

Nitration of *o*-xylene over rare earth cations exchanged zeolite- β with nitric acid and acetic anhydride

V.N. Sheemol, B. Tyagi, R.V. Jasra *

Silicates and Catalysis Discipline, Central Salt and Marine Chemicals Research Institute, G.B. Marg, Bhavnagar 364002, Gujarat, India

Received 15 December 2005; received in revised form 25 January 2006; accepted 26 January 2006

Available online 31 March 2006

Abstract

Liquid phase nitration of *o*-xylene was studied with sulfated silica, sulfated zirconia, zeolite H- β and rare earth cations exchanged zeolite- β with nitric acid and acetic anhydride/1,2-dichloroethane as solvent. H- β and rare earth exchanged zeolite- β were found to be efficient solid acid catalysts both in acetic anhydride and 1,2-dichloroethane. Nitration with nitric acid and acetic anhydride via acetyl nitrate as nitrating species is efficient and preferable rather than reaction in 1,2-dichloroethane solvent. Among the lanthanides studied Ce- β gave maximum conversion 86% with 58% *para* selectivity in acetic anhydride. The catalyst can be easily recovered and regenerated thus providing economic and environmentally friendly method for nitration reaction.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Nitration; *o*-Xylene; H- β ; Rare earth cations exchanged zeolite- β

1. Introduction

Nitration of aromatic substrates is one of the widely studied organic reactions as nitro aromatic compounds are industrially important intermediates during the synthesis of dyes, plastics and pharmaceuticals [1]. The nitro derivatives of xylene isomers are used as intermediates for the production of vitamins, agrochemicals, fragrance and dyes. The classical nitration with a mixture of concentrated nitric and sulfuric acid gives predominantly *ortho* and *para* products in 2:1 ratio [2]. As *para* nitro-products are commercially more useful, *para* selective nitration is desirable. The disadvantages of classical nitration methodology include corrosive nitrating reagents, formation of environmentally unfriendly waste that is expensive to dispose off, over nitration, poor selectivity and oxidation of by-products. This has prompted research efforts for exploring methods alternative to classical nitration using solid acid catalysts, organic nitrating agents or other source of nitronium ions.

Zeolite-based solid acid catalysts are potentially attractive due to their three dimensional crystalline microporous structure with well-defined cages and channels resulting into possible

shape selectivity, recovery and re-use of the catalyst. Zeolites mordenite [3,4,9], ZSM-5 [3,4], ZSM-11 [5], X [6], Y [3,4,6] and beta [3,4,7,8] have been studied for nitration of various activated as well as deactivated aromatic substrates such as benzene [3], mono-substituted benzene namely toluene [3,4,7,9,25,26], halo-benzene [3,4], phenol [6], anisole [3] and di-substituted benzene [4,8,27] with enhanced *para* selectivity. The concept of shape selectivity seems to be responsible for *para* selective nitration with zeolite catalysts. Among the zeolites studied, zeolite- β is reported to give higher regioselectivity for *para*-isomer [4,7,8]. The geometrical constraint of pore structure of beta is supposed to be responsible for higher selectivity that provides easy diffusion and also impose some order on the transition state [4]. Haouas et al. [10] suggested that high selectivity of zeolite- β could be linked to steric hindrance of *ortho* position induced by adsorption rather than to classical shape selectivity.

Besides zeolites, variety of other solid acids such as modified silica [9], sulfuric acid supported on silica [11] and silica gel [12], clay supported metal nitrates [13–16], metal exchanged clays [17], sulfonated polystyrene resin [18], Nafion-H [19], lanthanide triflates and sulfonates [20], modified zirconia and sulfated zirconia [11] have been studied for nitration of aromatic compounds. However, these are associated with the problem of leaching of acid from the support during reaction and even

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2567562.
E-mail address: rvjasra@csmcri.org (R.V. Jasra).

calcination, require higher diluted conditions, long reaction time and poor selectivity towards some aromatic compounds.

