Liquid phase selective benzoylation of chlorobenzene to 4,4′-dichlorobenzophenone over zeolite H-beta

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Selective formation of 4,4′-dichlorobenzophenone (>88%) at 19.8 wt% conversion level of 4-chlorobenzoylchloride (4-ClBC) and at 8.4×10^{-4} $s^{-1}mol_{Al}^{-1}$ turnover frequency (TOF) of 4-chlorobenzoylchloride is reported for the first time in the benzoylation of chlorobenzene using 4-ClBC as benzoylating agent and zeolite H-beta as the catalyst.

**KEY WORDS:** benzoylation of chlorobenzene; 4,4′-dichlorobenzophenone; H-beta

1. Introduction

4,4′-dichlorobenzophenone (4,4′-DCBP) is used as photosensitizer and applied to UV-curable coatings or UV-curable inks. Substituted diphenylketones are also used as intermediates for pharmaceutical and agricultural chemicals [1]. 4,4′-DCBP is usually produced by the Friedel–Crafts reactions of chlorobenzene (CB) with 4-chlorobenzoylchloride using Lewis acid catalysts such as AlCl₃, BF₃, TiCl₄, ZnCl₂, *etc.* [2–6], however, these catalysts have several disadvantages; wasting a lot of Lewis acid catalyst AlCl₃, because of the reaction being mostly equimolar and of the difficulty of recycling it after use, and corrosion of containers by evolved acidic gases. In order to overcome these difficulties of Lewis acid catalysts, solid acidic zeolite catalysts meet the requirement for industrial processing of organic chemicals taking into account their environmental advantage. In addition, zeolites are well known shape-selective and thermally stable materials. A number of reactions such as acylation [7–22], alkylation [23], halogenation [24–28] have been described using zeolites as catalyst under liquid phase conditions. However, there is no report in the open literature for the synthesis of 4,4′-DCBP using zeolite H-beta as catalyst. In this paper we disclose the report for the first time of our studies on the catalytic activity of a stable and recyclable H-beta catalyst in the benzoylation of chlorobenzene with 4-ClBC at atmospheric pressure (scheme 1). The influence of catalyst concentration, reaction temperature, CB/4-ClBC molar ratio and recycling of H-beta is also examined on the conversion of 4-ClBC using H-beta. The results obtained over H-beta are compared with that over AlCl₃.

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2. Experimental

Zeolites beta, mordenite and Na-Y were synthesized hydrothermally according to the procedure described elsewhere [29–31]. Del.H-Y was supplied by PQ corporation (CBV 720). The synthesized zeolites were calcined at 823 K in an air stream and changed into their H⁺-forms by repeated exchanges with solution of NH₄NO₃ (1 M solution, 10 ml g⁻¹ zeolite, temperature 353 K, duration 6 h, pH = 7–8; three exchanges). The procedure for the exchange of RE³⁺ into Na-Y has been reported elsewhere [14]. The washed zeolites were dried at 383 K for 2 h and calcined at 773 K for 8 h. The zeolites were characterised by wet chemical analyses and AAS (Hitachi 800) for their chemical composition, X-ray powder diffraction (Rigaku D-Max/III-VC model, Cu Kα radiation) for crystallinity and phase purity and scanning electron microscope (Cambridge
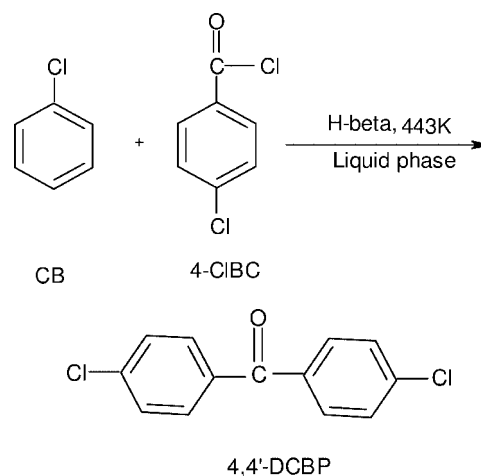
Scheme 1.

