

# Acylation of toluene using rare earth cation exchanged zeolite $\beta$ as solid acid catalyst

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Received 25 September 2003; received in revised form 16 January 2004; accepted 3 February 2004

## Abstract

The catalytic activity of rare earth cations exchanged zeolite  $\beta$  was studied for the acylation of toluene with acetic anhydride as an acylating agent and nitrobenzene, *o*-dichlorobenzene and dichloroethane as the solvent in liquid phase in the temperature range of 368–408 K. The rare earth cation exchanged zeolites were observed to have the catalytic activity in the following order: La- $\beta$  > H- $\beta$  = Ce- $\beta$  > Dy- $\beta$  > Eu- $\beta$  > Sm- $\beta$  > Gd- $\beta$  > Nd- $\beta$  > Pr- $\beta$  with more than 95% selectivity towards the *p*-isomer. Among the solvents studied, nitrobenzene is the most favored for toluene acylation reaction. The correlation of catalytic activities of the different catalysts with the cyclohexanol dehydration as well as DRIFT spectroscopy showed that the toluene acylation is a Brønsted acid catalyzed reaction.

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**Keywords:** Acylation; Toluene; Rare earth cation; Zeolite  $\beta$ ; Brønsted acidity

## 1. Introduction

The acylated aromatic compounds are prominent intermediates in many of the organic syntheses especially in pharmaceutical and fine chemical industry. Presently, Friedel–Crafts acylation of aromatic compounds is commercially done [1] using Lewis acids such as AlCl<sub>3</sub>, BF<sub>3</sub>, ZnCl<sub>2</sub>, TiCl<sub>4</sub>, FeCl<sub>3</sub> as well as Brønsted acids like polyphosphoric acid and hydrofluoric acid. However, these traditional catalysts have limitations such as environmental pollution hazards arising from the disposal of potential toxic wastes, reactor corrosion and difficulty in handling. Furthermore, the catalyst amount to be employed is more than the stoichiometric quantity required as the catalyst has a tendency for complex formation either with the reactants or products [2]. Therefore, considerable research efforts are directed to develop alternative suitable catalysts to overcome these drawbacks. Zeolites, clays, and ionic resins are potential solid acid materials for developing catalysts to overcome above-mentioned limitations. Zeolites, particularly, exhibit good thermal stability, shape selectivity, and ease to modify their surface acidity by simpler processes like cation exchange. The present study

reports the liquid phase acylation of toluene with rare earth exchanged zeolite  $\beta$  using acetic anhydride as an acylating agent. Methyl-*p*-tolylketone, *p*-isomer of acylated toluene is a colorless liquid with a penetrating floral fruity odor and finds applications in perfumery, flavors and fragrance industry. There are some reports on the acylation of toluene with different acylating agents using solid acids. For example, Chiche et al. [3] has reported the acylation of toluene with C<sub>2</sub> to C<sub>22</sub> alkanolic acids with CeNa-Y (70% cation exchange) and reported the maximum yield for C<sub>12</sub> and C<sub>14</sub> acids. Acetic acid was not observed to be effective for acylation. Gauthier et al. [4] from their study of acylation of toluene with octanoic acid and cation exchanged zeolite-Y concluded that acylation can also be catalyzed by Brønsted acid sites. Phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) supported on silica was shown [5] to be more active than zeolite-Y and  $\beta$  for acylation of toluene with crotonic acid. The acylation of lower aromatics with ion-exchanged montmorillonite clay has been discussed by Chiche et al. [6] and showed that Al<sup>3+</sup> exchanged clay was most active for acylation. It is reported that, the activity of La-exchanged zeolite-Y increases with an increase of La<sup>3+</sup> content in the zeolite for the acylation of toluene with acetyl chloride as an acylating agent [7]. It was observed from earlier studies on the acylation of aromatic compounds like anisole, veratrole and isobutylbenzene [8,9] that rare earth cations exchanged zeolites and

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acid activated clays display potential activity for acylation of aromatic compounds. Therefore, the present work was undertaken to explore the potential of rare earth cations ( $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ ) exchanged zeolite  $\beta$  for the acylation of toluene. Acetic anhydride was used as an acylating agent. Acetyl chloride, despite its high activity as a potential acylating agent is applied rarely because of the hydrogen chloride emission during the acylation reaction, which decreases the catalytic activity [10].

## 2. Experimental

### 2.1. Materials

La, Ce, Dy, Eu, Sm, Gd, Nd and Pr acetates used for cation exchange were procured from M/S Aldrich Chemicals, USA. Toluene, acetic anhydride and nitrobenzene, *o*-dichlorobenzene, dichloroethane and ammonium chloride were supplied by M/S S.D. Fine Chem. Ltd., India, and the reagents employed were of analytical grade purity. Na- $\beta$  procured from Zeocat, Switzerland, was having Si/Al ratio = 24, BET surface area  $612 \text{ m}^2/\text{g}$  and crystallite size of 0.2–0.4  $\mu\text{m}$ .