Furthermore, alternative nitrating agents such as nitric acid in mixed acids [21a], nitronium salts in organic media [21], metal nitrates of sodium [22], titanium, zirconium, iron [23] and cerium [24], dinitrogen tetraoxide [25,26] and dinitrogen pentoxide [27,28], organic nitrating agents such as acetyl nitrates [4,7,11,29] and alkyl nitrates [12,25] have been studied. Besides the organic solvents, ionic liquids have also been used as solvents [30].

The conventional process for nitration of *o*-xylene gives a mixture of *p*-nitro-xylene (31–55%) and *o*-nitro-xylene (45–69%) [8]. The earlier studies of nitration of xylene isomers along with other benzene derivatives, reported by Olah et al. [21] using conventional mixed acid, mixed acid in organic solvents, nitronium salts in organic solvents such as tetramethylene sulfone and nitromethane resulted into lower *p*-selectivity. Uemura et al. [22] used sodium nitrite/sodium nitrate and trifluoro acetic acid resulting into good yield, however, only *o*- and *m*-products were formed. Coombes and Russell [23] reported higher *p*-selectivity with transition metal nitrate compounds in carbon tetrachloride. However, this involves expensive and extremely hygroscopic reagents and the use of hazardous chlorinated compounds. Nitration of xylene isomers over sulfuric acid supported silica gel [12] resulted into good conversion; however, *p*-selectivity was not significantly high. Recently, Choudary and co-workers [8] reported good *p*-selectivity with solid acid catalyst, zeolite- β , using chlorinated solvents. In the present studies, we report nitration of *o*-xylene with nitric acid using various solid acids such as sulfated silica, sulfated zirconia and zeolites and 1,2-dichloroethane as a solvent using Dean Stark assembly for azeotropic removal of water formed during the reaction and present in nitric acid. Encouraging results for *p*-selective nitration with zeolite- β prompted us to extend our studies over zeolite-based catalysts particularly with rare earth cations (La^{3+} , Ce^{3+} , Dy^{3+} , Eu^{3+} , Sm^{3+} , Gd^{3+} , Nd^{3+} , Pr^{3+}) exchanged zeolite- β with nitric acid in acetic anhydride and 1,2-dichloroethane as solvents. To our knowledge, this is the first study with rare earth cations exchanged zeolite- β as catalysts for nitration of *o*-xylene. Zeolite- β was particularly chosen for *o*-xylene nitration in this study as Bernasconi et al. [7] from their study on nitration of toluene using various zeolites have shown that only with zeolite- β heterogeneously catalyzed nitration competes effectively with homogenous nitration in liquid phase.

2. Experimental

2.1. Materials

La, Ce, Dy, Eu, Sm, Gd, Nd and Pr acetates used for cation exchange in zeolites were procured from M/S. Aldrich Chemicals, USA. Ammonium chloride, propanol-1, aqueous ammonia (25%), *o*-xylene, acetic anhydride, 1,2-dichloroethane, concentrated nitric acid (70%) and sulfuric acid (98%) were purchased from M/S. S.D. Fine Chem. Ltd., India and were used as such. Zirconium propoxide (70 wt% in propanol-1) was procured from Sigma-Aldrich. Silica (60–120 mesh), silica (300 mesh) and

precipitated silica were obtained from M/S. Kadvani Chemicals Jamnagar, India.

Na- β having Si/Al ratio = 24, BET surface area 612 m²/g and crystallite size of 0.2–0.4 μm was procured from Zeocat, Switzerland.

2.2. Catalyst preparation and characterization

Sulfated silica: sulfuric acid supported silica catalysts (SS) were prepared following a reported procedure [11]. Typically, silica was activated at 400 °C for 18 h, cooled in a desiccator and treated with 1.8 g H₂SO₄ solution/g silica for 15 min under magnetic stirring. The samples were kept for 2 days, filtered and dried at 120 °C for 18 h. The samples prepared using silica (60–120 mesh), silica (300 mesh) and precipitated silica are designated as SS-1, SS-2 and SS-3, respectively.