Table 1
Properties and acidity 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] ($m^2\,g^{-1}$)	NH_3 chemisorbed at 303 K[c] ($mmol\,g^{-1}$)
H-Beta	26.0	>98	0.5	745	0.75
H-mordenite	22.0	>98	1.0	552	0.71
Del.H-Y	30.0	>98	0.5	665	0.56
H-REY[d]	4.1	>70.6	1.0	659	0.74

[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 ($mmol\,g^{-1}$).

[d] 70.6% RE^{3+}-exchange in NH_4-Y-zeolite.

Table 2
Benzoylation of chlorobenzene to 4,4′-dichlorobenzophenone.[a]

Catalyst	Conv. of 4-ClBC[b] (wt%)	TOF[c] ($10^{-4}\,s^{-1}\,mol_{Al}^{-1}$)	Product distribution (wt%)[d]		
			2,4′-DCBP	4,4′-DCBP	Others
H-beta	19.8	8.4	6	88	6
H-Y	12.4	6.0	10	87	3
RE-Y[e]	1.5	0.1	7	83	10
H-mordenite	1.8	0.6	8	85	7
$AlCl_3$[f]	22.0	6.0	2	84	14

[a] Reaction conditions: catalyst = 0.3 g; catalyst/4-ClBC = 0.078 wt/wt; CB/4-ClBC = 2; chlorobenzene = 0.044 mol; 4-ClBC = 0.022 mol; reaction temperature = 443 K; reaction time = 4 h.

[b] 4-ClBC = 4-chlorobenzoyl chloride.

[c] Turnover rates are expressed as turnover frequency (TOF, moles of 4-ClBC converted $s^{-1}\,mol_{Al}^{-1}$).

[d] 2,4′-DCBP = 2,4′-dichlorobenzophenone; 4,4′-DCBP = 4,4′-dichlorobenzophenone; others = consecutive products.

[e] 70.6% RE^{3+}-exchange in NH_4-Y-zeolite.

[f] Reaction time = 1 h.

Stereoscan 400) for morphology and crystal size. The surface area of the zeolites was measured by the nitrogen BET method using an Omnisorb 100 CX apparatus. The acidity of the zeolites was measured by the procedure described in [14–18,32]. The properties of the zeolites used in this study are given in table 1. The zeolite samples were activated at 438 K for at least 2 h before use in the experiments so as to keep dry reaction conditions.

The catalytic reactions were carried out in a three necked flask (capacity, 50 ml) fitted with condenser, gas supply tube and a septum. The temperature of the reaction vessel was maintained using an oil bath. In the reaction flask, 0.044 mol of chlorobenzene and 0.3 g of zeolite (activated at 438 K for 2 h) and 0.022 mol of 4-chlorobenzoyl chloride were introduced The reaction mixture was stirred and heated to attain the reaction temperature (443 K) in the presence of nitrogen gas. The reaction was monitored by taking the samples of reaction mixture at suitable intervals. The analysis of the reaction mixture was done using a gas chromatograph (HP 6890 series II) with a flame ionisation detector and a 50 m × 0.2 mm capillary column of methyl silicone gum. The products were also identified by GC-MS and compared with authentic samples.

3. Results and discussion

3.1. Influence of various catalysts

Table 2 lists typical values of benzoylation of chlorobenzene by 4-chlorobenzoylchloride over various acidic zeolites. The results obtained over various catalysts are compared under identical reaction conditions with the homogeneous catalyst, $AlCl_3$. The main product of the reaction is 4,4′-dichlorobenzophenone (4,4′-DCBP). Small amounts of 2,4′-dichlorobenzophenone (2,4′-DCBP) and others (dibenzoylated products) are also detected. The formation of 2,4′- and 4,4′-DCBP results from the aromatic substitution of CB by parallel reactions while others are obtained by the consecutive reactions of 2,4′- and 4,4′-DCBP [16,19]. The activities of various zeolite catalysts are compared using data after the 4 h of reaction time under similar reaction conditions whereas the activity and selectivity of $AlCl_3$ is compared after 1 h of reaction time owing to its higher activity and rate of reaction than that of zeolite catalysts. As can be seen from table 2, H-beta exhibits the higher catalytic activity and rate of 4-ClBC conversion (TOF = turnover frequency) among zeolite catalysts. The rate of 4-ClBC conversion (TOF) was found to be several

