Selective benzoylation of biphenyl to 4-phenylbenzophenone over zeolite H-beta

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Abstract

Liquid phase benzoylation of biphenyl (BP) to 4-phenylbenzophenone (4-PBP) with benzoyl chloride (BOC) has been investigated at atmospheric pressure in the presence of various zeolite catalysts. Conventional homogeneous catalyst, $AlCl_3$, is also included for comparison. Under identical reaction conditions, zeolite H-beta is considerably more active than the other zeolite catalysts, whereas $AlCl_3$ shows higher PBP yield but less selectivity than the H-beta in the benzoylation of BP. The conversion of BP, rate of BP conversion (TOF: turnover frequency), selectivity to 4-PBP and 4-PBP/2-PBP ratio over H-beta after 6 h of reaction time and at 443 K are ca. 41.0%, 31.7 (10^{-5} s^{-1} mol^{-1} Al), 97.4% and 37.4, respectively. For comparison, the conversion of BP, TOF, selectivity to 4-PBP and 4-PBP/2-PBP ratio over $AlCl_3$ after 0.5 h of reaction time, under identical reaction conditions, are estimated to be 48.6%, 72.1 (10^{-5} s^{-1} mol^{-1} Al), 80% and 4.0, respectively. A higher amount of 2-PBP (20%) is achieved over non-shape-selective $AlCl_3$ as compared to the zeolite H-beta (2.6%). Acidity and structure of the zeolites play an important role in the conversion of BP, rate of BP conversion and products distribution. Acidity of the zeolite catalysts is measured by the temperature-programmed desorption of ammonia. The effect of reaction time, catalyst concentration, reaction temperature and BOC/BP molar ratio on the catalyst performance is examined in order to optimise the conversion of BP and selectivity to 4-PBP. The conversion of BP using zeolite H-beta is increased significantly with the increases in reaction time, catalyst concentration, reaction temperature and BOC to BP molar ratio. The acetylation and propionylation of BP is also investigated over zeolite H-beta catalyst. In addition, the influence of various acylating agents (BOC, benzoic anhydride, propionyl chloride, propionic anhydride, acetyl chloride, acetic anhydride) is also seen on the conversion of BP and selectivity for the *para*-products. In the acylation reactions, the conversion of BP decreases in the following order: benzoylation > propionylation > acetylation. H-beta is recycled two times (fresh plus two cycles) and a decrease in BP conversion is observed after each cycle, which is related to the minor dealumination of zeolite catalyst by HCl (formed during reaction). The formation of acylated products of BP is explained by an electrophilic attack of acyl cation ($R–CO^+$; where $R = C_6H_5–$ or $CH_3CH_2–$ or $CH_3–$) on the BP ring, whose formation is facilitated by acid sites of the zeolite catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzoylation of biphenyl; 4-Phenylbenzophenone; Zeolite H-beta

1. Introduction

4-Phenylbenzophenone (4-PBP) is used as an important intermediate in the pharmaceutical industry [1]. It is also used in the synthesis of antifungal

