Benzoylation of benzene to benzophenone over zeolite catalysts

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The liquid phase benzoylation of benzene with benzoyl chloride (BOC) to benzophenone is catalyzed by various zeolites at 353 K. Zeolite H-beta is found to be more active than the other zeolites. The conversion of benzoyl chloride to benzophenone over H-beta increases significantly with increase in the reaction time, temperature, catalyst/BOC (wt/wt) and benzene/BOC (mole) ratios. The yield of benzophenone decreases with increase in SiO_2/Al_2O_3 ratio and isomorphous substitution of Al- by Ga- and Fe- in zeolite H-Al-beta in the following order: Al- > Ga- > Fe-H-beta suggesting that high density of acidic centers along with strong acid sites are required for the reaction.

Keywords: benzoylation of benzene; preparation of benzophenone; zeolite beta;

1. Introduction

Benzophenone is used as a fixative for heavy perfumes and in the manufacture of antihistamines and insecticides [1]. It is usually produced by the Friedel–Crafts acylation of benzene with benzoyl chloride in the presence of $AlCl_3$ [2,3]. Other processes for the synthesis of benzophenone include atmospheric oxidation of diphenylmethane and decarboxylation of *o*-benzoylbenzoic acid over copper catalysts [4–6]. Several types of insoluble heterogeneous catalysts have recently been used in liquid phase Friedel–Crafts reactions, in the place of the conventional homogeneous catalyst such as $AlCl_3$ and H_2SO_4, which often pose difficult operational problems of corrosion, catalyst removal from the product and requirement of a stoichiometric amount of the catalyst. In order to overcome the difficulties of the homogeneous system, the development and utilization of a solid catalyst is important. Zeolites, due to their thermostability and shape selectivity, have been used in organic synthesis [7]. However, relatively little attention has been paid to the use of zeolites in acylation reactions [8–12]. In this paper, we report the benzoylation of

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benzene with benzoyl chloride over zeolite catalysts for the first time. The influence of isomorphous substitution in zeolite beta, variation of SiO_2/Al_2O_3 ratio, reaction temperature, catalyst/BOC (wt/wt) and benzene/BOC (mole) ratios on the conversion of BOC to benzophenone over zeolite H-beta is examined. The results obtained over different catalysts are compared with that over the conventional catalyst, $AlCl_3$.

2. Experimental

Zeolites beta and ZSM-12 were prepared based on literature procedures [13,14]. Na-Y was obtained from Laporte Inorganics, Cheshire, UK. The procedures for cation exchange (to obtain H- and RE-zeolites) have been reported elsewhere [12,15]. The chemical analyses of the zeolites were carried out by a combination of wet chemical and atomic absorption (Hitachi Z-800) methods. The properties of zeolites used in this study are given in table 1. Prior to the addition of reactants to the flask, the catalyst was activated at 473 K under a stream of nitrogen (30 ml/min) for 4 h. The reactants (AnalaR grade) were dried over 4A molecular sieves.

The acidity of the zeolites was established by the temperature programmed desorption (TPD) of NH_3 (table 2) [16,17]. 1.0 g of sample was put in a quartz reactor and activated with N_2 at 823 K for 4 h. NH_3 was adsorbed at 303 K for 30 min, then the physically adsorbed NH_3 was desorbed by passing N_2 for 15 h (50 ml/min). Acid strength distribution was obtained by raising the catalyst temperature (10°C/min) from 303 to 773 K in a number of steps in a flow of N_2 (10 ml/min). The NH_3 evolved was trapped in a HCl solution and titrated with a standard NaOH solution.

Table 1
Characterization and catalytic activity data of catalysts [a]

Catalyst	SiO_2/Al_2O_3 (mole ratio)	Degree of H^+ or RE^{3+} exchange (%)	Crystal size (μm)	Surface area (m^2/g)	Micropore volume [b,c]	Mesopore volume [b]	Activity [d] (mmol/g h)
H-ZSM-12	100	>98.5	0.6	456	0.169	0.051	0.25
H-RE-Y (70.6) [e]	4.1	>70.6	1.0	712	0.236	0.072	0.27
H-beta	26.0	>98.7	0.5	745	0.265	0.074	5.76
$AlCl_3$	–	–	–	–	–	–	6.30

[a] Reaction conditions: see footnotes to fig. 1.

[b] N_2 adsorption.

[c] Obtained from de Boer *t*-plots.

[d] Activity = (amount of benzoyl chloride reacted)/(weight of catalyst × time of reaction) (h^{-1}); activity is based on the consumption of benzoyl chloride in the 1 h reaction time.

[e] Percent of RE (rare earth) exchange.