Sulfated zirconia: sulfated zirconia samples (SZ) were prepared by one-step sol-gel technique reported earlier [31]. In the one-step method, addition of sulfuric acid was done by two ways: (i) an aqueous solution of concentrated sulfuric acid was added drop-wise into the 30 wt% solution of zirconium propoxide in propanol; (ii) concentrated sulfuric acid was added to the 30 wt% solution of zirconium propoxide in propanol; water was then added drop-wise to complete the hydrolysis. The samples were dried at 110 °C for 12 h after filtration and calcined at 600 °C for 4 h. The samples are designated as SZ-1 and SZ-2, respectively.

Zeolite H- β and rare earth cation exchanged zeolite- β : 10 g of Na- β was treated with 1M aqueous ammonium chloride (with solid to aqueous solution ratio of 10) at 80 °C for 6 h followed by filtration of the sample and washing with distilled water till the filtrate showed the absence of chloride ions. The sample obtained was oven dried at 110 °C for 10 h followed by calcination at 550 °C for 6 h in air atmosphere. The H- β thus prepared was further ion-exchanged with 0.01M aqueous solution of rare earth acetate salts (with solid to aqueous solution ratio of 20) at 80 °C for 6 h. After ion-exchange, the samples were thoroughly washed with water to remove acetate anions followed by oven drying at 110 °C for 12 h and was calcined at 550 °C for 6 h under air atmosphere at a heating rate of 5 °C min⁻¹ in a programmable tubular furnace. The degree of cation exchange in the zeolite H- β 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 an indicator.

The crystallinity of the ion-exchanged zeolites was determined from X-ray powder diffraction data measured on Phillips X'Pert MPD system using Cu K α ($\lambda = 1.54056 \text{ \AA}$). FT-IR transmittance spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer at ambient temperature in the range of 400–4000 cm⁻¹ as KBr pellets. Diffuse reflectance infrared spectra were recorded on the above spectrophotometer, equipped with 'The Selector' DRIFT accessory (Graseby Specac, P/N 19900 series), an environmental chamber (EC) (Graseby Specac, P/N 19930 series), an automatic temperature controller (Graseby Specac, P/N 20130 series) and a water circulator system (Julabo, model F-25, HD). DRIFT spectra were recorded at 200 °C in the

range of 400–4000 cm^{-1} using dry N_2 ($30 \text{ cm}^3 \text{ min}^{-1}$) as a carrier gas.

The electron microscopic study was done with scanning electron microscope (Leo series VP1430) equipped with Oxford Instruments EDX facility, having silicon detector under a pressure of $>1.34 \times 10^{-2}$ 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. Cyclohexanol dehydration

Dehydration of cyclohexanol was carried out as a model reaction for measuring Brønsted acidity of zeolite catalyst samples using a fixed bed flow reactor. The zeolite sample (0.2 g) was packed in a glass reactor bed. Inert glass beads (2.3 g) were added with the samples for proper packing of the catalyst bed to avoid channeling and ensure plug flow. Catalyst samples were activated in situ for 2 h at 450°C under N_2 flow ($30 \text{ cm}^3 \text{ min}^{-1}$). Catalyst bed temperature was brought down to reaction temperature of 175°C and cyclohexanol (4 cm^3) was delivered using a syringe pump (Cole Parmer, 74900 series) with a flow rate of $0.033 \text{ cm}^3 \text{ min}^{-1}$. Product samples were collected after 1 h and analyzed by Gas Chromatograph (GC) (Hewlett Packard 6890 Model, USA) having a flame ionisation detector and HP-5 capillary column of 30 m length and 0.32 mm diameter, programmed oven temperature of (50 – 200°C) and N_2 ($30 \text{ cm}^3 \text{ h}^{-1}$) as a carrier gas. Calibration of GC peaks was done using standard mixture of cyclohexanol and cyclohexene under similar conditions. The conversion was calculated using following equation:

Conversion (wt%)

$$= 100 \times \frac{\text{initial wt\% of cyclohexanol} - \text{final wt\% of cyclohexanol}}{\text{initial wt\% of cyclohexanol}}$$