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bifonazole, a skin-penetrating fungicide, by reducing 4-PBP with NaBH$_4$, chlorinating the resulting compound with SO$_2$Cl$_2$ and then refluxing with imidazole [2,3]. The photochromic benzopyran compounds are prepared when 4-PBP was treated with Li acetylide in THF and the product was refluxed with 2-hydroxydibenzofuran [4]. In addition, 4-PBP is also used in the synthesis of photochromic naphthopyran compounds for coatings, lenses and other optical materials [5], fungicidal (arylmethyl) imidazoles [6] and as a photoinitiator [7]. Acylation of biphenyl with acyl halides, which is a typical example of Friedel–Crafts acylation, is generally known to proceed over the homogeneous Lewis acid catalyst AlCl$_3$ [8]. 4-PBP is prepared in 74% yield by treatment of benzoyl chloride with AlCl$_3$ in CHCl$_3$ at room temperature, followed by addition of biphenyl into refluxing solution of complex of benzoyl chloride with AlCl$_3$ [1]. Improved synthesis of 4-PBP is carried out by stirring benzoyl chloride with biphenyl and AlCl$_3$ in the presence of nitrobenzene at 343–393 K, which gave 94.2% yield of 4-PBP [9]. Trace amounts of FeCl$_3$, Fe acetylacetonate and salicylate, powder of Fe and Fe$_2$(SO$_4$)$_3$ also catalyse the benzoylation of biphenyl, giving 61–84% yield of 4-PBP with 100% selectivity at 393–448 K [10]. The only detailed investigation of Friedel–Crafts reactions on biphenyl was carried out by Adam [11], who studied the reactions of several halogenated hydrocarbons and acid derivatives. Several ketones have been prepared by various workers [12–14]. The *ortho*- and *meta*-phenylacetophenones were prepared from acetic anhydride by the low temperature Grignard procedure of Newman and Booth [15] and Campaigne and Reid [16]. In a rather extensive investigation Silver and Lowy [17] and Long and Henze [18] have shown conclusively that acyl halides reacts with biphenyl in the Friedel–Crafts reactions to form 4-monoacetylbiphenyl and 4,4′-diacetylbiphenyl products. 4-Phenylacetophenone (4-PAP) is also prepared by the acetylation of biphenyl with acetic anhydride in the presence of anhydrous HF and BF$_3$ [19]. The use of Lewis acid catalysts is fraught with problems, such as their handling, the necessity of using large amounts with substrates and separation from the products. Some catalysts are toxic. In addition, halides of iron and aluminium, being strong Lewis acids also, catalyse other undesirable reactions such as isomerisation and *trans*-alkylation reactions [20]. In view of the above, it was of interest to develop a new solid catalyst for the selective synthesis of 4-PBP, 4-phenylpropiophenone (4-PPP) and 4-PAP. Zeolite catalysts, due to their shape-selectivity, thermostability, the easy separation from the products and the possibility of regeneration of the deactivated catalysts, are used extensively in the petroleum refining and petrochemical industries for various cracking, hydrocracking, isomerisation, alkylation, dehydrogenation and rearrangement reactions of hydrocarbons and their derivatives. The use of zeolite catalysts in the synthesis of fine chemicals is of growing importance in recent years [21]. Recently, zeolite catalysts were found to be active in the acylation of aromatics [22–34]. However, the utility of zeolite catalysts in the acylation of biphenyl has not been reported till date and hence in this paper we report the benzoylation of biphenyl with benzoyl chloride over zeolite H-beta for the first time (Scheme 1).

The objective of the study is to replace the conventional homogeneous Lewis acid catalyst, AlCl$_3$, by the shape-selective and recyclable solid zeolite H-beta catalyst and to enhance the conversion of biphenyl and yield of 4-PBP in the benzoylation of biphenyl
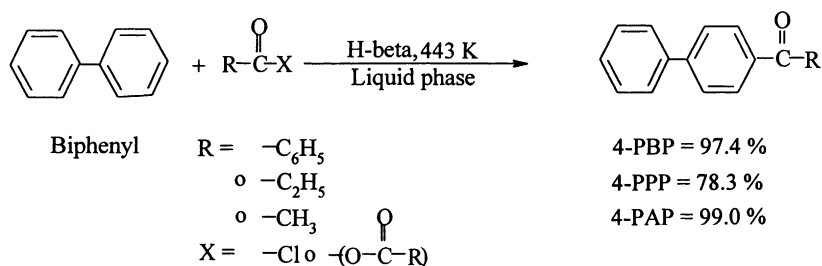
Scheme 1.

(Scheme 1). Here, we also report the results obtained for the benzoylation of biphenyl under various reaction conditions and the effect of some variables on the catalyst performance. Further, the acetylation and propionylation of BP is also investigated using zeolite H-beta as catalyst (Scheme 1). The results obtained over H-beta are compared with those obtained using the Lewis acid catalyst, AlCl₃.

2. Experimental

2.1. Materials

Zeolites Na-Y, mordenite, H-beta and ZSM-5 were prepared using the methods described in [35–38]. The synthesised zeolites were washed with deionised water, dried and calcined at 813 K for 16 h in the presence of air to eliminate the organic templates from the zeolite channels. The resulting forms of calcined zeolites were thrice NH_4^+-exchanged using the following conditions: 10 ml NH_4NO_3 (1 M)/g zeolite; 353 K; 8 h exchanged run; pH 7–8. The NH_4^+-exchanged samples were again calcined at 823 K for 8 h to get their protonic forms. The procedure for the exchange of RE^+ into NH_4^+-Y has been reported elsewhere [29].

2.2. Characterisation

The SiO_2/Al_2O_3 ratio of various zeolites and degree of ion-exchange were estimated by a combination of wet and atomic absorption methods (Hitachi 800). X-ray powder diffraction (XRD) was carried out on a Rigaku D-Max/III-VC model using the Cu Kα radiation and was used to evaluate the peak positions of various zeolite samples. The surface area of the samples was measured by nitrogen BET method using an area meter. The size and morphology of the zeolite catalysts were measured with a scanning electron microscope (SEM, Cambridge Stereoscan 400). Acidity of the zeolite catalysts was measured by the temperature-programmed desorption of ammonia. The procedure for the measurement of acidity of the zeolite samples is reported in [39].