Table 2
Desorption of ammonia (chemisorbed at 303 K) in different temperature steps

Catalyst	SiO_2/Al_2O_3 (mole ratio)	NH_3 desorbed (mmol/g)					NH_3 chemisorbed at 303 K (mmol/g)
		303–353 K	353–433 K	433–513 K	513–653 K	653–773 K	
H-ZSM-12	100	0.04	0.01	0.08	0.03	0.1	0.26
H-RE-Y (70.6)	4.1	0.17	0.10	0.26	0.11	0.10	0.74
H-beta	26.0	0.14	0.24	0.05	0.16	0.16	0.75

Catalytic reactions were performed in a three-necked flask (capacity 50 ml) fitted with a condenser, gas supply tube and a septum. 0.1 mol of benzene, 0.02 mol of benzoyl chloride and 33 wt% of catalyst (based on the amount of BOC) were taken in the flask and heated in an oil bath to the reaction temperature under stirring. Samples were withdrawn periodically and analyzed with a gas-chromatograph (Blue Star, India model 421) equipped with a 50 m × 0.2 mm capillary column with methyl silicone gum. Product identification was done by comparison with authentic samples and GC mass spectrometry (Shimadzu GC-MS-QP-2000A).

3. Results and discussion

Table 1 summarises the catalytic activities of H-beta, H-ZSM-12, H-RE-Y (70.6) and the conventional catalyst, $AlCl_3$, in the benzoylation of benzene at similar reaction conditions. The only product obtained in the reaction was benzophenone. Among the zeolite catalysts, H-beta was found to be the most effective catalyst. H-ZSM-12 and H-RE-Y (70.6) exhibited very low activities; the catalytic activities of H-ZSM-12, H-RE-Y (70.6) and H-beta were 0.25, 0.27 and 5.76 (mmol/g h), respectively. It has already been reported that H-beta is more active than the other zeolite catalysts in the alkylation reaction [10]. The higher activity of H-beta may be attributed to its stronger acid sites (table 2) and mesoporous system (table 1) [10,11]. Generally, acylation of aromatics takes place by electrophilic aromatic substitution [18]. It is reported [19,20] that an acidic catalyst is required for the formation of $C_6H_5CO^+$ cation from the C_6H_5COCl which attacks the aromatic ring and produces the respective ketone.

The reaction profiles of the conversion of benzoyl chloride to benzophenone with reaction time are illustrated in fig. 1. The conventional catalyst, $AlCl_3$, was found to be more active than the zeolite catalyst at 1 h reaction time, however, H-beta performed better than $AlCl_3$ after 2.5 h. The lower conversion of benzoyl chloride over $AlCl_3$ after 2.5 h compared to the H-beta may be due to the lower amount of $AlCl_3$ used in the reaction (less than stoichiometric in relation to BOC).

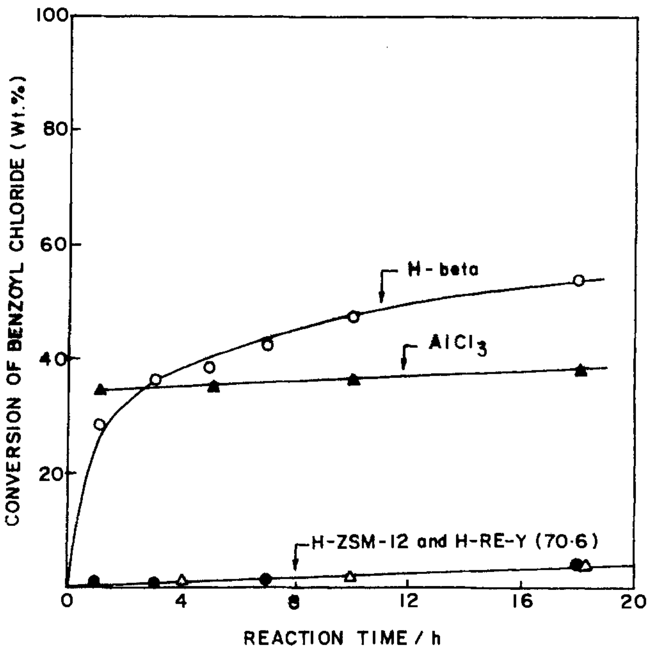

Fig. 1. Benzoyl chloride conversion vs. reaction time. Reaction conditions: catalyst/C_6H_5COCl = 0.33; reaction temperature (K) = 353; C_6H_6/C_6H_5COCl (mole ratio) = 5; C_6H_6 (mol) = 0.09.

The results of the preceding section have revealed that H-beta is the best catalyst for the formation of benzophenone. The influence of various parameters on the benzoyl chloride conversion over H-beta is reported in the following sections.

3.1. EFFECT OF ISOMORPHOUS SUBSTITUTION

The influence of H-Al-beta, H-Ga-beta and H-Fe-beta in the benzoylation of benzene with benzoyl chloride is illustrated in table 3. At similar reaction conditions, the conversion of BOC to benzophenone followed the order Al- > Ga- > Fe-. The acid strength of metallosilicates molecular sieves also decreases in the same order (Al- > Ga- > Fe-) [21,22] which indicates that strong acid sites are required for the benzoylation of benzene.