times higher over H-beta than that of the RE-Y and H-mordenite, whereas dealuminated H-Y (Del.H-Y) is found to be active compared to the RE-Y and H-mordenite. The conversions of 4-ClBC over H-beta, Del.H-Y, RE-Y and H-mordenite are found to be 19.8, 12.4, 1.5 and 1.8 wt%, respectively. The corresponding TOF (10^{-4} s^{-1} mol$_{Al}^{-1}$) are 8.4, 6.0, 0.1 and 0.6×10^{-4} s^{-1} mol$_{Al}^{-1}$, respectively. The homogeneous Lewis acid catalyst, AlCl$_3$, is found to be most active catalyst due to its strong Lewis acidity and the conversion of 4-ClBC, TOF and selectivity for 4,4′-DCBP are found to be 22.0 wt%, 6.0 (10^{-4} s^{-1} mol$_{Al}^{-1}$) and 84.0 wt%, respectively. In addition, the results show that the selectivity for 4,4′-DCBP over H-beta is higher (88.0 wt%) than over the other catalysts. A higher amount of consecutive products formation is observed over AlCl$_3$ due to its non-shape-selective character. From the data in table 2, it is clear that the performance of the catalyst is governed by the acidity and the structure of the zeolites. The higher conversion of 4-ClBC and TOF over H-beta and Del.H-Y seem to be due to the fact that the H-beta exhibits the stronger Brønsted acid sites compared to the other catalysts [8,15,18]. These results indicate that acid strength is the most important factor for the polarisation of ClC$_6$H$_5$COCl (4-ClBC) into an electrophile (ClC$_6$H$_5$CO$^+$) which attacks the CB ring and produces the DCBPs (dichlorobenzophenones) [8,14,33–36]. The little higher selectivity for 4,4′-DCBP over H-beta might be attributed to its peculiar pore opening (5.5 × 7.5 Å) than H-Y (7.4 Å) and H-mordenite (6.5 × 7.0 Å).

The results of the preceding section have revealed that H-beta is the best catalyst for the benzoylation of chlorobenzene to 4,4′-DCBP. The influence of various parameters on the conversion of 4-ClBC and product distribution over H-beta is reported in the following section.

3.2. Influence of catalyst concentration

Figure 1 displays the conversion of 4-ClBC, rate of 4-ClBC conversion (TOF) and product distribution at 4 h reaction time as a function of H-beta/4-ClBC ratio. The different ratios of H-beta/4-ClBC ratio were obtained by varying the amount of the catalyst (H-beta, SiO$_2$/Al$_2$O$_3$ = 26) and keeping the concentration of 4-ClBC constant. A linear increase in the conversion of 4-ClBC from 3.1 to 23.8 wt% was observed when catalyst to 4-ClBC ratio was increased from 0 to 0.131, respectively. The corresponding TOF decreases from 14.9 to 6.0 (10^{-4} s^{-1} mol$_{Al}^{-1}$) due to the increase in aluminium content when H-beta/4-ClBC ratio was increased from 0.026 to 0.131, respectively. However, the selectivity for 4,4′-DCBP remains mostly unaffected even after the change in catalyst to 4-ClBC ratio. The yields of the products increase with the increase in the catalyst concentration due to the increase of moles of Al in the total amount of zeolite H-beta. These results indicate that with an increase in catalyst loading the conversion of 4-ClBC increases linearly because of the increase in the total number of acid sites available for the reaction.
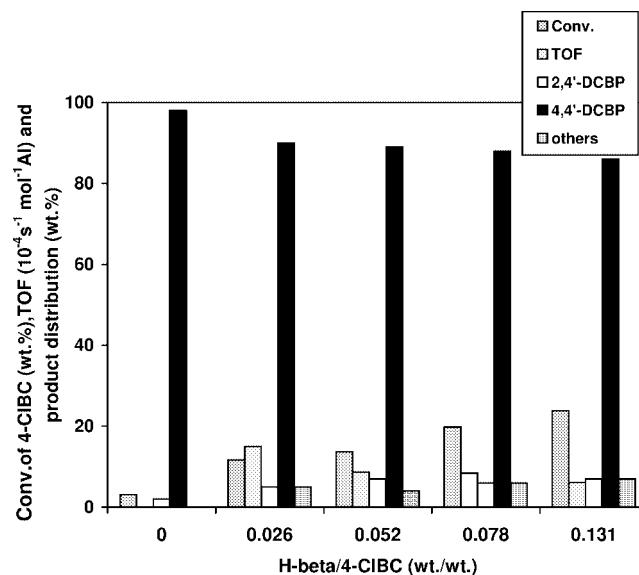