2.3. Catalytic reaction experiments

Anhydrous AR grade chemicals were used without further purification. The liquid phase acylation of biphenyl with acylating agent was carried out in a 50 ml two necked flask attached to a condenser and a septum. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, biphenyl and acylating agent were added in a required molar ratio to the activated zeolite catalyst (0.5 g). The reaction mixture was magnetically stirred and heated to the required temperature at atmospheric pressure. The product samples were withdrawn at regular intervals of time and analysed periodically on a gas chromatograph (HP 6890) equipped with a flame ionisation detector and a capillary column (5 μm thick cross-linked methyl silicone gum, 0.2 mm × 50 m long). The products were also identified by injecting authentic samples and GCMS (Shimadzu 2000 A) analysis.

Finally, the percentage conversion of biphenyl is defined as the total percentage of biphenyl transformed. The rate of biphenyl conversion (TOF: turnover frequency, $10^{-5}\,s^{-1}\,mol^{-1}\,Al$) was calculated as moles of BP converted per second per mole of aluminium. The selectivity to a product is expressed as the amount of a particular product divided by the amount of total products and multiplied by 100.

3. Results and discussion

3.1. Catalyst characterisation

Table 1 lists the SiO_2/Al_2O_3 ratios, percentage of H^+- or RE^{3+}-exchange, crystal size and surface area of zeolites. These data reveal that zeolite samples are highly crystalline. No reflections of a dense phase or any other impurity are found. Table 1 also illustrates the amount of NH_3 desorbed from zeolites in different temperature steps.

3.2. Catalytic activity of various catalysts

The results of the catalytic activities in the benzoylation of biphenyl with benzoyl chloride using H-beta, H-ZSM-5, H-Y and RE-Y are depicted in Table 2. The results with Lewis acid catalyst, AlCl₃, are compared under identical reaction conditions. The main product of the reaction is 4-PBP. A small amount of 2-PBP is also observed in some cases. The formation of 2-PBP and 4-PBP results from the aromatic substitution of

Table 1
Properties and acid strength distribution of zeolite catalysts

Catalyst	SiO_2/Al_2O_3 (molar ratio)	Degree of H^+- or RE^{3+}-exchange[a] (%)	Crystal size (μm)	Surface area[b] (m^2/g)	NH$_3$ desorbed (mmol/mol Al) in various steps					NH$_3$ chemisorbed at 303 K[c] (mmol/mol Al)
					303–353 K	353–433 K	433–513 K	513–653 K	653–773 K	
H-beta	26.0	>98	0.5	745	116.7	200.0	41.7	133.3	133.3	625.0
H-ZSM-5	41.0	>98	0.4	413	689.2	200.5	62.7	325.8	263.2	1516.3
H-Y	4.1	>98	1.0	615	50.9	96.5	86.0	19.3	1.8	254.4
H-RE-Y[d] (70.6)	4.1	>70.6	1.0	659	29.8	17.5	45.6	19.3	17.5	129.8

[a] Cation-exchange (H^+ or RE^{3+}) values reported as percent of the total cation sites, taken as the aluminium content 100%.

[b] Measured by N_2 adsorption.

[c] NH$_3$ chemisorbed at 303 K (mmol/mol Al).

[d] Value given in parentheses represents the percentage of RE^{3+}-exchange in Na-Y zeolite.

Table 2
Benzoylation of biphenyl[a]

Catalyst	Reaction time (h)	Biphenyl conversion (%)	TOF[b] $(10^{-5} \, s^{-1} \, mol^{-1} \, Al)$	Product distribution[c] (%)		4-PBP/2-PBP
				2-PBP	4-PBP	
H-beta	6	41.0	31.7	2.6	97.4	37.4
	12	58.3	22.5	2.7	97.3	36.1
H-ZSM-5	6	5.2	6.0	0	100	0
	12	9.0	5.2	0	100	0
RE[d]-Y	6	3.4	0.5	0	100	0
	12	7.5	0.6	0	100	0
H-Y	6	3.2	0.5	0	100	0
	12	5.6	0.5	0	100	0
AlCl$_3$	0.5	48.6	72.1	20	80	4.0
	1	63.2	46.8	20	80	4.0

[a] Reaction conditions: catalyst 0.5 g; biphenyl 0.01 mol; benzoyl chloride 0.01 mol; reaction temperature 443 K.
[b] TOF is given as moles of BP transformed per second per mole of aluminium.
[c] 2-PBP: 2-phenylbenzophenone; 4-PBP: 4-phenylbenzophenone.
[d] 70.6% RE^{3+}-exchange in NH_4-Y zeolite.

biphenyl by parallel reactions. The activities of catalysts are compared using data after 6 h runs.