### 2.2. Catalyst preparation and characterization

10 g of Na- $\beta$  was taken in a 250 ml round bottom flask and treated with 100 ml of aqueous ammonium chloride (1 M) at 353 K for 6 h followed by filtration of the sample and washing with copious amount of distilled water till the filtrate showed the absence of chloride ions. The sample obtained was oven dried at 383 K for 10 h followed by calcination in air atmosphere for 6 h at 823 K in a muffle furnace. The H- $\beta$  thus prepared was further ion-exchanged; 2.5 g of H- $\beta$  with 50 ml aqueous solution of rare earth acetate salts (0.01 M) heated at 353 K for 6 h. After ion-exchange the samples were thoroughly washed with water to remove acetate anions followed by oven drying at 383 K for 10 h. Thus dried sample was calcined for 6 h at 823 K under air atmosphere at a heating rate of 5 K/min in a programmable tubular furnace. The degree of cation exchange in the zeolite H- $\beta$  was determined by the analysis of rare earth cations taken in the starting solution and those remaining in the filtrate after the cation exchange volumetrically by EDTA titration using xylenol orange as indicator.

The crystallinity of the ion-exchanged zeolites was ascertained using X-ray powder diffraction on Phillips X'Pert MPD system using  $\text{Cu K}\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ). Diffuse reflectance infrared spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer at 473 K with  $\text{N}_2$  (40 ml/min) as a carrier gas.

The electron microscopic study has been done with scanning electron microscope (Leo series VP1430) equipped with Oxford instruments EDX facility, having silicon de-

tector under a pressure of  $>1.34 \times 10^{-2} \text{ Pa}$ . The samples were coated with gold using a polaron sputter coater. Surface chemical analysis by EDX was carried out at an accelerating voltage of 20 kV and probe current of 102 pA.

### 2.3. The catalytic reaction for acylation of toluene

The acylation reaction was carried out in liquid phase as a batch reaction. Typically, a 50 ml round bottom flask equipped with an efficient water condenser, is kept in a constant temperature oil bath whose temperature was maintained within  $\pm 0.5 \text{ K}$ . A mixture of toluene and acetic anhydride (molar ratio = 1:2) along with solvent (10 ml) and catalyst (0.25 g), pre-activated at 673 K for 2 h, were added to the flask. The reaction mixture was magnetically stirred at 400 rpm. It was ensured that the reaction mixture was well agitated at atmospheric pressure and reflux conditions so that there is no mass transfer resistance due to liquid film formed around the external surface of the catalyst. Under similar conditions the reaction was studied in three solvents namely nitrobenzene, *o*-dichlorobenzene and ethylene dichloride. The product samples were drawn at regular intervals and analyzed with a gas chromatograph (GC) (Hewlett-Packard Model 6890, USA) having a flame ionization detector and HP-5 capillary column (30 m length and 0.32 mm diameter, packed with silica-based supel cosil), programmed oven (temperature range 323–473 K), and 30 ml/h flow rate of  $\text{N}_2$  as carrier gas. Reaction kinetics was monitored by withdrawing the sample using a microsyringe from the reaction flask at different time intervals and measuring its composition by GC analysis. Calibration of GC peak areas was carried out by taking solutions of known compositions. The conversion was calculated on the basis of mole percent of substrate; the initial mole percent of toluene was divided by initial area percent (toluene peak area from GC) to get the response factor. The unreacted moles of toluene remaining in the reaction mixture were calculated by multiplying response factor with the area percentage of the GC peak for toluene obtained after the reaction. The conversion and selectivity was calculated as follows:

$$\text{conversion (mol\%)} = \frac{\text{initial mol\%} - \text{final mol\%}}{\text{initial mol\%}} \times 100$$

$$\begin{aligned} \text{selectivity of } p\text{-acylated product} \\ = \frac{\text{GC peak area of } p\text{-product}}{\text{sum of the GC peak area of } o\text{- and } p\text{-products}} \times 100 \end{aligned}$$

### 2.4. The catalytic reaction for cyclohexanol dehydration

Dehydration of cyclohexanol was carried out as a model reaction for acidity measurement of the catalyst samples in a fixed bed flow reactor. The catalyst samples (0.2 g) were diluted with 2.3 g of completely inert glass beads and packed in a glass reactor bed. Inert alumina was packed on the top of the catalyst to avoid channeling and ensure plug flow.

Catalyst samples were activated in situ for 2 h at 673 K under  $N_2$  flow (30 ml/min). Catalyst bed temperature was brought down to reaction temperature of 448 K and cyclohexanol (4 ml) was delivered using a syringe pump (Cole Parmer, 74900 series) with a flow rate of 0.033 ml/min. Product samples were collected after 1 h and analyzed by GC. Calibration of GC peaks was done using standard mixture of cyclohexanol and cyclohexene under similar conditions.

### 2.5. Catalyst regeneration

The spent catalyst was recovered from the reaction mixture by filtration and thoroughly washed with acetone. The recovered catalyst was then thermally treated at 673 and 823 K in air atmosphere for 4 h in a muffle furnace.

