# Selective acylation of aromatics using zeolite catalysts

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#### Abstract

Environmentally friendly, recyclable, selective solid catalysts have been developed for the acetylation of toluene to 4-methylacetophenone, propionylation of phenol to 4hydroxypropiophenone, veratrole to 3,4-dimethoxypropiophenone, benzoylation of phenol to 4-hydroxybenzophenone, chlorobenzene to 4,4'-dichlorobenzophenone and biphenyl to 4-phenylbenzophenone.

Keywords: acylation, zeolites, phenol, toluene, veratrole, chlorobenzene, biphenyl, chlorophenol.

## **1. INTRODUCTION**

Selective acylation of aromatics is of considerable interest due to its commercial importance in the production of fine chemicals [1-3]. In order to overcome the difficulties associated with homogeneous systems and to ensure an environmentally clean process, the development and utilization of solid catalysts are important. Recently, the use of solid catalysts, such as Nafion-H, clay, heteropoly acids and metal oxides promoted by sulphate ions have been reported for the acylation of aromatics [4-7]. Zeolites are wellmicroporous defined crystalline materials and have been investigated extensively and applied as solid catalysts in the manufacture of petrochemicals [8]. Zeolite catalysts are known to various synthetic catalvze organic transformations more effectively and selectively than Lewis acid catalysts. Zeolites are also efficient for the acylation reactions due to their acidity, shape-selectivity and regenerability [9-201.

Zeolites are widely used for acidcatalysed reactions and adsorptive separations. From the industrial point of view, heterogeneous catalysts such as zeolites offer the advantages of simple

separations and recovery in both gas and liquid-phase operations. Zeolites have a reasonable thermal stability and provide shape selectivity by possessing identical, well-defined reaction cavities. The less obvious benefit of using zeolites involves their controlled variability. More importantly, the properties of the zeolites could be altered through a process such as cation exchange and metal framework substitution. Here, we report our studies on selective acylation of activated (veratrole, phenol, toluene) non-activated and aromatics (chlorobenzene, biphenyl) with zeolite catalysts [21-27].

#### 2. EXPERIMENTAL 2.1. Materials

Zeolites Na-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, and U.K. The synthesis of Nabeta and Na-ZSM-5 were carried out hydro thermally using fumed silica (99 %, Sigma, USA), tetraethyl ammonium hydroxide (TEOH; 35 wt % aqueous solution, Aldrich), tetrapropyl ammonium hydroxide (TPA; 20 wt% aqueous solution. Aldrich, USA). aluminum sulfate, sodium hydroxide, potassium hydroxide, ammonium nitrate

and rare earth chloride (5 wt.% aqueous solution). For catalytic reactions, Phenol, toluene, veratrole, acetylchloride, acetic anhydride, propionic anhydride, propionyl chloride, benzovlchloride, 4chlorobenzoylchloride and benzoic anhydride were purchased from Aldrich and used without further purification. Anhvdrous AR grade solvents (chlorobenzene, nitrobenzene) were purchased from s-d Fine chemicals and used without further purification.

# 2.2. Synthesis of Catalysts

Zeolites H-ZSM-5 and H-beta were prepared by following the methods described in the literature [28-29]. The synthesized zeolites were washed with deionized water, dried at373 K for overnight and calcined at 813 K for 16 h in the presence of air to eliminate the organic templates from the zeolite channels. The resultant samples were exchanged thrice with 1 M NH<sub>4</sub>NO<sub>3</sub> solution for 8 h at 353 K. The  $NH_4^+$ exchanged samples were dried and calcined at 823 K for 8 h to get their protonic forms. RE-Y was prepared from Na-Y by exchanging with 1 M NH<sub>4</sub>NO<sub>3</sub> (three exchanges, 353 K, 8 h) and then the resulting NH<sub>4</sub>-Y was treated with 5 % rare earth chloride solution for 8 h at 353 K. The  $RE^+$ -exchanged samples were again calcined at 823 K for 8 h get their RE<sup>+</sup> forms. The catalyst materials used in this work are the hydrogen forms of zeolites. Most of the attention has been focused on the importance of the Brønsted-acid sites, which are generated as a result of protons balancing the charge associated with framework substitution of Al<sup>+3</sup> for Si<sup>+4</sup>. Brønsted sites are generally accepted to be the active sites for many important reactions [30].