The most interesting feature of the reaction is that conversion of BP, rate of BP conversion, product distribution and 4-PBP to 2-PBP ratio depend on the type of zeolite used. As can be seen from Table 2, zeolite H-beta is found to be more active than any other zeolite. The H-ZSM-5, RE-Y and H-Y are less active and have almost identical activities. The conversion of BP, rate of BP conversion and selectivity for 4-PBP over H-beta, H-ZSM-5, RE-Y and H-Y after 6 h of reaction time are found to be 41.0, 5.2, 3.4 and 3.2%; 31.7, 6.0, 0.5 and 0.5 ($10^{-5} \, s^{-1} \, mol^{-1}$ Al), and 97.4, 100, 100 and 100%, respectively. AlCl$_3$ produces 20% 2-PBP and 80% 4-PBP at 48.6% conversion level of BP after 0.5 h reaction time. The 4-PBP/2-PBP ratio over H-beta was found to be about 10 times higher (4-PBP/2-PBP = 37.4) than that of non-shape-selective AlCl$_3$ (4-PBP/2-PBP = 4.0). Among the zeolites studied, H-beta revealed the highest PBP yield and rate of BP conversion, which may be attributed to its stronger acid sites (Table 1) as seen from NH$_3$ desorption experiment. In order to gain an understanding of the acidity of the catalyst, the desorption of NH$_3$ was carried out in five steps (303–353, 353–433, 433–513, 513–653 and 653–773 K) after allowing the catalyst to adsorb ammonia at room

temperature and flushed with nitrogen to remove physisorbed ammonia. The results of the NH$_3$ desorption are listed in Table 1. With the increase in the amount of strong acid sites, the conversion of BP enhances, which means that medium and strong acid sites of H-beta promoted the reaction. Being large pore and weaker acid sites, HY and RE-Y showed less PBP yield for the same reaction. The lower yield of PBP over H-ZSM-5 in the benzoylation of BP may be attributed to its pore openings being smaller than the size of the products. The catalysts used in this study, show the following decreasing order of activity after 6 h of reaction time: AlCl$_3$ > H-beta > H-ZSM-5 > RE-Y ≈ H-Y. The results indicate that mainly *ortho*- and *para*-substitutions take place over zeolite H-beta, which is expected for an electrophilic aromatic substitution pathway [40]. Acidic zeolites polarise the benzoyl chloride into an electrophile ($C_6H_5CO^+$), which attacks on the aromatic ring, resulting in the formation of phenylbenzophenones [40–42].

3.3. Duration of the run

The influence of duration of the run on the performance of various catalysts under identical reaction conditions in the benzoylation of biphenyl was also tested (Fig. 1). Increasing reaction time increased
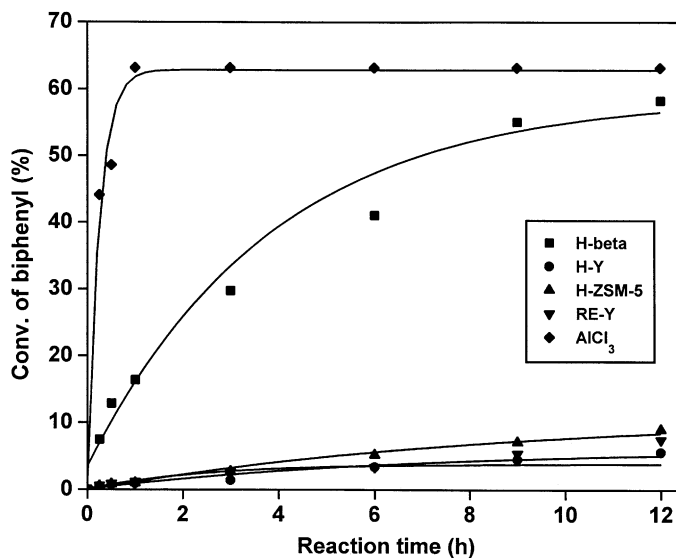
Fig. 1. Conversion of BP (%) vs. reaction time over various catalysts. Reaction conditions as in Footnote 'a' of Table 2.

the conversion of biphenyl over all catalysts. H-beta yielded a considerably superior performance throughout the reaction and its PBP yield was found to be higher compared with those of other zeolite catalysts. The reason could be the, the higher strength of acid sites of zeolite H-beta. The other catalysts (H-ZSM-5, RE-Y and H-Y) are found to be much less active. $AlCl_3$ is the most active catalyst and within 1 h a high yield of PBP (63.2% conversion of BP) is obtained in the benzoylation of BP. The catalytic activity of various catalysts used in this study after 12 h of reaction time can be arranged in the following order: $AlCl_3 >$ H-beta > H-ZSM-5 > RE-Y > H-Y.