## 3. Results and discussion

The X-ray diffraction patterns of all zeolite  $\beta$  samples are given in Fig. 1. All the samples show the reflections at  $2\theta$ , 22.5 and 7.5, typical of zeolite  $\beta$  structure even after the cation exchange. However, SEM images show some morphological variations in cation exchanged samples compared to Na- $\beta$  (Fig. 2). For example, Na- $\beta$  sample (Fig. 2a) shows distinct particles with less than 1  $\mu\text{m}$  size, whereas H- $\beta$  and other rare earth cation exchanged samples display aggregated particles (Fig. 2b–d). This agglomeration may be due to the de-alumination taking place during the cation exchange process with alumina binding the zeolite particles. Agglomeration might be promoted by lanthanide cations present on the external surface of the zeolite crystallites. It has already been reported [11] that de-alumination in zeolite  $\beta$  occurs easily during the cation exchange and calci-

Table 1

Si/Al ratio as determined from EDX and crystallinity (%) of Na- $\beta$  and cation exchanged zeolite  $\beta$

Catalyst	Si/Al ratio	Crystallinity (%)
Na- $\beta$	24	100
H- $\beta$	29	97
La- $\beta$	32	97
Ce- $\beta$	29	83
Dy- $\beta$	27	89
Eu- $\beta$	31	65
Sm- $\beta$	27	65
Gd- $\beta$	31	77
Nd- $\beta$	30	86
Pr- $\beta$	34	94

The chemical composition of zeolite  $\beta$  is  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 48\text{SiO}_2\cdot\text{H}_2\text{O}$ .

nation processes. Therefore, to confirm the occurrence of de-alumination from zeolite  $\beta$  during cation exchange, surface Si/Al ratio was analyzed using EDX facility. EDX data given in Table 1 for Na- $\beta$  and rare earth cation exchanged samples support de-alumination during cation exchange process, in which Si/Al ratio increases from 24 (Na- $\beta$ ) to 26–34 for other exchanged samples. Partial loss of crystallinity in zeolite structure upon rare earth cation exchange in Na- $\beta$  is also confirmed from the X-ray diffraction data (Table 1). For example, the decrease in crystallinity compared to Na- $\beta$  for Eu- $\beta$  (35%), Sm- $\beta$  (35%), Gd- $\beta$  (23%) zeolites is substantial.

The acylation reaction of toluene was carried out over H- $\beta$  and Ce- $\beta$  at three different temperatures (368, 398 and 408 K). The toluene conversion data given in Table 2 shows that highest conversion is obtained at 408 K among the range of temperature studied.

The toluene acylation kinetics over H- $\beta$  and La- $\beta$  in nitrobenzene was studied at 408 K to determine the optimum

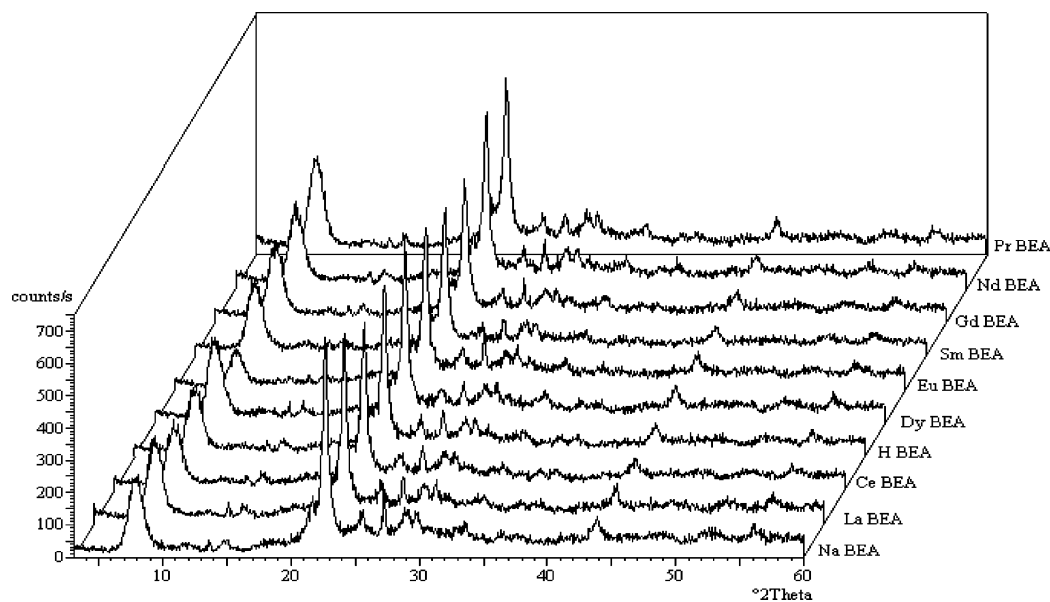


Fig. 1. XRD pattern of Na- $\beta$ , H- $\beta$  and rare earth cation exchanged zeolite  $\beta$ .