## 2.3. Characterization

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of various zeolites and degree of ion- exchange were found out by a combination of wet and atomic absorption methods (Hitachi 800). X-ray powder diffraction (XRD) was carried out on a Rigaku, Miniflex model (CuK<sub>a</sub> radiation) and was used to evaluate the peak positions of various zeolite The surface area of the samples. catalysts was measured by nitrogen adsorption (BET method). The size and morphology of the zeolite catalysts were estimated by scanning electron microscope (Cambridge Stereoscan 400). The acidity of the materials was measured by temperature programmed desorption (TPD) of ammonia [31].

# 2.3.1 Acidity measurements

Temperature programmed desorption measurements were carried out to measure the acid strength of the zeolite catalysts using ammonia as an adsorbate (Fig. 1, Ref.22).

In a typical run, 1.0 g of a calcined sample was placed in a quartz tubular reactor and heated at 773 K under a nitrogen flow of 50ml/min. for 4 h. The reactor was then cooled to 303 K and adsorption conducted at that temperature by exposing the sample to ammonia (30 ml/min.) for 30 min. Physically adsorbed ammonia was removed by purging the sample with a nitrogen stream flowing at 50 ml/min. for 15 h at 303 K. Acid strength distribution was obtained by catalyst raising the temperature  $(10^{0} \text{C/min})$  from 303 K to 773 K in a number of steps with a flow of nitrogen (10 ml/min.). The NH<sub>3</sub> thus evolved was trapped in normalized hydrochloric acid solution and back titrated with a standard NaOH solution to find out decease in the strength of acid and by which the acid strength of the catalysts was calculated.



Fig. 1. Acid strength distribution of various zeolites.

# 2.4. Catalysis

## 2.4.1 Acetylation of toluene

The vapor phase reaction of acetyl chloride with toluene was carried out at atmospheric pressure in a quartz micro flow reactor with an inner diameter of 14mm. The catalyst was pretreated *in situ* for 4 h at 813 K. Then the catalyst temperature was brought down to 453 K and the mixture of toluene and acetyl chloride, was fed into the reactor by a syringe pump.

## 2.4.2 Propionylation of phenol

The propionylation reactions were carried out in a liquid phase batch reactor. 0.5 g of catalyst was introduced into the mixture of 0.106 moles of phenol and 0.035 moles of propionylchloride and the reaction was continued for 4 h at 413 K.

## 2.4.3 Propioylation of veratrole

The liquid phase propionylation of veratrole (VT) with propionylchloride (PC) was carried out in a 100 ml two necked flask attached to a condenser and septum (used to sample the reaction mixture). The temperature of the reaction vessel was maintained using an oil bath. An appropriate amount of VT (10mmol), PC (10mmol) and

chlorobenzene (20ml) of solvent were added to the activated (0.5g) catalyst.

## 2.4.4 Benzoylation of chlorobenzene

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-chlrobenzoyl chlorides were introduced. The reaction mixture was stirred and heated to attain the reaction temperature (443 K).

## 2.4.5 Benzoylation of phenol

The reaction was carried out in a Parr reactor. A mixture of 0.21 moles of phenol, 0.01 moles benzoic anhydride and 0.5 g of catalyst were taken in a Parr reactor and heated to 493 K for 20 h under autogeneous pressure.

## 2.4.6 Benzoylation of biphenyl

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. 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.

Samples were collected periodically in all the reactions and analyzed by a gaschromatograph (HP 6890) equipped with flame ionization detector and a capillary column (50m x 0.2mm) with methyl silicone gum. The products were identified on a Shimadzu GC-MS, QP 2000 A gas-chromatograph- mass spectrometer and <sup>1</sup>H and <sup>13</sup>C-NMR techniques.

#### **3. RESULTS AND DISCUSSION**

The physicochemical properties of the zeolite catalysts are given in Table 1. The X-ray diffraction patterns of the zeolites match well with those reported in the literature and are found to be highly crystalline. The scanning electron microscopy and surface area show that there is no pore blocking or amorphous material inside the channels and also on the external surface of the zeolites.