Figure 1. Influence of H-beta/4-ClBC (wt/wt) ratio on the 4-ClBC conversion, TOF and product distribution. Reaction conditions: see the footnotes to table 2.
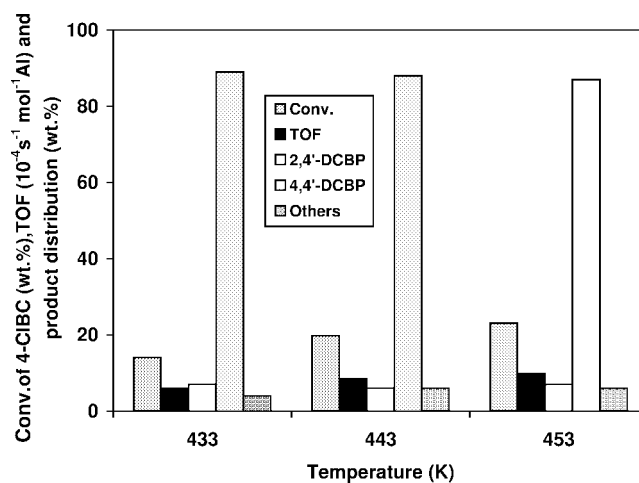

Figure 2. Influence of reaction temperature on the conversion of 4-ClBC, TOF and product distribution. Reaction conditions: see the footnotes to table 2.

3.3. Influence of reaction temperature

Figure 2 shows the variation of conversion of 4-ClBC (wt%), rate of 4-ClBC conversion (10^{-4} s^{-1} mol$_{Al}^{-1}$) and product distribution (wt%) as a function of reaction temperature. A significant increase in the conversion of 4-ClBC and rate of 4-ClBC conversion is achieved with the increase in reaction temperature. The conversion of 4-ClBC and rate of 4-ClBC conversion increases from 14.1 to 23.1 wt% and 6.0 to 9.8 (10^{-4} s^{-1} mol$_{Al}^{-1}$), respectively. However, the selectivity for 4,4′-ClBC remains nearly constant in all experiments. One of the reasons for the increased rates at higher temperature may be attributed to an enhancement of the rate of diffusion of 4-ClBC inside the channel of the H-beta; however, reaction rates are usually more temperature dependent than rate of diffusion [37,38].
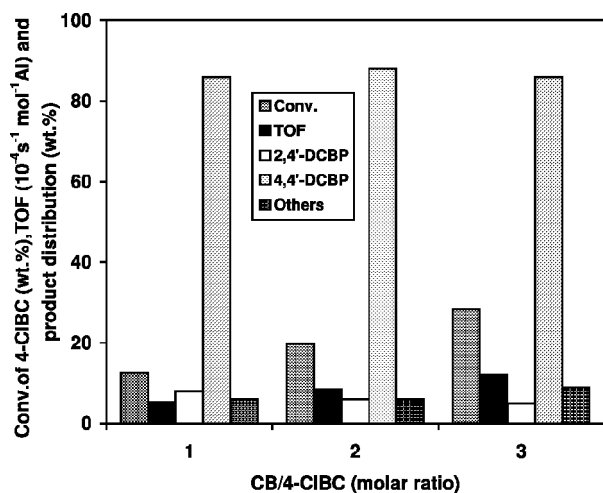
Figure 3. Influence of CB/4-ClBC molar ratio on the conversion of 4-ClBC, TOF and product distribution. Reaction conditions: see the footnotes to table 2.

Figure 4. Influence of recycling of H-beta on the conversion of 4-ClBC, TOF and product distribution. Reaction conditions: see the footnotes to table 2.