2.4. Nitration of *o*-xylene

The nitration of *o*-xylene was done in liquid phase as a batch reaction. Typically, a 50 ml two-neck round bottom flask equipped with Dean Stark apparatus was immersed in a constant temperature oil bath. The temperature of oil bath was maintained within $\pm 0.5^\circ\text{C}$. This system was attached with an efficient water condenser. Catalyst (0.1 g, pre-activated at requisite temperature) was added to a mixture of *o*-xylene (12 mmol) and solvent (1:4, v/v) to the flask. The same solvent was also taken in the Dean Stark apparatus. The reaction was carried out at temperatures in the range from 90 to 105°C with continuous magnetic stirring (400 rpm). Concentrated nitric acid (15 mmol) was added to this mixture drop-wise so that the addition was completed in 1 h and the reaction was carried out for another 2 h. The product samples were drawn at regular intervals and analyzed with GC (Hewlett Packard 6890 Model, USA) using same conditions as used for cyclohexene analysis. Calibration of GC peak areas was carried out by taking solutions of known compositions of *o*-xylene and solvent. The conversion and selec-

tivity for *p*-nitro-xylene isomer was calculated using following equation:

Conversion (wt%)

$$= 100 \times \frac{[\text{initial wt\% of } o\text{-xylene} - \text{final wt\% of } o\text{-xylene}]}{[\text{initial wt\% of } o\text{-xylene}]}$$

p-Selectivity (wt%)

$$= 100 \times \frac{\text{GC peak area of } p\text{-product}}{\sum \text{ of GC peak area of } o\text{-, } p\text{- and other product}}$$

2.5. Catalyst regeneration

The spent zeolite catalyst was recovered from the reaction mixture by filtration. The recovered catalyst was washed thoroughly with acetone and dried in the oven at 120°C for 12 h. Thus, dried catalyst was tested for the nitration reaction as such and after activation at 550°C for 6 h to study the regeneration of the catalyst.

3. Results and discussion

Nitration of *o*-xylene with sulfated silica, sulfated zirconia and zeolite H- β (Table 1) showed *o*-xylene conversion from 20% to 58% with selectivity for *p*-nitro-xylene isomer ranging from 42% to 50%. As sulfated silica (SS-3) and zeolite H- β gave higher selectivity for *p*-nitro-xylene isomer, therefore, further studies were carried out with these two samples. To optimize the reaction time for maximum conversion and *p*-selectivity, samples were analyzed immediately after the completion of addition of nitric acid (i.e. 1 h) and successively after every 1 h of the reaction. The result (Table 2) showed that the conversion of *o*-xylene increases with time, however, *p*-selectivity decreases after 3 h of the reaction. Therefore, total time for nitration reaction along with the addition of nitric acid was optimized to 3 h.

To optimize the reaction temperature, nitration of *o*-xylene was studied with H- β at varied temperature ranging from 95 to 105°C . The data (Table 3) showed that highest conversion and *p*-selectivity is obtained at 100°C . As among the solid catalysts studied, zeolite H- β showed encouraging (60%) *p*-selectivity,

Table 1
Nitration of *o*-xylene over various solid acid catalysts

Catalyst	Conversion (wt%)	Selectivity (wt%)	
		<i>p</i> -Nitro-xylene	<i>o</i> -Nitro-xylene
SS-1	49	45	47
SS-2	58	47	47
SS-3	54	50	41
SZ-1	49	43	49
SZ-2	51	42	41
H- β	20	50	47

SS, sulfated silica, 1 (60–120), 2 (300) and 3 (precipitated silica), respectively; SZ, sulfated zirconia catalyst. Reaction conditions: *o*-xylene:1,2-dichloroethane = 1:4 (v/v), *o*-xylene: HNO_3 = 1:1.2 ratio; reaction temperature = 90°C ; reaction time = 3 h; catalyst 0.1 g after activation of SS catalysts at 120°C for 18 h, SZ and H- β catalysts at 450°C for 2 h.