#### 3.1. Acetylation of toluene

Figure 2. shows the catalytic activity of different catalysts in the acetylation of toluene. The main products are 4-methyl acetophenone (4-MACP) and 2-methyl acetophenone (2-MACP). H-ZSM-5 performed better than others with respect to conversion of chloride (60.2 acetvl wt.%) and selectivity for 4-MACP (88.3%). The turnover frequencies (TOF) are found to be 7.5, 0.7 and 0.08  $*10^{-4}$  s<sup>-1</sup> mol<sup>-1</sup> Al for H-ZSM-5, H-mordenite and REY zeolites, respectively. The corresponding isomer ratios (4-MACP/2-MACP) are 9.8, 4.7 and 4.0, respectively, showing that H-ZSM-5 exhibited the highest activity and selectivity in the acetylation of toluene.



Fig. 2 Acetylation of toluene over various catalysts. Reaction conditions: catalyst weight=2 g; toluene/CH3COCI (molar ratio)=2; feet rate= 2 ml h<sup>-1</sup>; reaction temperature=453 K; 4-MACP: 4-methylacetophenone; 2-MACP: 2-methylacetophenone; others: di and tri-acetylated products (Ref.24)

The acid strength of H-ZSM-5 is found to be higher than the H-mordenite and RE-Y zeolite catalysts (Table 1) and it is likely that the stronger acid sites of the H-ZSM-5 result in higher rate of acetyl chloride conversion in the acetylation of toluene. The results from Fig. 2, show that geometrical constraints produced by H-ZSM-5 did not allow the formation of bulkier 2-MACP and consecutive products in the small channels of H-ZSM-5. Hence a higher selectivity for 4-MACP is achieved over H-ZSM-5 than other zeolites.

Catalysts	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Degree of <sup>a</sup> H <sup>+</sup> or RE <sup>3+</sup> exchange (%)	Crystal size (µm)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	Acid strength (mmolg <sup>-1</sup> )
H-beta	26.0	>98	0.5	745	0.75
H-ZSM-5	41.0	> 98	0.4	413	1.21
H-mordenite	22.0	> 98	1.0	552	0.71
H-Y	4.1	>98	1.0	615	1.45
H-REY <sup>d</sup>	4.1	> 70.6	1.0	659	0.74

#### Table 1. Physicochemical properties of zeolite catalysts (Ref.22)

<sup>a</sup>Cation-exchange (H<sup>+</sup>- or  $RE^{3+}$ -) values reported as percent of the total cation sites, taken as the aluminium content 100%

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

 $^{\circ}NH_3$  chemisorbed at 303 K (m mol g<sup>-1</sup>); detail in Table 1a.

<sup>d</sup>70.6% RE<sup>3+</sup>-exchange in NH<sub>4</sub>-Y-zeolite

#### 3.2. Propionylation of phenol

The liquid phase propionylation of phenol (Ph) with propionyl chloride (PC) has been studied over zeolite Hbeta, RE-Y, H-Y, mordenite, H-ZSM-5 and AlCl<sub>3</sub> at 413 K. H-beta is found to be superior to other zeolite and AlCl<sub>3</sub> catalysts [Fig. 3, Ref.21]. The main products are 2-hydroxypropiophenone (2-HPP) and 4-hydroxypropiophenone (4-HPP). The conventional catalyst, AlCl<sub>3</sub>, is less active and selective (4-HPP/2-HPP = 0.9) than H-beta and a higher yield of others (3.6 wt.%) is obtained due to its non shape-selective character. RE-Y produced lower yields of 2-HPP (1.0 wt.%) and 4-HPP (0.8 wt.%) than H-beta. However, RE-Y was found to be more active than H-Y, H-

Mordenite and H-ZSM-5. The higher activity of RE-Y in the formation of 2-HPP and 4-HPP compared to H-Y may be attributed to its higher strength of acid sites, which are generated by the exchange of RE<sup>3+</sup>-cations in H-Y (Table 1). The lower activity of H-ZSM-5 in the formation of 2-HPP and 4-HPP may be due to its small pore openings than the various size of the reactants (intermediates), which are formed by different reaction pathways in the propionylation of phenol i.e. both intra and inter molecular Fries rearrangement. The catalysts used in the study show the decreasing order of activity in the formation of hydroxypropiophenones (2-HPP and 4-HPP): H-Beta >  $AlCl_3$  > RE-Y > H-Mordenite > H-ZSM-5 > H-Y. 2HPP is produced through the Fries rearrangement of phenyl propionate (PP), propionylation of phenol with PP and direct C-propionylation of phenol with propionylchloride (PC). Small amount of 4-HPP is also produced through the direct propionylation phenol with PC and propionylation of phenol with PP.



