

# Selective benzoylation of *o*-xylene to 3,4-dimethylbenzophenone using various zeolite catalysts

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## Abstract

The liquid phase benzoylation of *o*-xylene with benzoyl chloride (BOC) over various zeolite catalysts is studied in a batch reactor at atmospheric pressure and 411 K. The results obtained over different zeolite catalysts are compared with the homogeneous Lewis acid catalyst, AlCl<sub>3</sub> and amorphous silica–alumina. The protonic form of zeolite beta is found to be an efficient catalyst compared to other zeolites in the benzoylation of *o*-xylene. The conversion of BOC, turnover rate of BOC conversion (TOF) and selectivity for 3,4-dimethylbenzophenone (3,4-DMBP) over zeolite H-beta are found to be 52.8 wt.%,  $69.7 \times 10^{-5} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$  and 94.7 wt.%, respectively, at the following reaction conditions [H-beta to BOC (w/w) = 0.28, *o*-xylene to BOC (molar ratio) = 5; 411 K; 1 atm]. The non-shape selective AlCl<sub>3</sub> catalyst produces higher amount of consecutive products (16.2 wt.%) and hence gives lower selectivity for 3,4-DMBP (76.5 wt.%). The acidity and pore structure of H-beta appeared to be responsible for good performance. Increase in reaction time, catalyst concentration, reaction temperature, *o*-xylene to BOC molar ratio enhances the conversion of BOC, whereas it decreases with the increase in degree of Na-exchange and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of H-beta. The zeolite H-beta is recycled three times without the loss of 3,4-DMBP selectivity but with a decline in the catalytic activity of H-beta. Additionally, the benzoylation of *m*-xylene and *p*-xylene is also investigated using H-beta. The Friedel–Crafts acylation reaction mechanism involves the formation of an electrophile (C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>) over an acidic zeolite catalyst which attacks the xylene ring resulting in the formation of dimethyl benzophenones. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Benzoylation of *o*-xylene; 3,4-Dimethylbenzophenone; Zeolite H-beta

## 1. Introduction

3,4-Dimethylbenzophenone is used for the production of dyes and several organic intermediates for the production of fine chemicals. Traditionally, these reactions are carried out using

homogeneous Lewis acid catalysts such as AlCl<sub>3</sub>, TiCl<sub>4</sub>, FeCl<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [1]. Homogeneous catalysts have several disadvantages: difficulty in catalyst recovery, separation of the final product from the catalyst and use of stoichiometric amounts of the catalyst with respect to the benzoylating agent. In addition, these halides of iron and aluminium, being strong Lewis acids, also catalyze other undesirable side

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reaction like production of a substantial amounts of consecutive products. In addition, the use of  $\text{Fe}(\text{CO})_5$  [2],  $\text{Fe}(\text{II})$  phthalocyanine [3] and metal oxides like  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{MoO}_3$  and  $\text{Na}_2\text{WO}_4$  etc. [4] have been reported for the benzylation of *o*-xylene with benzoyl chloride. This reaction is also known to proceed over  $\text{AgNO}_3$  catalyst using acid chloride as the acylating agent [5]. These non-shape selective catalysts gave a lower selectivity for 3,4-DMBP.

Zeolite catalysts have been widely used in the field of petrochemistry [6,7] due to their shape-selectivity, thermostability, the easy separation from the products and the possibility of regeneration of the deactivated catalysts. However, their use in fine organic synthesis has been limited [8–10]. Recently, zeolite catalysts were found to be active in the acylation of aromatics [11–20]. However, there is no report to date on the benzylation of *o*-xylene using zeolite H-beta as catalyst. The objective of the present work is to replace the homogeneous non shape-selective Lewis acid catalyst,  $\text{AlCl}_3$ , by the shape-selective and environmentally friendly zeolite catalyst. The another objective is to enhance the selectivity for 3,4-DMBP and consequently to minimize the formation of consecutive products using zeolite catalysts.

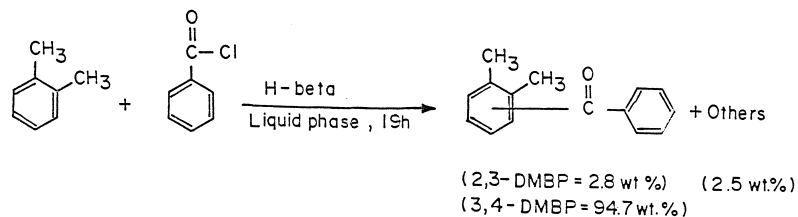
In this paper, we disclose a new catalytic method for the selective benzylation of *o*-xylene to 3,4-DMBP using zeolite H-beta as catalyst and benzoyl chloride as benzoylating agent (Scheme 1). The catalyst and process parameters are optimized to enhance the conversion of BOC and selectivity to 3,4-DMBP. The

results obtained over zeolite catalysts are compared with the conventional catalyst  $\text{AlCl}_3$  and amorphous  $\text{SiO}_2\text{-Al}_2\text{O}_3$ .