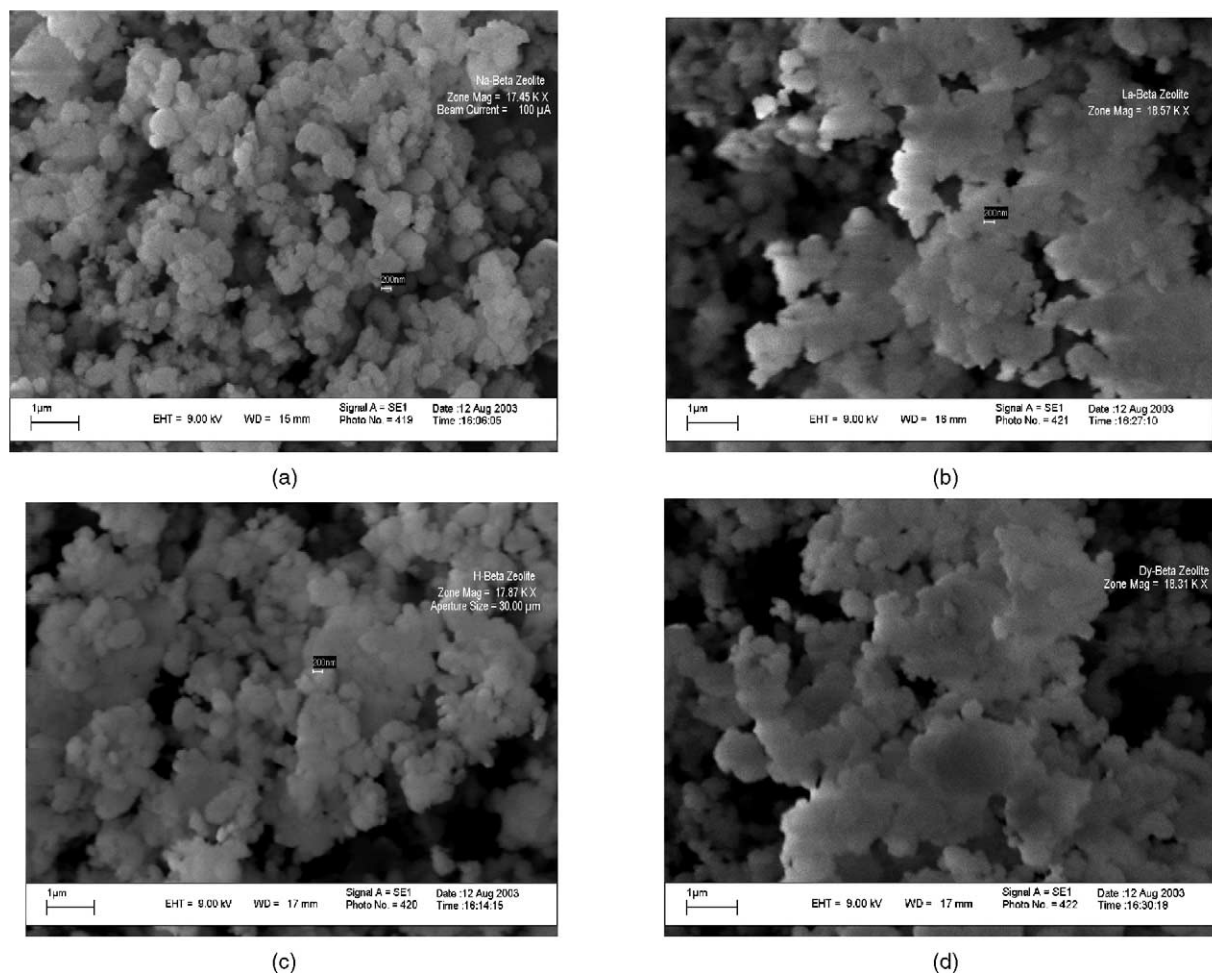


Fig. 2. (a) SEM images of zeolite Na- $\beta$ ; (b) SEM images of zeolite La- $\beta$ ; (c) SEM images of zeolite H- $\beta$ ; (d) SEM images of zeolite Dy- $\beta$ .

contact time. Table 3 shows that for both the catalysts, conversion increases with time up to 6 h after that there is a decrease in conversion indicating the optimum reaction time for maximum conversion is 6 h under specified conditions. The observed decrease in conversion after 6 h may be attributed to de-acylation reaction during longer reaction period and also due to coke formation on the surface of the zeolites which might affect the catalytically active sites present on the zeolite surface [10].

Toluene conversion and selectivity data for Na- $\beta$ , H- $\beta$  and various rare earth exchanged zeolite  $\beta$  are given in

Table 2

Conversion data of toluene acylation at different temperatures for zeolites H- $\beta$  and Ce- $\beta$

Temperature (K)	Conversion (mol%)	
	H- $\beta$	Ce- $\beta$
368	14	16
398	31	32
408	50	51

Toluene: 0.01 mol; acetic anhydride: 0.02 mol; nitrobenzene solvent: 10 ml; catalyst: 0.25 g; reaction time: 6 h.