The apparent activation energy of 4-ClBC conversion over H-beta is estimated to be 40.4 kJ mol^{-1} in the temperature range 433–453 K.

3.4. Influence of CB/4-ClBC molar ratio

The CB/4-ClBC ratios were changed by keeping the amount of CB constant. The increase in CB/4-ClBC ratio up to 3 gave a linear rise in the conversion of 4-ClBC and rate of 4-ClBC conversion (figure 3). The conversion of 4-ClBC and rate of 4-ClBC conversion increased from 12.6 to 28.3 wt% and 5.3 to 12.0 (10^{-4} s^{-1} mol$_{Al}^{-1}$), respectively, as the CB/4-ClBC molar ratio increased from 1 to 3. The selectivity for the products was not influenced by the change in molar ratios (figure 3).

3.5. Recycling

H-beta sample used in the benzoylation of CB was recycled three times (fresh and two cycles) in order to check the activity and stability of the catalyst. After reaction of each cycle, the catalyst was filtered off, washed with acetone and calcined at 773 K in the presence of air for 16 h. Figure 4 lists the results of these experiments. H-beta shows an immediate but little decrease in the activity after each cycle. The conversion of 4-ClBC decreased from 19.8 to 17.0 wt% when the catalyst was recycled from fresh to 2nd cycle, respectively. However, the selectivity for the products remained unaffected. In order to check the structure of the catalyst after each reaction, X-ray diffraction patterns were recorded. XRD measurements indicated that the catalyst retains the H-beta structure. Chemical analysis of the reaction mixture as well as zeolite H-beta after each cycle revealed that minor amount of the aluminium leached out from the zeolite by the HCl (formed during the reaction). The SiO$_2$/Al$_2$O$_3$ molar ratio of the zeolite H-beta increases from 26 to 28.9 after fresh to 2nd cycle, respectively, due to the leaching of minor amount of aluminium from the struc-
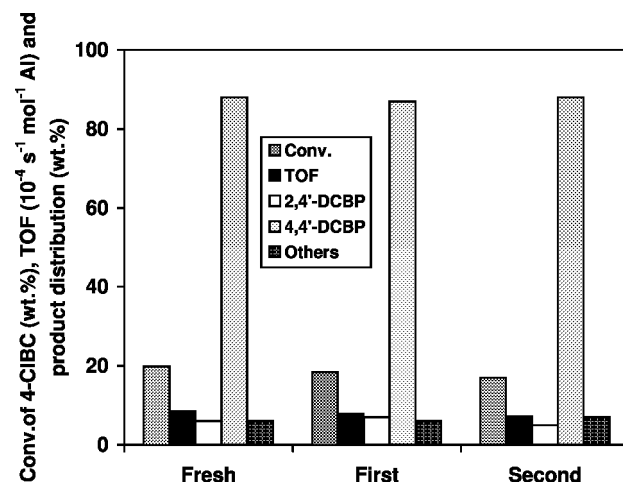
ture of the H-beta and hence a linear decrease in the activity of the catalyst is observed. The present study indicates that the catalyst can be recycled a number of times without losing its activity to a greater extent.

4. Conclusions

It is demonstrated for the first time that zeolite H-beta catalyzes the benzoylation of chlorobenzene with 4-ClBC efficiently, which leads to the formation of 4,4'-DCBP in high selectivity. At identical reaction conditions the activity (conversion of 4-ClBC) trend after 4 h reaction time is AlCl$_3$ > H-beta > Del.H-Y > H-mordenite ≈ RE-Y. H-mordenite and RE-Y are less active due to their weaker acid sites. It is concluded that the presence of strong Brønsted acid sites in the zeolite catalysts is very important for the polarisation of ClC$_6$H$_5$COCl (4-ClBC) into an electrophile (ClC$_6$H$_5$CO$^+$) which then attacks the chlorobenzene ring resulting in the formation of dichlorobenzophenones. The higher yield of the products can be achieved by increasing the values of the catalyst concentration, reaction temperature and CB/4-ClBC molar ratio. Recycling of the catalyst progressively decreases the 4-ClBC conversions to a little extent.

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