## 2. Experimental

### 2.1. Catalyst preparation

Zeolites ZSM-5 and beta were synthesized following the procedures described in literature [21,22]. Zeolites H-mordenite and Na-Y were obtained from Laporte Inorganics, Cheshire, UK. The as-synthesized ZSM-5 and beta samples were filtered, washed with deionized water and dried at 373 K for 2 h. Organic templates were eliminated from the zeolite channels by calcination in dry air at 773 K for 16 h. The resultant samples were thrice  $\text{NH}_4^+$ -exchanged using the following conditions:  $\text{NH}_4\text{NO}_3 = 1$  M, 10 ml  $\text{NH}_4\text{NO}_3$  per gram of zeolite, 353 K, 6 h exchange run, pH 7–8 and calcined at 823 K for 8 h to get the protonic form. The modified forms of H-beta such as H-Na (13.6) beta and H-Na (37.3) beta were obtained by exchange with 0.1 M and 1 M solutions of  $\text{NaNO}_3$ , respectively, at 353 K for 8 h. The preparation of H-Y was carried out by thermal decomposition of  $\text{NH}_4\text{-Y}$  zeolite following the experimental details described above. The H-RE(42.2)Y and H-RE(70.6)Y were prepared by treating  $\text{NH}_4\text{-Y}$  with 5% rare earth chloride solution [18,19].



Scheme 1.

Table 1  
Properties of zeolite catalysts

Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Degree of H <sup>+</sup> or RE <sup>3+</sup> exchange <sup>a</sup> (%)	Crystal size (μm)	Surface area <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	NH <sub>3</sub> desorbed <sup>c</sup> (mmol g <sup>-1</sup> )					NH <sub>3</sub> chemisorbed at 303 K (mmol g <sup>-1</sup> )
					303–353 K	353–433 K	433–513 K	513–653 K	653–773 K	
H-ZSM-5	41.0	> 98	0.4	413	0.55	0.16	0.05	0.26	0.21	1.23
H-beta	26.0	> 98	0.5	745	0.14	0.24	0.05	0.16	0.16	0.75
H-mordenite	22.0	> 98	1.0	552	0.20	0.17	0.15	0.12	0.07	0.71
H-Y	4.1	> 98	1.0	615	0.29	0.55	0.49	0.11	0.01	1.45
H·RE(42.2)Y <sup>d</sup>	4.1	> 42.2	1.0	712	0.19	0.45	0.12	0.10	0.04	0.90
H·RE(70.6)Y <sup>d</sup>	4.1	> 70.6	1.0	659	0.17	0.10	0.26	0.11	0.10	0.74

<sup>a</sup> Values are reported as percent of the total cation sites, taken as the aluminium content 100%.

<sup>b</sup> Measured by N<sub>2</sub> adsorption.

<sup>c</sup> Measured by temperature programmed desorption (TPD) of ammonia.

<sup>d</sup> Values in parenthesis represent the amount of RE<sup>3+</sup>-exchange in HY.

## 2.2. Catalyst characterization

The chemical analysis of the zeolites was carried out by a combination of wet chemical and atomic absorption (Hitachi Z-800) methods. The average particle size of zeolites was investigated using (Stereoscan 440: Cambridge, UK) scanning electron microscope. The crystallinity and phase purity of the zeolites were characterized by a Rigaku (model, D/MAX-VC, Japan) X-ray diffractometer using Ni filtered Cu K $\alpha$  radiation. The nitrogen BET surface areas were measured using an Omnisorb 100 CX apparatus. The properties of zeolites used in this study are given in Table 1.

The acidity of the zeolites was established by the temperature programmed desorption (TPD) of ammonia [18,23,24]. The sample 20–30 mesh

size ( $\sim 1$  g) was activated in a flow of dry N<sub>2</sub> at 773 K for 6 h and cooled in flowing N<sub>2</sub> (100 ml min<sup>-1</sup>) to room temperature. NH<sub>3</sub> gas (25 ml min<sup>-1</sup>) was then passed continuously for a period of 30 min, then the physically adsorbed NH<sub>3</sub> was desorbed by passing N<sub>2</sub> for 15 h (15 ml min<sup>-1</sup>). Acid strength distribution was obtained by raising the catalyst temperature (100°C min<sup>-1</sup>) from 303–773 K in a number of steps in a flow of N<sub>2</sub> (10 ml min<sup>-1</sup>). The NH<sub>3</sub> evolved was trapped in HCl solution and titrated with standard NaOH solution (Table 1).