3.4. Influence of reaction time using zeolite H-beta

A typical reaction course according to the time is pointed out in Fig. 2 for the transformation of biphenyl over zeolite H-beta at 443 K. The conversion of biphenyl increased almost linearly up to 8 h of reaction time and then a marginal increase in the conversion of BP is observed. BP leads mainly to 4-PBP in 97.6% selectivity at 0.25 reaction time and remains almost unchanged up to 12 h. A small amount of 2-PBP is also observed until the end of the reaction. The results show that the reaction time influenced the

conversion of BP, but did not affect the 4-PBP/2-PBP isomer ratio to a great extent.

3.5. Influence of H-beta/BP (w/w) ratio

In order to clarify the effects of catalyst concentration on the conversion of BP, rate of BP conversion and product distribution, the catalyst concentration (H-beta/BP ratio (w/w)) was increased from 0.06 to 0.49 (Fig. 3). A sharp increase in the conversion of BP is observed when H-beta/BP (w/w) ratio was raised from 0.06 to 0.19. Afterwards, a slow but steady increase in the conversion of BP is noticed in the benzoylation of BP. No change in the product distribution is seen due to the change in catalyst concentration. A marginal increase in the rate of BP conversion (TOF) is seen up to 0.19 ratio of H-beta to BP, whereas it decreases continuously and linearly due to the increase in catalyst concentration and a corresponding increase in the concentration of aluminium in the total amount of zeolite H-beta used in the benzoylation of BP.

Fig. 4 shows the conversion profile of BP versus reaction time using different catalyst concentrations (H-beta/BP ratio (w/w)). In Fig. 4, one may observe that the H-beta/BP (w/w) ratio had a strong effect on the conversion of BP and on the amount of 4-PBP
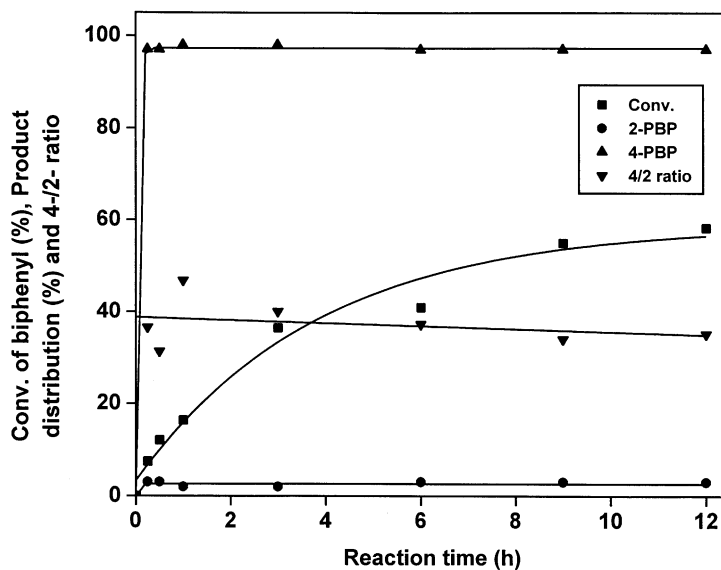
Fig. 2. Effect of reaction time on the conversion of BP (%), product distribution (%) and 4-PBP/2-PBP ratio using zeolite H-beta as catalyst. Reaction conditions as in Footnote 'a' of Table 2.

obtained. A rapid increase in the conversion of BP is observed at the early stages (up to 6 h) of the reaction on all H-beta/BP (w/w) ratios. The maximum increase in the conversion of BP with reaction time is found for a H-beta/BP (w/w) ratio of 0.49.

3.6. Influence of reaction temperature

The effect of reaction temperature is studied on the conversion of BP, rate of BP conversion and product distribution in the benzoylation of BP. The results are
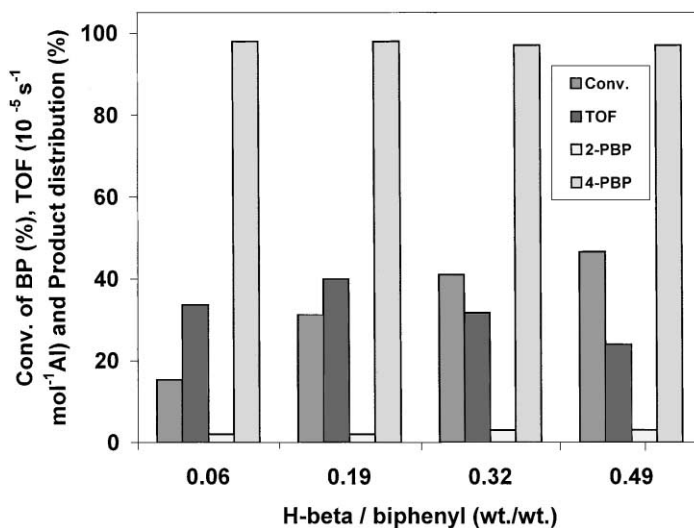