Table 4. H- $\beta$  and rare earth cation exchanged zeolite  $\beta$  showed 12–66% toluene conversion with very high selectivity (86–100%) towards *p*-isomer of the product. In the case of Na- $\beta$ , no conversion was obtained. Among the catalyst systems studied, La- $\beta$ , H- $\beta$ , Ce- $\beta$ , and Dy- $\beta$ , showed toluene conversion in the range of 46–66% with almost 100% selectivity (except Ce- $\beta$ ). Nd- $\beta$ , Sm- $\beta$ , Eu- $\beta$ , and Gd- $\beta$  catalysts gave lower toluene conversion ranging from 27 to 35% with almost 100% selectivity. Pr- $\beta$  has shown the least conversion (12%), even though the *p*-isomer selectivity is 100%. The EDX analysis shows the complete exchange of Na<sup>+</sup> ions with H<sup>+</sup> ions. The degree of rare earth

Table 3

Conversion data for acylation of toluene at different time

Catalyst	Conversion (mol%)				
	2 h	4 h	6 h	8 h	10 h
H- $\beta$	17	45	50	46	43
La- $\beta$	34	44	66	52	46

Toluene: 0.01 mol; acetic anhydride: 0.02 mol; nitrobenzene solvent: 10 ml; catalyst: 0.25 g; reaction temperature: 408 K.

Table 4

Toluene conversion and *p*-isomer selectivity for different cation exchanged zeolite  $\beta$  using acetic anhydride as an acylating agent and nitrobenzene solvent

Catalyst	Conversion (mol%)	<i>p</i> -Selectivity (wt.%)
Na- $\beta$	–	–
H- $\beta$	50	100
Ce- $\beta$	51	86
La- $\beta$	66	100
Dy- $\beta$	46	100
Eu- $\beta$	35	98
Sm- $\beta$	31	99
Gd- $\beta$	30	100
Nd- $\beta$	27	100
Pr- $\beta$	12	100

Toluene: 0.01 mol; acetic anhydride: 0.02 mol; nitrobenzene solvent: 10 ml; catalyst: 0.25 g; reaction temperature: 408 K for 6 h.

cation exchange in zeolite H- $\beta$  calculated from the EDTA volumetric analysis was in the range of 64%. The extent of exchange has been found similar, i.e. 64% in the case of all rare earth cations. Therefore, the observed difference in the catalytic activity for toluene acylation cannot be attributed to rare earth content alone of the zeolite. The cation location, crystallinity and acidity of zeolite samples also affect the catalytic activity as discussed later.

It is known that zeolites possess both Lewis and Brønsted acid sites, which are catalytically active sites for acylation and alkylation reactions [12]. Rare earth cation exchanged zeolites will display both the types of acidity due to high charge density rare earth cations, which generate acidic hydroxyl groups inside the zeolite cavities. The electrostatic field of the cation ionizes the water molecules, which lead to the formation of acidic hydroxyl group [13]. The strength and the number of such acidic hydroxyl groups generated

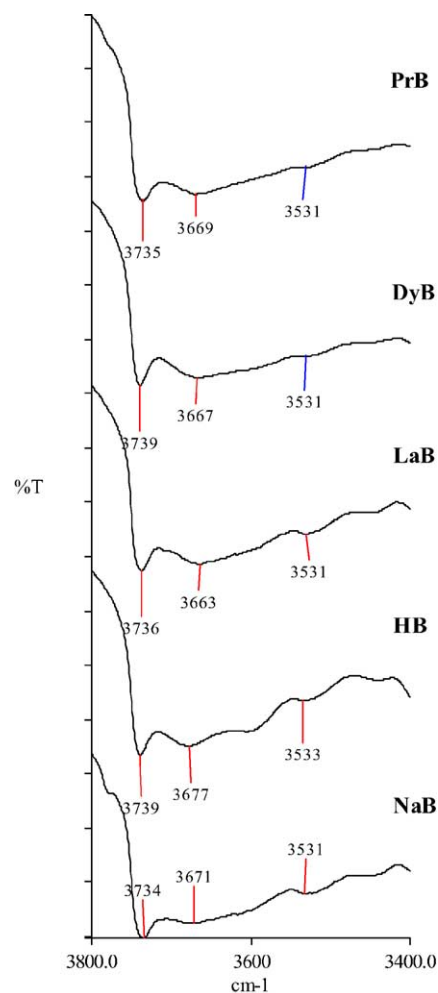


Fig. 3. FT-IR spectra of cation exchanged zeolite  $\beta$ .