Table 2
Nitration of *o*-xylene with sulfated silica catalyst

Catalyst	Time (h)	Conversion (wt%)	Selectivity (wt%)	
			<i>p</i> -Nitro-xylene	<i>o</i> -Nitro-xylene
SS-3	1	11	53	41
	2	44	49	47
	3	54	50	41
	4	56	41	53

SS-3, sulfated precipitated silica catalyst. *Reaction conditions:* *o*-xylene:1,2-dichloroethane = 1:4 (v/v), *o*-xylene:HNO₃ = 1:1.2 ratio; reaction temperature = 90 °C; catalyst 0.1 g after activation at 120 °C for 18 h; reaction time 1 h, immediately after the addition of nitric acid.

Table 3
Nitration of *o*-xylene with H-β catalyst at varied temperature

Catalyst	Temperature (°C)	Conversion (wt%)	Selectivity (wt%)	
			<i>p</i> -Nitro-xylene	<i>o</i> -Nitro-xylene
H-β	95	27	54	46
	100	53	60	40
	105	40	55	45

Reaction conditions: *o*-xylene:1,2-dichloroethane = 1:4 (v/v), *o*-xylene:HNO₃ = 1:1.2 ratio; reaction time = 3 h; catalyst 0.1 g after activation at 450 °C for 2 h.

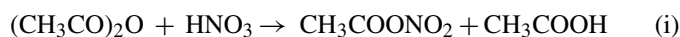
further studies were extended with H-β and a series of rare earth cations exchanged zeolite-β with 1,2-dichloroethane and acetic anhydride as a solvent. The conversion and selectivity data over H-β and various rare earth cations exchanged zeolite-β studied under optimized conditions of temperature and time are given in Table 4. The conversion and selectivity to *p*-isomer were found to be 40–65% and 51–65%, respectively, with 1,2-dichloroethane as a solvent. With acetic anhydride as a solvent the conversion values were significantly increased to 66–86%. Our results with H-β showing 74% conversion having 61% *p*-selectivity and 86% conversion with Ce-β having 58% *p*-selectivity are comparable to the results as reported by Smith et al. [4] showing 99% conversion and 44% *p*-selectivity over H-β with HNO₃ and acetic anhydride at 0 °C.

Table 4
Nitration of *o*-xylene with H-β and rare earth cation exchanged zeolites

Catalyst	Conversion (wt%)		Selectivity (wt%)			
	AC ₂ O	DCE	<i>p</i> -Nitro-xylene		<i>o</i> -Nitro-xylene	
			AC ₂ O	DCE	AC ₂ O	DCE
Ce-β	86	61	58	55	31	45
Gd-β	77	43	58	54	33	46
Sm-β	77	40	56	51	29	49
Pr-β	77	53	56	54	34	46
La-β	76	54	57	63	29	37
H-β	74	53	61	60	27	40
Dy-β	70	60	56	61	29	39
Nd-β	67	65	57	55	29	45
Eu-β	66	50	56	60	29	40

Reaction conditions: *o*-xylene:solvent = 1:4 (v/v), *o*-xylene:HNO₃ = 1:1.2 ratio; reaction temperature = 100 °C; reaction time = 3 h; catalyst 0.1 g after activation at 450 °C for 2 h.

Higher conversion with acetic anhydride is attributed to the in situ formation of acetyl nitrate as active nitrating species in presence of nitric acid [4,7,21a,29]. Acetic anhydride reacts with HNO₃ to form acetyl nitrate (AcONO₂) intermediate species as follows:



The other factors which could also have contributed towards higher conversion observed (Table 4) with acetic anhydride as a solvent include: (i) nitration reaction is accompanied with the release of water that will adversely affect the acidity of the zeolite. With acetic anhydride as a solvent, water molecules released during reaction will react with acetic anhydride to give acetic acid and thereby retaining the acidity of the zeolite. In dichloroethane, such a consumption of released water is not possible. (ii) Acetic anhydride could also act as a dehydrating reactant and consumes the water present in the 70% HNO₃ to form acetic acid thus increasing the concentration of nitric acid and thereby enhancing the conversion of the substrate.