Fig. 3. Effect of H-beta/BP (w/w) ratio on the conversion of BP (%), TOF ($10^{-5} s^{-1} mol^{-1} Al$) and product distribution (%). Reaction conditions as in Footnote 'a' of Table 2; reaction time 6 h.
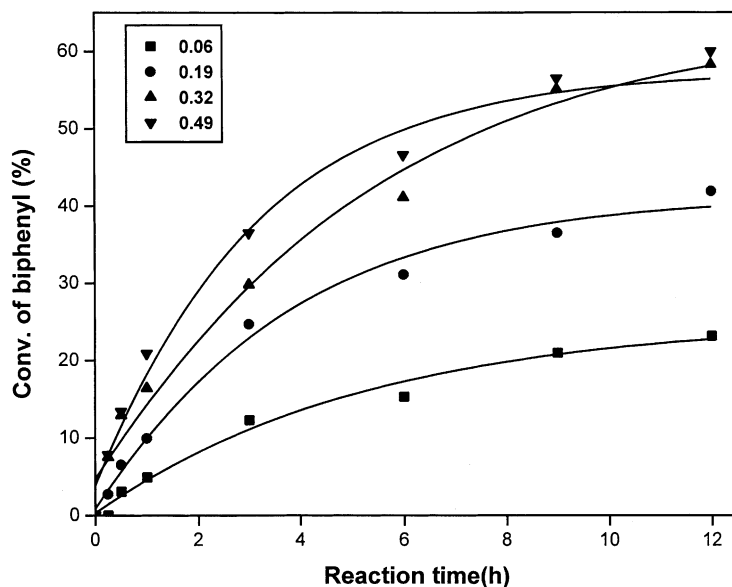
Fig. 4. Effect of different H-beta/BP (w/w) ratio on the conversion of BP (%) vs. reaction time (h). Reaction conditions as in Footnote 'a' of Table 2.

depicted in Fig. 5. When the temperature is increased from 433 to 453 K, both the conversion of BP and rate of BP conversion increased from 6.7 to 46.4%, and 5.2 to 35.8 $(10^{-5} \, s^{-1} \, mol^{-1} \, Al)$, respectively. However, the selectivity for 4-PBP remains nearly unchanged with the increase in reaction temperature, as shown in Fig. 5.

The conversion of BP at various reaction temperatures over a period of 12 h using zeolite H-beta increases sharply at the initial stages of the reaction and
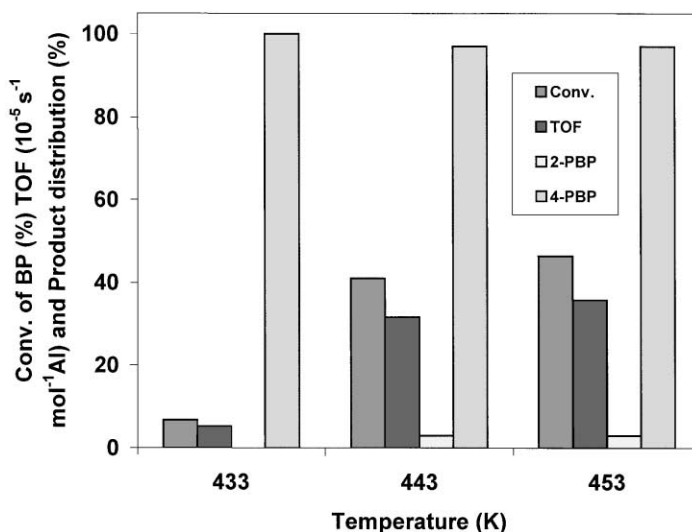

Fig. 5. Effect of reaction temperature on the conversion of BP (%), TOF $(10^{-5} \, s^{-1} \, mol^{-1} \, Al)$ and product distribution (%). Reaction conditions as in Footnote 'a' of Table 2; reaction time 6 h.

Fig. 6. Effect of BOC/BP molar ratio on the conversion of BP (%), TOF ($10^{-5}\,s^{-1}\,mol^{-1}$ Al) and product distribution (%). Reaction conditions as in Footnote 'a' of Table 2; reaction time 6 h.

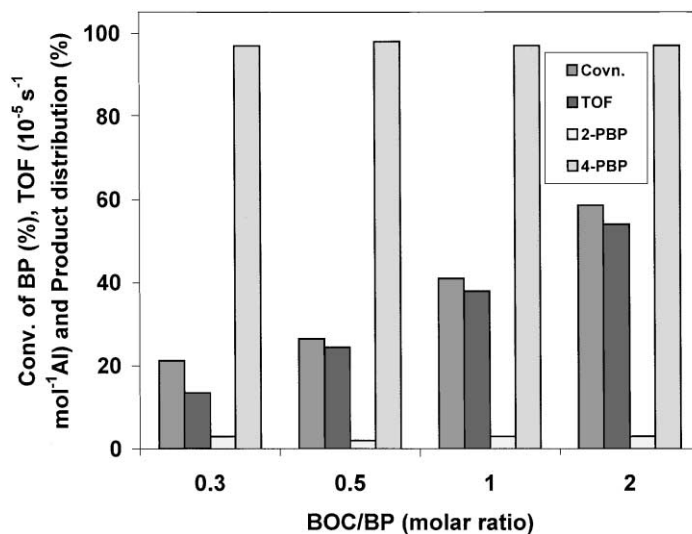finally reaches a relatively steady-state value over all temperatures.