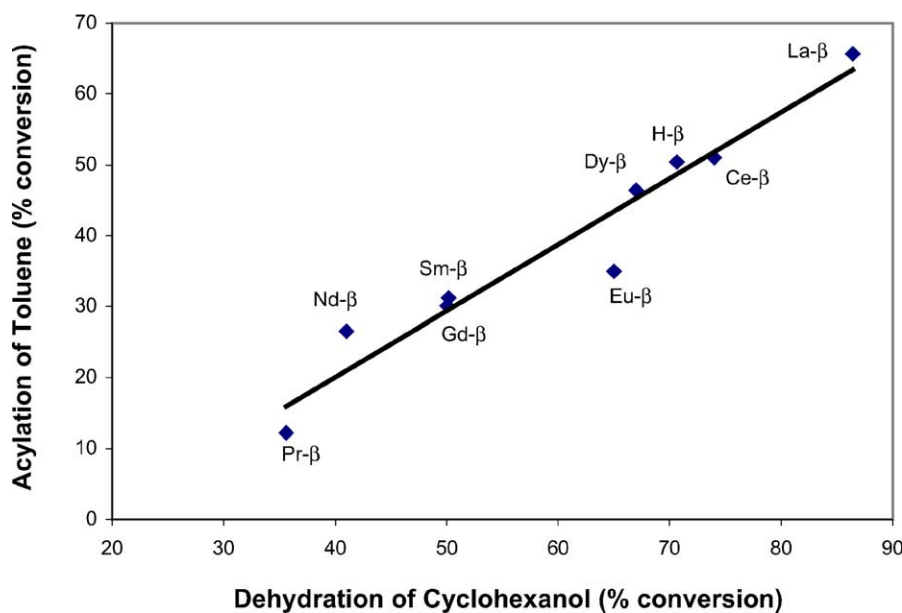


Fig. 4. Plot of toluene acylation conversion vs. cyclohexanol dehydration over cation exchanged zeolites  $\beta$ .



Table 5

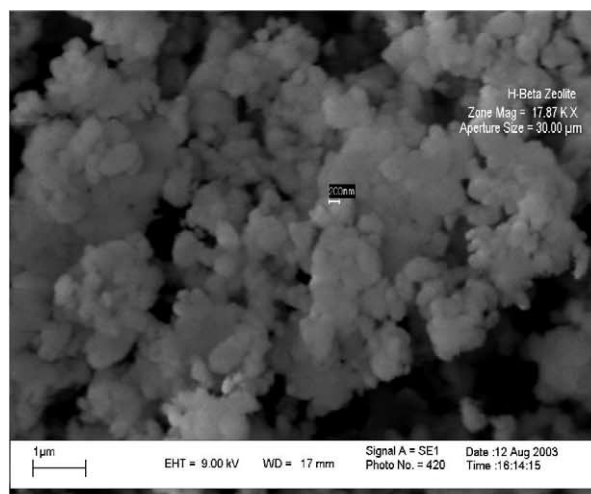
Cyclohexanol dehydration data for various rare earth cation exchanged zeolite  $\beta$ 

Catalyst	Conversion (mol%)
H- $\beta$	71
La- $\beta$	86
Ce- $\beta$	74
Dy- $\beta$	67
Eu- $\beta$	65
Sm- $\beta$	50
Gd- $\beta$	50
Nd- $\beta$	41
Pr- $\beta$	36

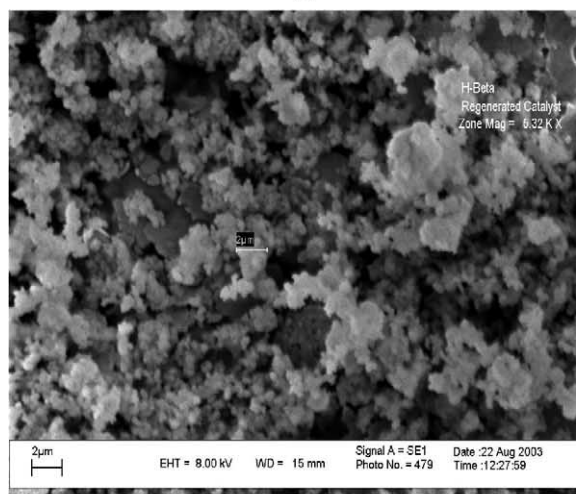
Cyclohexanol: 4 ml; catalyst: 0.2 g; activation temperature: 673 K for 2 h; reaction temperature: 448 K; reaction time: 1 h.

inside the cavities will depend upon the nature and number of rare earth cations [14]. The presence of acidic hydroxyl group has been ascertained using FT-IR spectroscopy. DRIFT spectra of all the zeolite samples obtained at ambient temperature do not show the well-resolved peaks in hydroxyl region ( $3400\text{--}3600\text{ cm}^{-1}$ ) due to the presence of physisorbed water. After heating at 473 K, H- $\beta$  and all the rare earth exchanged zeolite samples showed the bands at around  $3734$ ,  $3662\text{--}3680$  and  $3535\text{ cm}^{-1}$  (Fig. 3). The band at  $3734\text{ cm}^{-1}$  is attributed to terminal SiOH groups. The well-resolved band at around  $3662\text{ cm}^{-1}$  is attributed to acidic hydroxyl groups showing the presence of Brønsted acidity. The band at  $3535\text{ cm}^{-1}$  is attributed to non-acidic hydroxyl groups. The lower intensity of  $3535\text{ cm}^{-1}$  band in all these samples show that the exchanged cations first replace  $\text{H}^+$  ions corresponds to accessible sites representing the band at  $3662\text{ cm}^{-1}$ . Cyclohexanol dehydration is one of the model reactions generally carried out to characterize the Brønsted acidity of the solid acids [4]. Therefore, the cyclohexanol dehydration reaction was carried out, over all the zeolite samples studied here for toluene acylation reaction. The cyclohexanol conversion data for these samples are given in Table 5. Linear correlation of toluene acylation with cyclohexanol dehydration, shown in Fig. 4, strongly suggests that acylation of toluene over cation exchanged zeolite  $\beta$  is a Brønsted acid catalyzed reaction.