Fig. 3. Propionylation of phenol over various catalysts. Reaction conditions: catalyst = 0.5 g; phenol = 0.106 mol; PC = 0.035 mol; phenol:PC molar ratio = 3 mol; reaction temperature = 413 K; reaction time = 4 h. PP = phenylpropionate; Ph = phenol; 2-HPP = 2-hydroxypropiophenone; 4-HPP = 4-hydroxypropiophenone; 4-PXPP = 4-propionyloxypropiophenone; 4-: 2- = isomer ratio of 4-HPP:2-HPP.

#### 3.3. Propionylation of veratrole

The catalytic liquid phase propionylation of veratrole (VT, 1,2dimethoxybenzene (1,2-DMB)) to 3,4dimethoxypropiophenone (3,4-DMPP) was investigated over a number of zeolite catalysts such as H-beta, H-Y, RE-Y, H-Mordenite and H-ZSM-5 [Fig. 4]. H- beta was found to be an effective catalyst for the selective conversion of VT to 3,4-DMPP. The conversion of VT, rate of VT conversion (TOF) and selectivity for 3,4-DMPP over zeolite H- beta after 1 h reaction time are 40.8 wt. %, 18.8  $(10^{-4}s^{-1}mol^{-1}Al)$  and 89 wt.%, respectively. Under identical reaction conditions, conversion of VT, rate of VT conversion and selectivity for 3,4-DMPP over AlCl<sub>3</sub> are found to be 48.5 wt. %, 3.6  $(10^{-4}s^{-1}mol^{-1}Al)$  and 68.9 wt. %, respectively. Presumably, the higher activity of H-beta may be attributed to its stronger acid sites compared to other zeolite catalysts. The lower activity of H-ZSM-5 (< 1 wt.% conversion of VT)

compared to other zeolite catalysts may be attributed to its small pore openings than the size of veratrole and the reaction products. When H-Y is exchanged to H-RE (70.6)-Y. the catalytic activity enhanced is considerably, which may be due to the higher strength of acid sites generated by  $RE^{3+}$ -cations. Compared to AlCl<sub>3</sub> catalyst, all zeolite catalysts show higher selectivity for 3.4-DMPP.



Fig. 4. Propionylation of VT over various catalysts. Reaction conditions: catalyst (g) =0.5; catalyst/PC (wt.wt.<sup>-1</sup>) = 0.53; VT/PC (molar ratio) =1; VT(mol) = 0.01; chlorobenzene (ml) =20; reaction temperature(K)=403; reaction time (h)=1 (Ref.22).

#### 3.4. Benzoylation of chlorobenzene

The catalytic liquid phase benzoylation of chlorobenzene (CB) to 4,4'-dichlorobenzophenone (4,4'-DCBP) with 4-chlorobenzoylchloride (4-ClBC) as benzoylating agent was investigated over a number of zeolite catalysts such as H-beta, H-Y, RE-Y, H-Mordenite and H-ZSM-5. It was found that selective formation of 4,4'-DCBP (>88%) at 19.8 wt.% conversion level of 4-ClBC and at  $8.4 \times 10^{-4} s^{-1} mol^{-1} Al$  turn over frequency of 4-ClBC over zeolite H-beta. Table 2 shows the catalytic activity of different catalysts on the conversion of chlorobenzene and product distribution in the benzoylation reaction. H-beta exhibits higher catalytic activity and rate of 4-ClBC conversion (TOF) 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 active compared to the RE-Y and H-mordenite. The conversion of 4-ClBC over H-beta, .H-Y, RE-Y and Hmordenite are found to be 19.8, 12.4, 1.5 and 1.8 wt. %, respectively. The corresponding TOF  $(10^{-4} \text{ s}^{-1} \text{mol}^{-1} \text{Al})$  are 8.4, 6.0, 0.1 and 0.6 x 10<sup>-4</sup> s<sup>-1</sup>mol<sup>-1</sup>Al, respectively. The homogeneous Lewis acid catalyst, AlCl<sub>3</sub>, is found to be the 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  $(10^{-4} \text{ s}^{-1} \text{mol}^{-1} \text{Al})$ 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 the other catalysts. A higher amount of