## 2.3. Catalytic testing

High purity (> 99%) *o*-, *m*- and *p*-xylene were used in the reaction. The liquid phase catalytic runs were carried out batchwise in a

Table 2  
Benzoylation of *o*-xylene<sup>a</sup>

Catalyst	Reaction time (h)	Conversion of BOC <sup>b</sup> (wt.%)	TOF of BOC conversion <sup>c</sup> (10 <sup>-5</sup> s <sup>-1</sup> mol <sup>-1</sup> Al)	Product distribution <sup>d</sup> (wt.%)		
				2,3-DMBP	3,4-DMBP	Others
H-ZSM-5	1	0.8	7.2	–	35.1	64.9
	19	4.4	–	–	47.3	52.7
H-beta	1	12.0	69.7	–	100.0	–
	19	52.8	16.1	2.8	94.7	2.5
H-Na (13.6) beta <sup>e</sup>	1	4.7	27.3	–	100.0	–
	19	29.4	–	1.8	94.9	3.3
H-Na (37.3) beta <sup>e</sup>	1	3.1	18.0	–	94.5	5.5
	19	6.3	–	–	92.3	7.7
H-mordenite	1	0.7	3.5	–	100.0	–
	19	7.7	–	1.1	75.0	23.9
H-Y	1	3.4	4.2	6.8	75.2	18.0
	19	12.6	–	7.5	79.1	13.4
H-RE (42.2)Y <sup>f</sup>	1	7.1	8.7	6.1	64.9	29.0
	19	32.7	–	8.8	81.2	10.0
H-RE (70.6)Y <sup>f</sup>	1	11.6	14.2	7.7	76.2	16.1
	19	49.6	–	8.8	87.7	3.5
AlCl <sub>3</sub>	1	64.4	59.8	7.3	76.5	16.2
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (amorphous)	1	1.9	12.7	67.8	24.4	7.8
	19	3.5	–	53.9	30.6	15.5

<sup>a</sup>Reaction conditions: catalyst (g) = 0.75; catalyst/C<sub>6</sub>H<sub>5</sub>COCl (w/w) = 0.28; *o*-xylene/C<sub>6</sub>H<sub>5</sub>COCl (molar ratio) = 5; *o*-xylene (mol) = 0.09; reaction temperature (K) = 411.

<sup>b</sup>BOC = benzoyl chloride (C<sub>6</sub>H<sub>5</sub>COCl).

<sup>c</sup>Turnover rates are expressed as turnover frequency (TOF, moles of BOC converted s<sup>-1</sup> mol<sup>-1</sup> Al).

<sup>d</sup>2,3-DMBP = 2,3-dimethylbenzophenone; 3,4-DMBP = 3,4-dimethylbenzophenone; others = secondary benzoylated products (consecutive products).

<sup>e</sup>Values in parenthesis represents the percentage of Na exchanged in the H-beta.

<sup>f</sup>Values in parenthesis represents the percentage of RE<sup>3+</sup>-exchanged in zeolite H-Y.

mechanically stirred, closed 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, appropriate amounts of *o*-xylene and benzoyl chloride (5:1 molar ratio) was charged in the reactor along with 0.75 g catalyst. The reaction mixture was heated to 411 K under stirring. Samples were withdrawn periodically and analysed with a gas chromatograph (HP 6890) fitted with a flame ionization detector and a capillary column (50 m  $\times$  0.2 mm) with methyl silicon gum. Some selected runs were analysed by GC-MS (Shimadzu-MS QP-2000A) for product identification. The composition of the reaction mixture was also determined by comparing their gas chromatograph with those of authentic samples.

Conversion of BOC is reported as the weight percent of the BOC is consumed. The turnover rates for BOC conversion ( $\text{TOF} = 10^{-5} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$ ) indicates moles of BOC converted per second per mole of aluminum. The product distribution (selectivity) weight percent for a product is expressed as the amount of the partic-

ular product divided by the amount of total products and multiplied by 100.

### 3. Results and discussion

#### 3.1. Catalyst characterization

The zeolites used in this study and their physico-chemical properties are presented in Table 1. The crystallinity and phase purity of the zeolite samples as well as the absence of amorphous matter within their pore structure were first ensured. The X-ray diffraction of all zeolites matched with those in the literature. In addition, XRD examination gave no evidence of structure damage or change of the zeolites as a result of various treatments. The surface area and scanning electron micrographs showed the absence of amorphous matter inside the channel as well as on the external surface of the zeolites, respectively. All the samples consisted of particles of about 0.4–1.0  $\mu\text{m}$ . Table 1 also lists the chemical composition and acidity data of zeolites used in the present study.