3.7. Influence of BOC/BP molar ratio

Fig. 6 exhibits the effect of the BOC/BP molar ratio on the catalytic activity of H-beta. The ratio is changed while keeping the amount of biphenyl constant. The data at 443 K show that, as the BOC/BP molar ratio is increased from 0.3 to 2, the conversion of BP and rate of BP conversion increase linearly from 21.2 to 58.6%, and 16.4 to 45.2 ($10^{-5}\,s^{-1}\,mol^{-1}$ Al), respectively. In addition, the selectivity to 4-PBP is found to be unaffected over the wide range of BOC/BP ratio. The conversion of BP versus reaction time increased with all molar ratios of BOC/BP, and the fact that the conversion of BP is also stabilised from an early stage till 7 h of the reaction time. A higher increase in the BP conversion with reaction time is observed when BOC/BP molar ratio of two is used in the benzoylation of biphenyl.

3.8. Acetylation, propionylation and benzoylation of biphenyl

The results of the benzoylation of biphenyl are compared at 443 K with the results of propionylation and

acetylation of biphenyl using zeolite H-beta as catalysts and acyl halides (benzoyl chloride, propionyl chloride, and acetyl chloride, respectively) as acylating agents (Table 3). The propionylation and acetylation of biphenyl lead to the formation of 2-PPP, 4-PPP and 2-PAP and 4-PAP, respectively. The conversion and rate of BP conversion in the acylation reactions under similar reaction conditions decrease in the following order: benzoylation > propionylation > acetylation. The conversion of BP and rate of BP conversion in the benzoylation, propionylation and acetylation of biphenyl using acyl halides as acylating agents over zeolite H-beta are found to be 41.0, 11.1 and 6.7%, and 31.7, 8.6 and 5.2 ($10^{-5}\,s^{-1}\,mol^{-1}$ Al), respectively. The corresponding selectivities for 4-PBP, 4-PPP and 4-PAP are 97.4, 78.3 and 99.0%, respectively.

Acid anhydrides (benzoic anhydride, propionic anhydride and acetic anhydride) are also employed as acylating agents instead of acyl chlorides in the acylation of biphenyl. Acid anhydrides are also capable of acylating biphenyl. The conversion of BP and rate of BP conversion in the acylation of biphenyl with benzoic anhydride, propionic anhydride and acetic anhydride are found to be 30.3, 10.1 and 4.2%, and 23.4, 7.8 and 3.2 ($10^{-5}\,s^{-1}\,mol^{-1}$ Al), respectively. The corresponding selectivities for 4-PBP, 4-PPP and 4-PAP are 98, 100 and 99%, respectively. The yield of PBP

Table 3
Influence of acylating agent[a]

Agent	Conversion of BP (%)	TOF[b] $(10^{-5} s^{-1} mol^{-1} Al)$	Product distribution (%)[c]						4-PBP/ 2-PBP
			2-PBP	4-PBP	2-PPP	4-PPP	2-PAP	4-PAP	
C_6H_5COCl	41.0	31.7	2.6	97.4	–	–	–	–	37.4
$(C_6H_5CO)_2O$	30.3	23.4	2.0	98.0	–	–	–	–	49.0
C_2H_5COCl	11.1	8.6	–	–	21.7	78.3	–	–	3.6
$(C_2H_5CO)_2O$	10.1	7.8	–	–	0	100	–	–	0
CH_3COCl	6.7	5.2	–	–	–	–	1.0	99.0	99.0
$(CH_3CO)_2O$[d]	4.2	3.2	–	–	–	–	1.0	99.0	99.0

[a] Reaction conditions: catalyst 0.5 g; biphenyl 0.01 mol; acylating agent 0.01 mol; reaction temperature 443 K; reaction time 6 h.

[b] TOF is given as moles of BP transformed per second per mole of aluminium.

[c] 2-PBP: 2-phenylbenzophenone; 4-PBP: 4-phenylbenzophenone; 2-PPP: 2-phenylpropiophenone; 4-PPP: 4-phenyipropiophenone; 2-PAP: 2-phenylacetophenone; 4-PAP: 4-phenylacetophenone.

