1

[a] Reaction conditions are the same as those given in Table 2.
[b] Initial reaction rate is based on the consumption of benzoyl chloride at 1 h reaction time.
[c] See footnotes to Table 2.

3.7. Effect of mole ratio of the reactants

The results of the influence of toluene/BOC molar ratios on the benzoyl chloride conversion and product distribution are summarised in Table 6. The ratios were changed by keeping the amount of BOC constant. When toluene is used in large excess (toluene/BOC = 5 to 8) hardly any disubstituted product is obtained and the para-isomer (4-MBP) of the monosubstituted derivatives is the major product.

3.8. Catalyst recycle

Table 7 depicts the recycling of zeolite H-beta in the benzoylation of toluene. The catalyst was reused by separating the catalyst, washing with acetone and calcining at 773 K for 16 h before use in the next experiment. A slight decline was observed in the benzoyl chloride conversion after each reuse. The chemical analyses (Table 7) of the used catalysts show that the slight decrease in the catalytic activity is most probably due to some

Table 6
Influence of the molar ratio (toluene/benzoyl chloride) on the benzoyl chloride conversion and product distribution at 388 K over H-beta [a]

Toluene/benzoyl chloride (molar ratio)	Conversion of benzoyl chloride [b] (wt%)	Product distribution (wt%) [c]			
		2-MBP	3-MBP	4-MBP	Others [d]
1	43.3	5.3	1.8	92.0	0.8
2	69.5	4.7	2.6	92.3	0.4
5	83.4	3.4	1.3	95.3	–
7	89.3	3.3	2.0	94.7	–
8	90.5	3.8	2.3	93.9	–

[a+b+c] See footnotes to Table 2.
[d] Others = dibenzoyltoluenes.

Table 7
Influence of catalyst (H-beta) reuse in the benzoylation of toluene with benzoyl chloride [a]

Repeated run number	Change in SiO_2/Al_2O_3 (mol)	Conversion [b] of benzoyl chloride (wt%)	Product distribution [c]		
			2-MBP	3-MBP	4-MBP
0 (fresh)	26.0	83.4	3.4	1.3	95.3
1	25.9	82.1	3.2	3.4	93.4
2	25.8	80.7	3.6	3.7	92.7
3	25.7	79.8	3.8	3.9	92.3

[a+c] See footnotes to Table 2.
[b] Conversion of benzoyl chloride at 18 h reaction time.

dealumination of the zeolite framework by HCl (formed during the reaction).

4. Conclusions

Acidic zeolites are active in the benzoylation of toluene with benzoyl chloride. The results obtained in this study show that the zeolite H-beta leads to both high activity and selectivity among zeolite catalysts. H-ZSM-12 is also an active and selective catalyst. $AlCl_3$ gave lower conversion of benzoyl chloride compared to the H-beta at 18 h reaction time. Total acidity obtained at 303 K of the zeolites does not show any correlation between acidity and catalytic activity of the zeolites, however, strong acid sites of the H-beta and RE^{3+}-exchanged zeolites Y enhanced the benzoyl chloride conversion considerably. The change of the values of different parameters such as duration of the run, catalyst concentration, reaction temperature and molar ratios of the reactants increased the benzoyl chloride conversion to methylbenzophenones. An increase in the SiO_2/Al_2O_3 ratio and reuse of the H-beta decrease the formation of methylbenzophenones.

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