AcONO₂ is reported to form a surface bound complex with zeolite lattice aluminium and thereby resulting into enhanced *p*-selectivity [7]. However, in our case *p*-selectivity observed with acetic anhydride was not significantly different from those observed with dichloroethane wherein NO₂⁺ as the nitrating species is formed as follows:



To rule out the possibility of acylation of *o*-xylene in presence of acetic anhydride and nitric acid, the reaction was also carried out in absence of nitric acid under similar conditions. The samples were drawn at regular intervals and analyzed by GC. The GC results showed the presence of a peak of acylated product after 3 h of the reaction; during early phases of the reaction starting from 10 min the peak of acylated product was absent. When the reaction was carried out after adding nitric acid, the peak of acylated product was not observed. It confirms that acylation of *o*-xylene is not occurring with acetic anhydride and nitric acid.

Among all the rare earth exchanged zeolites, Ce-β was observed to give maximum conversion of 86% with 58% *p*-selectivity. The catalytic activity of exchanged zeolites is correlated with structural and textural properties of the zeolite. The X-ray diffraction patterns of all zeolite-β samples (Fig. 1) show the reflections at 2θ 22.5 and 7.4, typical of zeolite-β structure before and after the cation exchange. However, partial loss of crystallinity (65–97%) in zeolite structure as compared to Na-β (100%) and increase in Si/Al ratio from 24 (Na-β) to 27–34 for cation exchanged samples was observed from XRD and EDX analysis respectively. SEM images also show some morphological variations in cation exchanged samples compared to Na-β (Fig. 2). For example, Na-β sample (Fig. 2a) shows distinct particles of <1 μm size, whereas H-β and other rare earth cation exchanged samples display aggregated particles (Fig. 2c and d). This agglomeration may be due to the de-alumination taking place during the cation exchange process with alumina binding the zeolite particles. SEM images of Ce-β (Fig. 2b), however,

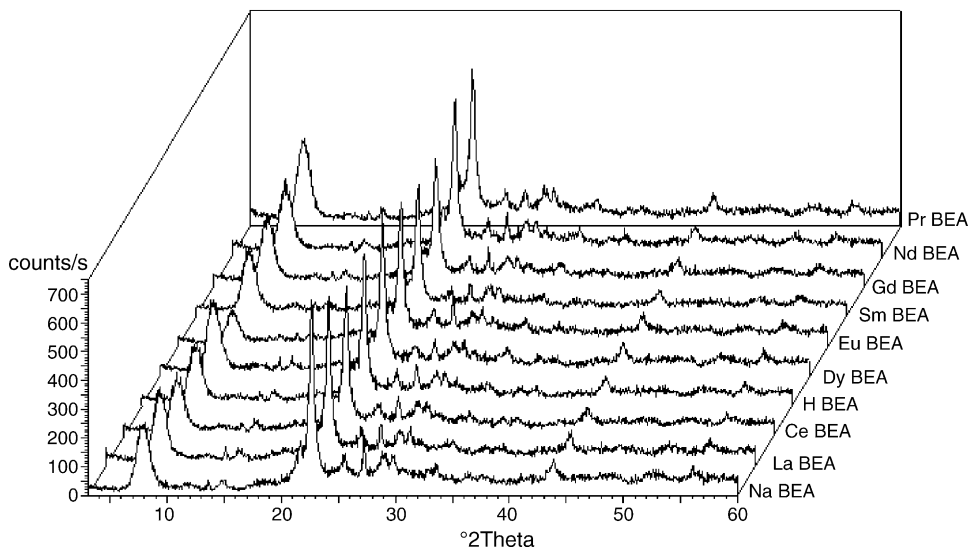


Fig. 1. XRD pattern of Na- β , H- β and rare earth cation exchanged zeolite- β .

show distinct particles rather than aggregated particles, which may be one of the factors responsible for higher catalytic activity for *o*-xylene conversion with Ce- β .