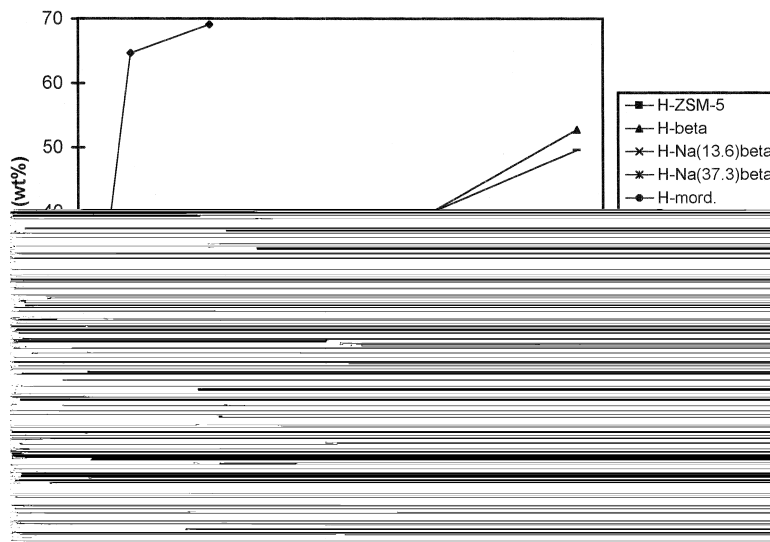


Fig. 1. Conversion of BOC versus reaction time over various zeolites. Reaction conditions: see table notes to Table 2.

Table 3  
Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of zeolite H-beta<sup>a</sup>

	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio		
	26	50	80
Reaction time (h)	6	6	6
Conversion of BOC (wt.%) <sup>b</sup>	25.9	7.6	3.9
Turnover rates of BOC conversion (TOF = 10 <sup>-5</sup> s <sup>-1</sup> mol <sup>-1</sup> Al) <sup>c</sup>	25.0	13.7	11.1
Product distribution (wt.%) <sup>d</sup>			
2,3-DMBP	1.2	–	–
3,4-DMBP	96.7	96.2	100
Others	2.1	3.8	–

<sup>a,b,c,d</sup>See table notes to Table 2.

### 3.2. Activity and selectivity of various catalysts

Table 2 shows the conversion of BOC (wt.%), turnover rates of BOC conversion (TOF = 10<sup>-5</sup> s<sup>-1</sup> mol<sup>-1</sup> Al) and the product distribution (wt.%) obtained over various catalysts in the benzylation of *o*-xylene. 3,4-Dimethylbenzophenone (3,4-DMBP) and 2,3-dimethylbenzophenone (2,3-DMBP) are the main reaction products. In some cases, a significant amount of dibenzoylated products (others) is also formed (Table 2). Both 2,3-DMBP and 3,4-DMBP are formed by parallel reactions while dibenzoylated products arise from secondary consecutive reactions of mono-benzoylated products [20]. H-beta catalyses the reaction efficiently and selectively to 3,4-DMBP and it is found to be superior compared to other zeolite catalysts. The conversion of BOC, turnover rates of BOC

conversion and selectivity for 3,4-DMBP over zeolite H-beta after 19 h of reaction time are found to be 52.8 wt.%, 16.1 × 10<sup>-5</sup> s<sup>-1</sup> mol<sup>-1</sup> Al and 94.7 wt.%, respectively. AlCl<sub>3</sub> gave 64.4 wt.% conversion of BOC with a selectivity of 76.5 wt.% for 3,4-DMBP. Presumably, the higher activity of H-beta may be attributed to its stronger acid sites compared to the other zeolite catalysts (Table 1) [12,17–19]. The higher selectivity of H-beta for 3,4-DMBP might be due to its smaller pore openings (7.5 × 5.5 Å) than H–Y (7.4 Å) zeolite catalysts. The small pores of zeolite H-beta prevent the secondary reactions in the zeolite channels and consequently the formation of dibenzoylated products of *o*-xylene. The lower activity of H-ZSM-5 compared to H-beta may be attributed to its small pore openings (5.4 × 5.6 and 5.1 × 5.5 Å) than the size of the *o*-xylene and reaction products. When H–Y is exchanged to H · RE(42.2)Y and H · RE(70.6)Y, the catalytic activities are enhanced considerably which may be due to the higher strength of acid sites generated by RE<sup>3+</sup>-cations [18,19]. The activity of H-beta decreases drastically with the increase in Na<sup>+</sup>-content of H-beta. The conversion of BOC (wt.%) over H-beta, H · Na(13.6)beta and H · Na(37.3)beta catalysts after 19 h of reaction time is found to be 52.8, 29.4 and 6.3 wt.%, respectively. The catalytic activity (conversion of BOC) of H · Na(13.6)beta and H–Y are found to be almost identical after 1 h of reaction time. However, the former was more selective due to the small pore openings than that of H–Y. The lower activity of Na-exchanged beta may be