3.2. EFFECT OF SiO_2/Al_2O_3 RATIO

The effect of the SiO_2/Al_2O_3 ratio of H-beta upon the BOC conversion was investigated and the results are shown in table 4. Increasing the SiO_2/Al_2O_3 ratio leads to a decrease in catalytic activity, which goes along with a loss in number of acid sites. The lower SiO_2/Al_2O_3 ratio (26.0) required proves that a high density of acidic centers along with strong acid sites are necessary for the reaction.

Table 3
Influence of isomorphous substitution

	Catalyst		
	H-Al-beta	H-Ga-beta	H-Fe-beta
SiO_2/M_2O_3 [a]	26.00	28.17	30.01
reaction conditions			
reaction temperature (K)	353	353	353
benzene / benzoyl chloride (mole)	5	5	5
catalyst / benzoyl chloride (wt / wt)	0.33	0.33	0.33
reaction time (h)	18	18	18
product yield (wt%) [b]			
benzophenone	54.0	32.8	19.0

[a] M = Al, Ga, Fe.

[b] Product yield is based on the benzoyl chloride conversion at 18 h.

3.3. EFFECT OF REACTION TEMPERATURE

The reaction of benzene with benzoyl chloride over H-beta was examined in the temperature range from 313 to 353 K. The results obtained are summarised in table 4. Lower temperature does not favour the formation of benzophenone, however, the yield of benzophenone increased sharply with the increase in reaction temperature and reached a value as high as 54% at 353 K.

3.4. EFFECT OF CATALYST/BOC RATIO

The catalyst/BOC (wt/wt) ratio was varied from 0.03 to 0.33, keeping the concentration of BOC constant (fig. 2). The total surface area available for the reaction depends on the catalyst loading. It is found that with an increase in

Table 4
Influence of reaction temperature and SiO_2/Al_2O_3 ratio of H-beta on the BOC conversion [a]

SiO_2/Al_2O_3 (molar ratio)	Reaction temperature (K)	Product yield [b] (wt%)
26.0	313	2.1
26.0	333	16.2
26.0	353	54.0
41.5	353	24.6
60.0	353	8.9

[a] Reaction conditions: catalyst/C_6H_5COCl = 0.33; benzene/BOC (mole ratio) = 5; benzene (mole) = 0.09.

[b] See footnote to table 3.

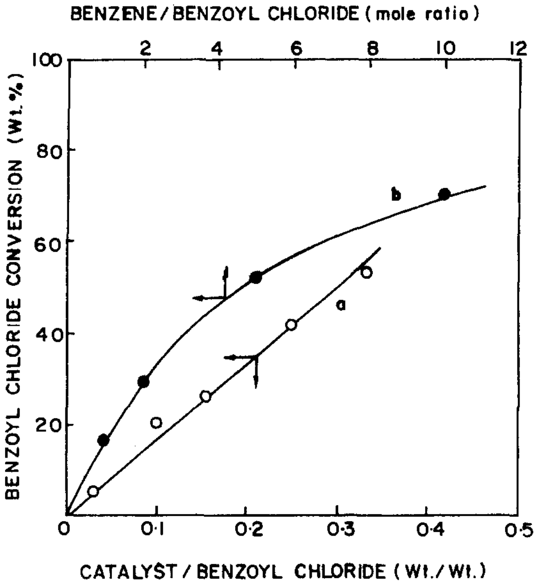

Fig. 2. Influence of (a) catalyst amount and (b) C_6H_6/C_6H_5COCl (mole ratio). Reaction conditions: reaction temperature (K) = 353; reaction time (h) = 18; C_6H_6 (mole) = 0.09; C_6H_6/C_6H_5COCl (mole ratio) for (a) = 5; catalyst/C_6H_5COCl (wt/wt) for (b) 0.33.

catalyst loading the conversion of benzoyl chloride increases linearly because of the increase in the total number of acid sites available for the reaction.

3.5. EFFECT OF BENZENE/BOC MOLE RATIO

The mole ratio of benzene to BOC was varied between 1 and 10, maintaining the amount of BOC constant (fig. 2). It is seen from the plot that, as the mole ratio is increased, the conversion of benzoyl chloride increases rapidly.

4. Conclusions

In summary, zeolite catalysts can catalyze the benzoylation of benzene to benzophenone. H-beta is found to be a more active catalyst than H-ZSM-12 and H-RE-Y (70.6). H-beta showed better activity in the reaction than $AlCl_3$, at longer contact times. A higher yield of benzophenone was obtained by increasing the reaction temperature, catalyst concentration and mole ratios of benzene/BOC. The yield of the product decreases with an increase in SiO_2/Al_2O_3 ratio of the H-beta. The isomorphous substitution of Al by Ga or Fe significantly decreases the yield of benzophenone probably due to the decrease in acid strength in the following order: H-Al-beta > H-Ga-beta > H-Fe-beta.

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