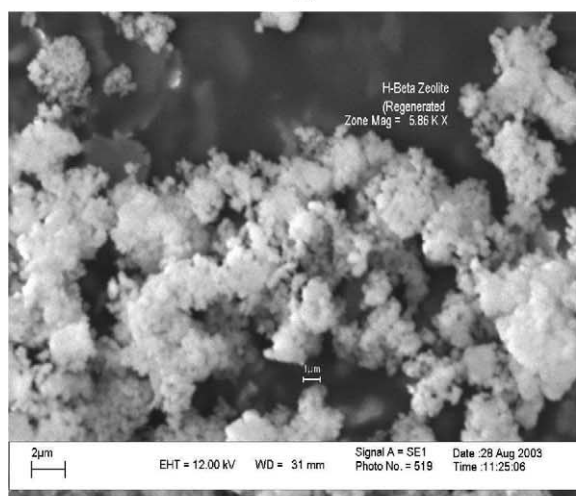
The difference in catalytic activity of these rare earth cation exchanged zeolite  $\beta$ ; with similar extent of cation exchange, may be due to the following reasons: (i) acidity of the sample, e.g. Nd- $\beta$  and Pr- $\beta$ , showed lowest activity in cyclohexanol dehydration (41–36%, respectively), representing the low Brønsted acidity and also showed least conversion for toluene acylation (27–12%, respectively). Na- $\beta$ , well known for its lower acidity, showed nil conversion for toluene acylation; (ii) Si/Al ratio and the crystallinity of the sample, as the total number of Brønsted acid sites decrease with the increase in Si/Al ratio [18]. Na- $\beta$ , having higher crystallinity shows no catalytic activity because of its lower acidity; (iii) cation position in the lattice [15], cations present at different positions in the lattice will result into different acidity depending on its immediate environment.



(a)



(b)



(c)

Fig. 5. (a) SEM image of fresh H- $\beta$ ; (b) SEM image of deactivated H- $\beta$ ; (c) SEM image of regenerated H- $\beta$ .

Table 6

Conversion and selectivity of toluene acylated using acetic anhydride in different solvents with zeolites H- $\beta$  and La- $\beta$

No.	Solvent	Conversion (mol%)		<i>p</i> -Selectivity (wt.%)	
		H- $\beta$	La- $\beta$	H- $\beta$	La- $\beta$
1	Nitrobenzene	50	66	100	100
2	<i>o</i> -Dichlorobenzene	17	18	89	91
3	Ethylene dichloride	0	0	0	0
4	Absence of solvent	19	13	100	88

Toluene: 0.01 mol; acetic anhydride: 0.02 mol; solvent: 10 ml; catalyst: 0.25 g; reaction temperature: 408 K for 6 h.

It is well known that rare earth cations like La<sup>3+</sup> and Ce<sup>3+</sup> occupy different sites in the zeolite faujasite even in hydrated and dehydrated form [10,16,17]. The rare earth cations present at an accessible or inaccessible will definitely affect the available surface acidity and in turn catalytic activity of the zeolite.

The acylation of toluene was studied over La- $\beta$  and H- $\beta$  in three solvents namely, nitrobenzene, *o*-dichlorobenzene and dichloroethane. Toluene conversion data (Table 6) shows that nitrobenzene is the favored medium for toluene acylation. The acylation of toluene in the presence of acid catalyst is an electrophilic substitution reaction wherein an acylium ion generated by interaction of acetic anhydride with the zeolite surface reacts with electron-rich aromatic ring to form an intermediate complex. This complex loses a proton to give a ketonic product. Polar solvents like nitrobenzene (dielectric constant = 34.82) and *o*-dichlorobenzene (dielectric constant = 10–10.99) might stabilize the acylium ion as well as the ionic intermediate ( $\sigma$ -complex) formed by the attack of acylium ion with the aromatic substrate and facilitate acylation reaction [19]. Nil conversion obtained with dichloroethane (dielectric constant = 9–9.99) and reason-

Table 7

Toluene conversion and *p*-isomer selectivity for cation exchanged zeolite  $\beta$  after regeneration

Catalyst	Conversion (mol%)	<i>p</i> -Selectivity (wt.%)
H- $\beta^a$	21	100
H- $\beta^b$	49	100
La- $\beta^a$	42	100
La- $\beta^b$	65	100
Dy- $\beta^a$	25	100
Dy- $\beta^b$	44	100

Toluene: 0.01 mol; acetic anhydride: 0.02 mol; nitrobenzene solvent: 10 ml; catalyst: 0.25 g; reaction temperature: 408 K for 6 h.

<sup>a</sup> Regenerated catalyst after the activation at 673 K.