Table 4  
Effect of reaction temperature<sup>a</sup>

Reaction temp. (K)	Conversion of BOC <sup>b</sup> (wt.%)	TOF of BOC conversion <sup>c</sup> (10 <sup>-5</sup> s <sup>-1</sup> mol <sup>-1</sup> Al)	Product distribution <sup>d</sup> (wt.%)		
			2,3-DMBP	3,4-DMBP	Others
393	4.8	21.0	–	100	–
400	9.1	39.7	–	100	–
411	20.8	90.8	1.9	96.0	2.1

<sup>a</sup>Reactions conditions: catalyst (H-beta) = 1 g; catalyst/C<sub>6</sub>H<sub>5</sub>COCl (w/w) = 0.38; *o*-xylene/C<sub>6</sub>H<sub>5</sub>COCl (molar ratio) = 5; *o*-xylene (mol) = 0.09; reaction time (h) = 1.

<sup>b,c,d</sup>See table notes to Table 2.

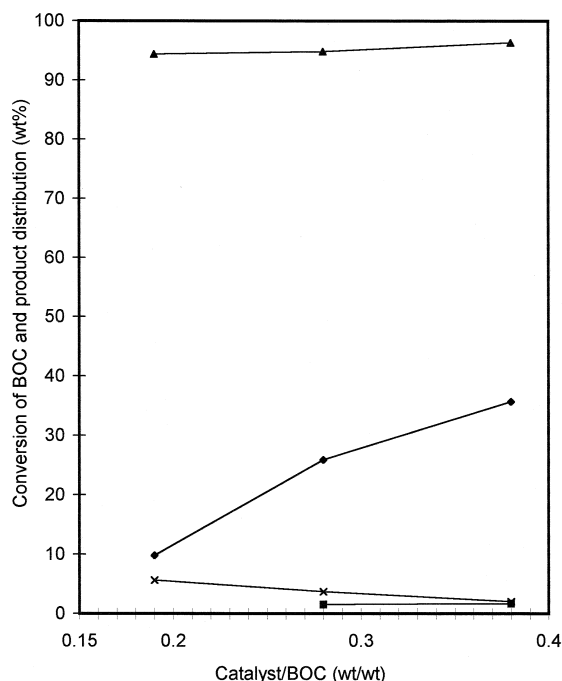


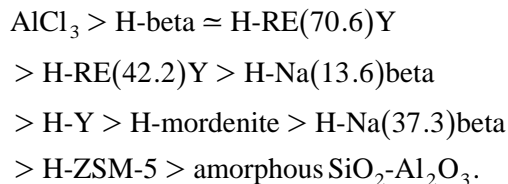
Fig. 2. Effect of catalyst/BOC molar ratio on the conversion of BOC (◆) and product distribution, 2,3-DMBP (■), 3,4-DMBP (▲) and others (X). Reaction conditions: see table notes to Table 2; reaction time (h) = 6.

attributed to the removal of some amount of stronger Bronsted acid sites by  $\text{Na}^+$  ion exchange in H-beta.

### 3.3. Duration of the run

The relationship between conversion of BOC (wt.%) and reaction time for the benzylation of *o*-xylene over various zeolite catalysts is illustrated in Fig. 1. Reaction conditions were those detailed in Table 2.  $\text{AlCl}_3$  gave higher conversion of BOC compared to other catalysts but it is a poor catalyst in terms of selectivity. The conversion of BOC over zeolite H-beta is found to be increased with the increase in reaction time and reaches a maximum (52.8 wt.%) in 19 h of the run. Zeolites H-ZSM-5, H-mordenite and amorphous  $\text{SiO}_2\text{-Al}_2\text{O}_3$  exhibit comparatively lower activities in this reaction. Based on the conversion of BOC after 19 h of reaction

time, the trend in activities for the catalysts studied is as follows:



The results of Section 3.2 have revealed that zeolite H-beta is the best catalyst for the benzylation of *o*-xylene to 3,4-DMBP. The influence of various parameters on the conversion of BOC, turnover rates of BOC conversion and product distribution over H-beta is reported in the following sections.