consecutive products formation is observed over AlCl<sub>3</sub> due to its non shape-selective character. From the data presented in Table 2, it is clear that that the performance of the catalyst is governed by the acidity and the structure of the zeolites. The higher conversion of 4-CIBC and TOF over H-beta and H-Y seem to be due the fact that the H-beta exhibits the stronger Bronsted acid sites compared to the other catalysts. These results indicate that acid strength is the important factor for most the polarisation of ClC<sub>6</sub>H<sub>5</sub>COCl (4-ClBC) into an electrophile ( $ClC_6H_5CO^+$ ), which attacks the CB ring and produces the DCBPs (dihalobenzophenones) [8,14]. The marginal higher selectivity for 4,4'-DCBP over H-beta might be attributed to its peculiar pore opening (5.5 x 7.5 Å) than H-Y (7.4 Å) and H-mordenite (6.5 x 7.0 Å).

 Table 2 Benzoylation of chlorobenzene to 4,4'-dichlorobenzophenone<sup>a</sup>(Ref.25)

Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Conv.of 4-ClBC <sup>b</sup>	$\frac{\text{TOF}}{(10^{-4}\text{s}^{-1}\text{mol}^{-1}\text{mol}^{-1}\text{mol}^{-1}\text{mol}^{-1})}$	Product distribution (wt.%) <sup>c</sup>		
	(molar ratio)	(wt.%)	<sup>1</sup> Al)	2,4'-	4,4'-	Others
				DCBP	DCBP	
H-beta	26.0	19.8	8.4	6	88	6
H-Y	4.1	12.4	6.0	10	87	3
RE-Y	4.1	1.5	0.1	7	83	10
H-Mordenite	21	1.8	0.6	8	85	7
AlCl <sub>3</sub>	-	22.0	6.0	2	84	14

<sup>a</sup> Reaction conditions: catalysts (g) = 0.3 ; chlorobenzene (mole)=0.044; 4-ClBC (mole)=0.022; catalyst (g)=0.3; reaction temperature (K)=443; reaction time (h)=4 ;<sup>b</sup> 4-ClBC = 4-Chlorobenzoyl chloride; <sup>c</sup> 2,4'-DCBP = 2,4'-dichlorobenzophenone ; 4,4'-DCBP = 4,4'- dichlorobenzopheneone; Others = consecutive products.

## 3.5. Benzoylation of phenol

The catalytic activities of different catalysts such as H-beta, H-Y, RE-Y, H-ZSM-5, H-mordenite and conventional catalyst, AlCl<sub>3</sub>, in the benzoylation of phenol at 493 K are summarised in Table 3. It is seen that all the catalysts readily produce phenyl benzoate (PB) as a major product by the

ortho-acylation of phenol. Further. mechanisms reaction have been proposed for the formation of nuclear products such as 2hydroxybenzophenone (2-HBP) and 4hydroxybenzophenone (4-HBP). Zeolite H-beta, H-Y and RE-Y were found to be the most active catalysts for the formation of nuclear products whereas the selectivity of H-beta was much higher (4-/2- = 2.1) than those of H-Y (4-/2=0.6) and RE-Y (4-/2=1.1). The most attractive shape-selectivity of Hbeta among the zeolites and conventional catalyst, AlCl<sub>3</sub>, is attributed to the three dimensional pore system with straight channels of *ca*. 7.3 \* 6.5 Å and tortuous channel of 5.5 \* 5.5 Å of H-beta. Very small amount of 2-HBP formed over H-mordenite. In was addition, the inactivity of H-ZSM-5 might be explained on the basis of its smaller pore size (5.4 \* 5.6 and 5.1 \* 5.5 Å) compared to the bulkier size of the products. For comparison, the results over conventional Lewis acid catalyst,

AlCl<sub>3</sub>, are also reported in the benzovlation of phenol. Obviously the catalyst demonstrates AlCl<sub>3</sub> the reasonable activity for nuclear products (lower than H-Y, RE-Y and H-beta) but lower selectivity for 4-HBP (4-/2-=0.6)than H-beta (4-/2=2.1). The Activity of various catalysts in the formation of 2-HBP and 4-HBP and others (consecutive products in the case of AlCl<sub>3</sub>) decreases in the sequence: H-Y > H-beta> RE-Y >H-mordenite whereas the  $AlCl_3 >$ selectivity for 4-HBP (4-/2- ratio) decreases in the following order: H-beta > RE-Y > H-Y  $\approx$  AlCl<sub>3</sub>.