[d] Reaction temperature 453 K.

over zeolite H-beta in the acylation of biphenyl with acid chlorides and acid anhydrides decreases in the following order: acid chlorides > acid anhydrides.

As a function of reaction time over zeolite H-beta using various acylating agents, benzoyl chloride exhibited higher conversion of BP compared to the other acylating agents. The total conversion of BP reached 58.3% in 12 h using benzoyl chloride as benzoylating agent. Benzoic anhydride was found to be less active than BOC and only 38.3% conversion of BP is noticed after 12 h of reaction time. Other acylating agents gave much less conversion of BP. The conversion of BP after 12 h of reaction time with various acylating agents decreases in the following order: benzoyl chloride > benzoic anhydride > propionyl chloride > propionic anhydride > acetyl chloride > acetic anhydride.

3.9. Catalyst recycling

In order to check the stability and catalytic activity of zeolite H-beta in the benzoylation of biphenyl, three reaction cycles (fresh and two cycles) were carried out using the same catalyst. The results are presented in Table 4. After workup of the reaction mixture, the zeolite H-beta was separated by filtration, washed with acetone and calcined for 16 h at 773 K in the presence of air before use in the next experiment. Thus, the recovered zeolite after each reaction was characterised for its chemical composition by atomic absorption spectroscopy (AAS) and crystallinity by XRD. AAS and XRD studies showed a downward trend in the content of aluminium and crystallinity of H-beta after each cycle. The 4-PBP yield decreases progressively on recycling and the conversion of BP decreases from 41 to 33.7% when H-beta was recycled from fresh to second cycle, respectively, in the benzoylation of biphenyl. The hydrogen halide liberated during the reaction probably promotes the extraction of aluminium to some extent from the framework positions of the zeolite H-beta. The loss of aluminium and a decrease in the crystallinity of zeolite H-beta may be attributed for the decrease in catalytic activity

Table 4
Effect of catalyst recycling[a]

Cycle	SiO_2/Al_2O_3 (molar ratio)	Conversion of BP[b] (%)	Product distribution[c] (%)		4-PBP/2-PBP	H-beta crystallinity (%)
			2-PBP	4-PBP		
Fresh	26.0	4.0	2.6	97.4	37.4	100
First recycle	27.1	35.0	2.0	98.0	43.0	100
Second recycle	33.7	33.0	3.0	97.0	37.3	92.8

[a] Reaction conditions: catalyst 0.5 g; biphenyl 0.01 mol; benzoyl chloride 0.01 mol; reaction temperature 443 K.

[b] TOF is given as moles of BP transformed per second per mole of aluminium.

[c] 2-PBP: 2-phenylbenzophenone; 4-PBP: 4-phenylbenzophenone.

after each cycle. The results reported here are in good agreement with the benzoylation of aromatics using zeolite catalysts [29,34].

4. Conclusions

Zeolite H-beta catalyses the benzoylation of biphenyl efficiently with benzoyl chloride as the benzoylating agent and is superior to other zeolite catalysts. The conventional homogeneous catalyst, $AlCl_3$, does not possess shape-selectivity and favours the formation of a fairly large amount of 2-PBP. A selectivity of the order of 97.4% to 4-PBP is achieved at 41.0% conversion of BP over H-beta, whereas $AlCl_3$ gave lower selectivity to 4-PBP (80%) under certain reaction conditions. A higher strength of acid sites and medium pore size of H-beta are the responsible for the conversion of BP. The effect of reaction time, catalyst concentration, reaction temperature and BOC/BP molar ratio on the catalyst performance is examined in order to optimise the conversion of BP and selectivity to 4-PBP. The conversion of BP using zeolite H-beta increased significantly with an increase in reaction time, catalyst concentration, reaction temperature and BOC to BP molar ratio. The acetylation and propionylation of BP are also investigated over zeolite H-beta catalyst. In addition, other acylating agents (BOC, benzoic anhydride, propionyl chloride, propionic anhydride, acetyl chloride and acetic anhydride) have been used in the conversion of BP for comparison. In the acylation reactions, the conversion of BP decreases in the following order: benzoylation > propionylation > acetylation. The yield of 4-PBP over zeolite H-beta in the acylation of biphenyl with acid chlorides and acid anhydrides decreases in the following order: acid chlorides > acid anhydrides. H-beta was recycled two times (fresh plus two cycles) and a decrease in BP conversion is observed after each cycle, which is related to a minor dealumination of zeolite catalyst and consequently a decrease in the crystallinity of H-beta due to the formation of HCl during the reaction. The formation of acylated products of BP is explained by an electrophilic attack of acyl cation ($R–CO^+$; where $R = C_6H_5–$ or $CH_3CH_2–$ or $CH_3–$) on the BP ring, whose formation is facilitated by acid sites of the zeolite catalysts.

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