### 3.4. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

The results obtained for the benzylation of *o*-xylene over different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of H-beta are presented in Table 3. It is shown that the conversion of BOC in the benzylation of

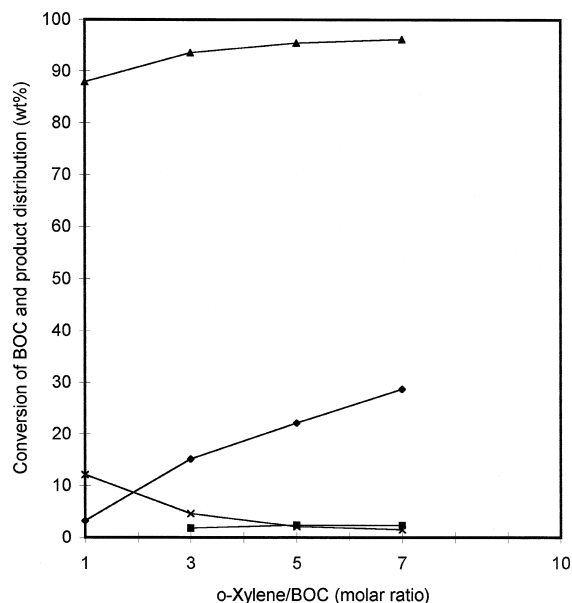


Fig. 3. Effect of *o*-xylene/BOC molar ratio on the conversion of BOC (◆) and product distribution, 2,3-DMBP (■), 3,4-DMBP (▲) and others (X). Reaction conditions: see table notes to Table 2; reaction time (h) = 4.

Table 5  
Recycling of H-beta in the benzylation of *o*-xylene<sup>a</sup>

Run	Change in SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Conversion of BOC <sup>b</sup> (wt.%)	TOF of BOC conv. <sup>c</sup> (10 <sup>-5</sup> s <sup>-1</sup> mol <sup>-1</sup> Al)	Product distribution <sup>d</sup> (wt.%)			Percentage of crystallinity of H-beta
				2,3-DMBP	3,4-DMBP	Others	
1 (parent catalyst)	26.0	25.9	25.0	1.2	96.7	2.1	100
2	27.4	12.4	11.2	–	96.8	3.2	80.5
3	29.2	8.1	8.7	–	96.7	3.3	71.4

<sup>a</sup>Reaction conditions same as given in Table 2; reaction time (h) = 6.

<sup>b,c,d</sup>See table notes to Table 2.

*o*-xylene is markedly affected by the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of H-beta. The higher the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of H-beta, the lower the BOC conversion. The conversion of BOC over 26, 50 and 80 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of H-beta is found to be 25.9, 7.6 and 3.9 wt.%, respectively. The corresponding selectivity for 3,4-DMBP is 96.7, 96.2 and 100 wt.%, respectively.

### 3.5. Effect of reaction temperature

The temperature dependency of this reaction is shown in Table 4. The turnover rates of BOC conversion over zeolite H-beta increases steadily from 21.0 to 90.8 × 10<sup>-5</sup> s<sup>-1</sup> mol<sup>-1</sup> Al as the temperature is raised from 393 to 411 K. The selectivity for 3,4-DMBP remains nearly constant through out the range of temperature studied. The apparent activation energy for BOC conversion over H-beta was found to be 89.0 KJ mol<sup>-1</sup>.

### 3.6. Effect of catalyst concentration

The effect of catalyst concentration in the range of 0.19–0.38 g mol<sup>-1</sup> of BOC on the conversion of BOC is studied at 411 K for 6 h of reaction over zeolite H-beta as catalyst. The catalyst to BOC ratios are changed by keeping the constant concentration of BOC in the reaction mixture. When the catalyst to BOC ratio is increased from 0.19 to 0.38, the conversion of BOC is also found to increase from 9.8 to 35.7 wt.%, respectively (Fig. 2). Furthermore, it is observed that the concentration of the unwanted products (others) decreases with the increase in

catalyst/BOC ratio. These results confirm that with an increase in catalyst loading the conversion of BOC increases linearly because of the increase in the total number of acid sites available for the reaction.

### 3.7. Effect of *o*-xylene / BOC molar ratio

Fig. 3 shows the effect of varying the *o*-xylene/BOC molar ratio in the reaction mixture on the activity of H-beta and product distribution at a fixed *o*-xylene concentration. Thus an increase in the conversion of BOC is observed with the increase in *o*-xylene/BOC molar ratio. The conversion of BOC at 1, 3, 5 and 7 molar ratios of *o*-xylene to BOC is found to be 3.2, 15.1, 22.1 and 28.7 wt.%, respectively. The selectivity for 3,4-DMBP remains roughly constant beyond the molar ratio of 3 (*o*-xylene/BOC). The formation of dibenzoylated