Catalyst <sup>a</sup>	Conv.	Product yields (wt%) <sup>c</sup>				4-/2-	
	BA (wt%)	PB	2-HBP	4-HBP	Others	ratio <sup>d</sup>	
H-beta	95.3	61.2	11.4	23.3	-	2.1	
H-Y	96.2	55.0	25.7	16.9	-	0.6	
RE-Y	87.3	56.5	16.5	16.5	-	1.1	
H-mordenite	87.8	87.0	0.7	-	-	-	
H-ZSM-5	86.1	86.1	-	-	-	-	
AlCl3	93.2	70.8	5.4	3.3	11.9	0.1	

 Table. 3. Benzoylation of phenol<sup>a</sup>(Ref.27)

<sup>a</sup> Reaction conditions : Catalyst (g) = 0.5 ; Phenol (mol) =0.21 ; BA (mol) = 0.01 ; phenol/BA(molar ratio) = 20 ; reaction temperature (K) = 493 ; reaction time (h) = 20 . <sup>c</sup> PB=phenylbenzoate; 4-HBP = 4-hydroxybenzophenone ; 2-HBP = 2hydroxybenzophenone; Others = consecutive products ; <sup>d</sup> 4-/2- = 4-HBP/2-HBP ratio.

# 3.6. Benzoylation of biphenyl

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 such as H-beta, H-ZSMand H-Y. Conventional 5, RE-Y homogeneous catalyst, AlCl<sub>3</sub> has been used for comparison. 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 the Table 4, 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, 3.2 (%), 31.7, 6.0, 0.5, 0.5 (10<sup>-5</sup>s<sup>-1</sup>mol<sup>-1</sup>Al) and 97.4, 100, 100, 100

(%), respectively. AlCl<sub>3</sub> 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 ten times higher (4-/2- = 37.4) than that of non shape-selective AlCl<sub>3</sub> (4-/2- = 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<sub>3</sub> desorption experiment. With the increase the amount of strong acid sites, the conversion of BP enhances, which means that strong acid sites of H-beta promoted the reaction. Being large pore and weaker acid sites, HY and RE-Y 
 Table 4. Benzovlation of biphenyl (Ref.26)
 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 6h of reaction time:  $AlCl_3 > H$ -beta > H-ZSM-5 > RE-Y  $\approx$  H-Y. The results indicate that mainly ortho- and parasubstitutions take place over zeolite Hwhich expected beta, is for an electrophilic aromatic substitution pathway. Acidic zeolites polarize the benzovl chloride into an electrophile  $(C_6H_5CO^+)$ , which attacks on the aromatic ring, resulting in the formation of phenylbenzophenones.

Catalyst	Reaction time (h)	Biphenyl Conv. (%)	TOFb(10-5 s-1mol-1Al)	Prod distribu (% 2-PBP	uct ution <sup>c</sup> ) 4-PBP	4-/2- <sup>d</sup> 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 <sup>e</sup> -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 <sub>3</sub>	0.5	48.6	72.1	20	80	4.0
	1	63.2	46.8	20	80	4.0

<sup>a</sup> Reaction conditions: Catalyst (g) = 0.5; Biphenyl (mol) = 0.01; Benzoyl chloride (mol) = 0.01; Reaction temperature (K) = 443; <sup>b</sup> TOF (turnover frequency) = moles of BP transformed per second per mol of aluminium; <sup>c</sup> 2-PBP = 2-Phenylbenzophenone; 4-PBP = 4-Phenylbenzophenone; <sup>d</sup> Ratio of 4-phenylbenzophenone; 70.6% RE<sup>3+</sup>-exchange in NH<sub>4</sub>.Y

# 4. CONCLUSION

In conclusion, various types of zeolites have been synthesized and characterized by XRD for crystallinity and N<sub>2</sub> adsorption study for the surface area measurements. The acidity of the synthesized catalysts was measured by temperature programmed desorption (TPD) of ammonia. All the synthesized zeolite catalysts were tested in acylation aromatics such of various as, acetylation of toluene 4to methylacetophenone, propionylation of phenol to 4-hydroxypropiophenone, veratrole 3.4to dimethoxypropiophenone, benzoylation 4,4'of chlorobenzene to dichlorobenzophenone, phenol to 4hydroxybenzophenone and biphenyl to 4-phenylbenzophenone. It is found that, in all reactions, H-beta was more active and selective catalyst except in the acetylation of toluene, where H-ZSM-5 was found to be more active and selective.

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