<sup>b</sup> Regenerated catalyst after the activation at 823 K.

ably high conversion in the absence of solvent shows that polarity may not be the only factor influencing the conversion of toluene. The acetic acid formed in the reaction cannot acylate the substrate, as one of the zeolite samples (La- $\beta$ ) was studied for acylation of toluene using acetic acid as acylating agent (instead of acetic anhydride) under the similar experimental conditions and that showed no conversion of toluene.

Toluene acylation studied with thermally regenerated catalyst, H- $\beta$ , La- $\beta$  and Dy- $\beta$  by heating at 673 K for 4 h does not fully regenerate the catalyst as seen from low conversion value (Table 7). Microscopic study (SEM, Fig. 5b) and surface chemical analysis (EDX) of the deactivated catalysts showed the carbon deposition 2.32, 5.41 and 1.84 wt.% for H- $\beta$ , La- $\beta$  and Dy- $\beta$ , respectively, on the surface of the catalysts, which might block the acidic sites of the catalyst, resulting in the lowering of conversion. The deactivation of zeolite catalyst is reported [18] to occur due to the adsorption of more polar acylated product on the acid sites restricting the reaction of toluene with these acid sites, which decreases the reaction rate. The nature of carbonaceous species on the

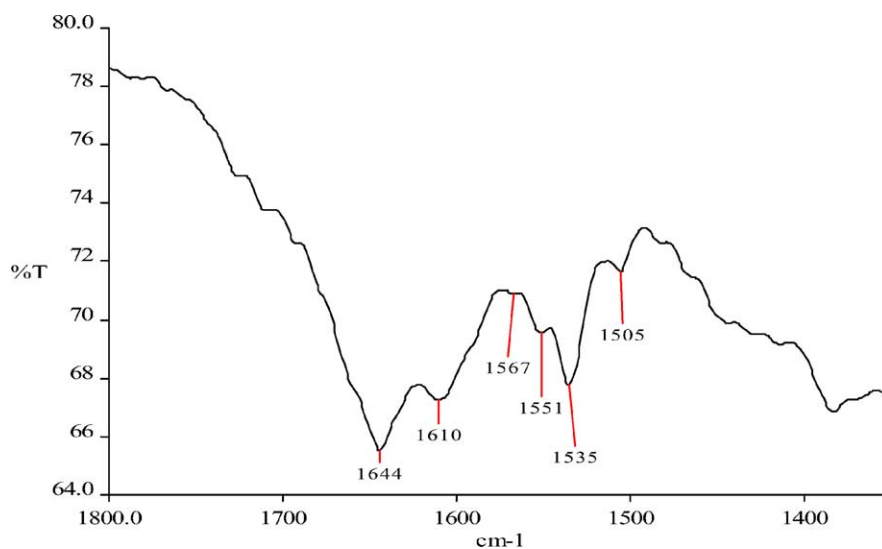
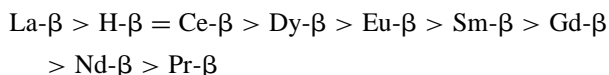


Fig. 6. FT-IR spectra of deactivated H- $\beta$ .

catalyst sites were ascertained from FT-IR spectra of the deactivated H- $\beta$ , La- $\beta$  and Dy- $\beta$ . The spectra were recorded at ambient temperature (as KBr pellet) after washing the catalysts with acetone and drying at 383 K. The spectra showed absorption bands in the range 1300–1800  $\text{cm}^{-1}$  (Fig. 6) at 1505, 1535, 1551, 1610 and 1664  $\text{cm}^{-1}$ . The formation of diketone and triketone has been demonstrated by Guignard et al. [20] during the acylation of veratrole and anisole with acetic anhydride and zeolites. The observed bands are attributed to adsorbed diketone (1505, 1535 and 1610  $\text{cm}^{-1}$ ) and triketone (1551 and 1664  $\text{cm}^{-1}$ ) formed during acylation of toluene. The SEM (Fig. 5c) and EDX data of the regenerated catalysts after activation at 823 K showed removal of carbon and morphological pattern similar to that of the fresh catalyst (Fig. 5a). The activity of these regenerated catalysts was also similar to that of fresh catalysts for toluene acylation reaction (Table 7).

#### 4. Conclusion

Rare earth cations exchanged zeolite  $\beta$  catalysts were found to be active for the liquid phase acylation of toluene with acetic anhydride in nitrobenzene solvent with >95% selectivity towards the *p*-isomer of the product. The order of activity of various rare earth cations exchanged beta is as follows:



It was further shown that acylation of toluene is Brönsted acid catalyzed reaction. Among the various solvents studied namely, nitrobenzene, *o*-dichlorobenzene, ethylene dichloride it was observed that nitrobenzene is the most efficient solvent for the acylation of toluene with acetic anhydride.

#### Acknowledgements

The authors thank CSIR's NMITLI program for financial assistance and Dr. P.K. Ghosh, Director, CSMCRI for his

encouragement. We are also thankful to Dr. (Mrs.) Pragyana Bhatt, Mr. V.B. Boricha and Mr. Chandrakanth C.K. for analytical support.

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