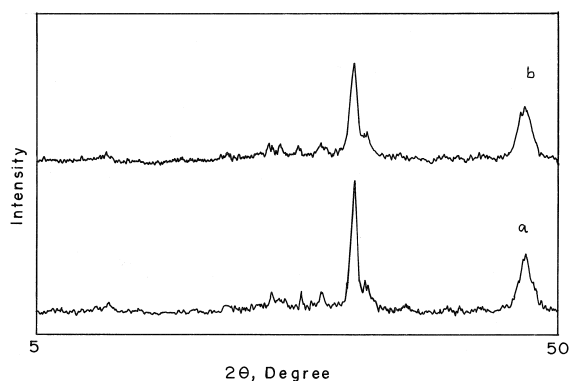


Fig. 4. X-ray diffraction patterns of fresh H-beta (a) and H-beta recycled third time (b).



products (others) is minimized with the increase of *o*-xylene to BOC molar ratios in the benzoylation of *o*-xylene (Fig. 3).

### 3.8. Catalyst recycle

The results of the catalyst recycling experiments using zeolite H-beta in the benzoylation of *o*-xylene are shown in Table 5. After completion of the reaction of each recycle for 6 h, the catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone, calcined at 773 K for 16 h in the presence of air and characterised for its chemical composition ( $\text{SiO}_2/\text{AlO}_3$ ) and crystallinity. The activity of the catalyst decreases progressively on recycling, however, selectivity for 3,4-DMBP remains unaffected (Table 5). In order to check the structure and crystallinity of the catalyst after reaction, X-ray powder diffraction patterns were recorded. XRD measurement indicated that the catalyst retains the H-beta structure and the crystallinity was found to be 71.4% (after third recycle) when compared to the parent catalyst (100% crystallinity) (Table 5, Fig. 4). The HCl liberated during the reaction promotes the extraction of aluminum to some extent from the framework positions of the zeolite H-beta. Such types of extractions and a little decrease in crystallinity of H-beta may be responsible for

the decrease in catalytic activity after each cycle. The results reported here are in good agreement with the earlier reported data for the acylation of aromatics using zeolite catalysts [18].

### 3.9. Benzoylation of isomeric xylenes (*o*-, *m*-, *p*-)

*Ortho*-, *meta*- and *para*-xylenes are separately acylated by benzoyl chloride over H-beta catalyst at 411 K under identical reaction conditions. The performance of zeolite H-beta is compared with that of conventional catalyst,  $\text{AlCl}_3$ , for each reaction. The results are shown in Table 6. The position of methyl groups on the benzene ring plays an important role in defining the type of products. The benzoylation of *o*-xylene leads to the formation of 3,4-DMBP in higher selectivity (94.7 wt.%). With  $\text{AlCl}_3$ , the benzoylation of *o*-xylene gave a conversion of BOC 64.4 wt.% and a product selectivity (3,4-DMBP) of 76.5 wt.%. With *m*-xylene, the reaction gives mainly 2,4-DMBP with a selectivity of 91 wt.%. For the same reaction,  $\text{AlCl}_3$  gave 91.3 wt.% selectivity and 78.2 wt.% conversion of BOC. Similarly, benzoylation of *p*-xylene gives almost single monoacylated product, i.e., 2,5-DMBP with a BOC conversion of 22.1 wt.% and a selectivity of 96.7 wt.%. With  $\text{AlCl}_3$ , the BOC conversion and selectivity are

Table 6  
Benzoylation of xylenes (*o*-, *m*-, *p*-)<sup>a</sup>

Xylenes	Catalyst	Reaction time (h)	Conversion of BOC <sup>b</sup> (wt.%)	TOF of BOC conversion <sup>c</sup> ( $10^{-5} \text{ s}^{-1} \text{ mmol}^{-1} \text{ Al}$ )	Product distribution <sup>d</sup> (wt.%)					
					2,3-DMBP	3,4-DMBP	2,6-DMBP	2,4-DMBP	2,5-DMBP	Others
<i>o</i> -xylene	H-beta	1	12.0	69.7	–	100.0	–	–	–	–
		19	52.8	–	2.8	94.7	–	–	–	2.5
<i>m</i> -xylene	$\text{AlCl}_3$	1	64.4	59.8	7.3	76.5	–	–	–	16.2
		H-beta	1	4.3	24.9	–	–	12.3	85.7	–
<i>p</i> -xylene	H-beta	19	15.5	–	–	–	7.0	91.0	–	2.0
		1	78.2	72.6	–	–	6.4	91.3	–	2.3
<i>p</i> -xylene	$\text{AlCl}_3$	1	6.2	36.0	–	–	–	–	93.3	6.7
		19	22.1	–	–	–	–	–	96.7	3.3
	$\text{AlCl}_3$	1	87.2	81.0	–	–	–	–	85.8	14.2

<sup>a,b,c</sup> See table notes to Table 2.

<sup>d</sup> 2,3-DMBP = 2,3-dimethylbenzophenone; 3,4-DMBP = 3,4-dimethylbenzophenone; 2,6-DMBP = 2,6-dimethylbenzophenone; 2,4-DMBP = 2,4-dimethylbenzophenone; 2,5-DMBP = 2,5-dimethylbenzophenone; others = consecutive products.

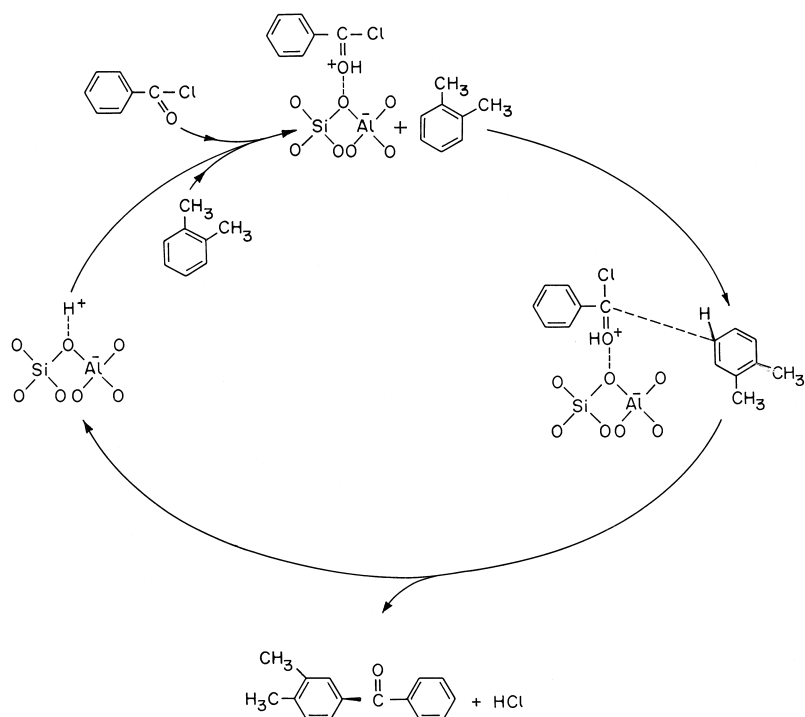


Fig. 5. A plausible mechanism for the benzoylation of *o*-xylene using zeolite catalyst and benzoyl chloride.

87.2 wt.% and 85.8 wt.%, respectively. It can be concluded that xylenes may be benzoylated to the corresponding ketones [26,27].

### 3.9.1. Mechanism

It seems reasonable from the results presented in this paper and earlier reports [12,18] that the benzoylation of *o*-xylene proceeds through electrophilic substitution. Fig. 5 shows the schematic diagram of the catalytic cycle which is in agreement with the reported data [12,18,25–29]. The figure suggests that acidic zeolite polarizes the benzoyl chloride molecule into an electrophile ( $C_6H_5CO^+$ ) which then attacks the *o*-xylene ring resulting in the formation of dimethylbenzophenones.

## 4. Conclusions

In summary, *o*-xylene can be benzoylated selectively to 3,4-DMBP using zeolites as cata-

lyst and benzoyl chloride as benzoylating agent. Zeolite H-beta exhibits higher activity and selectivity than that of the other zeolite catalysts. Conventional homogeneous non shape-selective Lewis acid catalyst  $AlCl_3$  produces a higher amount of dibenzoylated products (consecutive products) and lower amount of 3,4-DMBP under identical reaction conditions. The higher activity of H-beta may be attributed to its stronger acid sites and mesoporous system. The catalytic activity of H-Na (13.6) beta and H-Y were found to be almost identical. However, the former was more selective due to the small pore openings than that of H-Y.  $RE^{3+}$ -exchanged zeolite Y enhanced the conversion of BOC considerably due to the higher strength of acid sites generated by  $RE^{3+}$ -cations. H-ZSM-5 and H-mordenite were found to be less active compared to other zeolite catalysts. The higher yield of product can be achieved by increasing the values of the reaction parameters such as: reaction time, catalyst concentration and reaction

temperature, while the conversion is found to decrease with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio and  $\text{Na}^+$  ion exchange of H-beta. The decrease in activity with recycling experiments may be attributed in part to the changes in chemical composition and crystallinity of zeolite H-beta by HCl, which is a by-product of the reaction. The formation of dimethyl benzophenone is explained by an electrophilic attack of the benzoyl cation ( $\text{C}_6\text{H}_5\text{CO}^+$ ) on the *o*-xylene ring whose formation is facilitated by the stronger acid sites of catalyst.

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