The extent of rare earth cation exchange in zeolite- β is of similar range (64%) as observed from the EDTA volumetric analysis. Therefore, the observed difference in the catalytic activity for *o*-xylene nitration cannot be attributed to rare earth content of the zeolite. Zeolites possess both the Lewis and the Brønsted acid sites, which are catalytically active sites. 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 strength and the number of such acidic hydroxyl groups generated inside the cavities will depend upon the nature, number and location of rare earth cations. The presence of acidic hydroxyl group in zeolite samples has been ascertained using FT-IR spectroscopy. DRIFT spectra of all the zeolite samples, recorded after heating at 200 °C, showed a well resolved peak between 3660 and

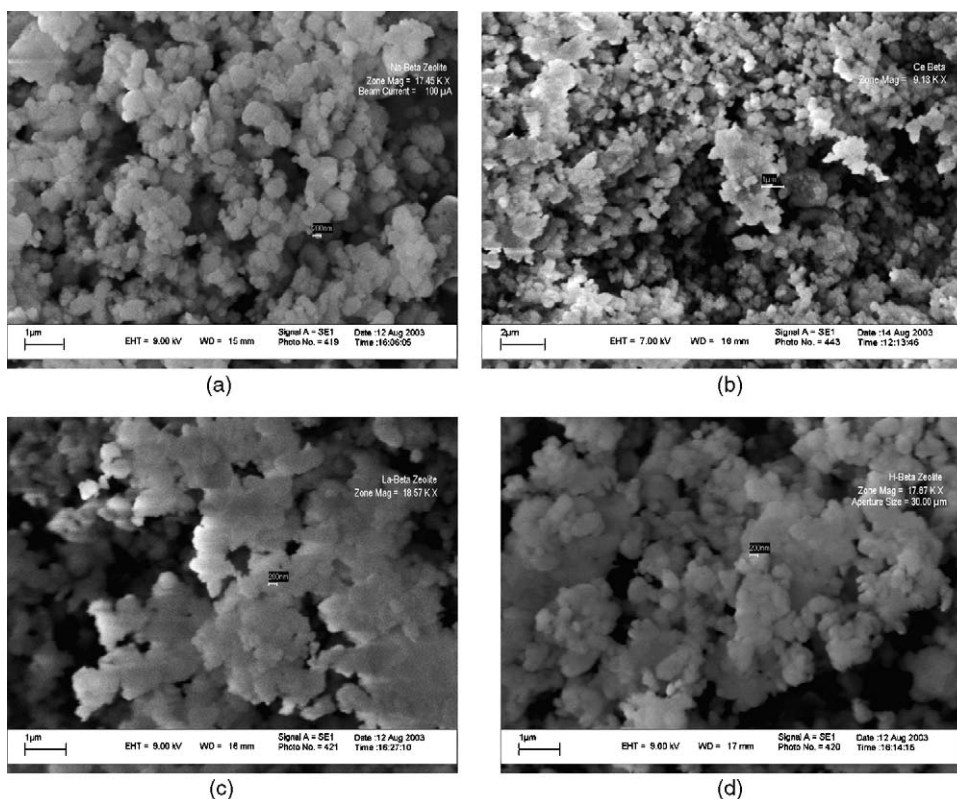


Fig. 2. SEM images of (a) Na- β , (b) Ce- β , (c) H- β , (d) La- β .

Table 5
Dehydration of cyclohexanol with H- β and rare earth cation exchanged zeolites

Catalyst	Conversion (wt%)
H- β	71
La- β	86
Ce- β	74
Dy- β	67
Eu- β	65
Sm- β	50
Gd- β	50
Nd- β	41
Pr- β	36

Reaction conditions: cyclohexanol = 4 ml; flow rate = $0.033 \text{ cm}^3 \text{ min}^{-1}$; catalyst 0.2 g, in situ activation at 450°C for 2 h; reaction temperature = 175°C ; reaction time = 1 h.

3680 cm^{-1} , which is attributed [32] to accessible acidic hydroxyl groups showing the presence of Brönsted acidity.

Brönsted acidity of these samples was also measured by cyclohexanol dehydration model reaction. The data of cyclohexanol conversion for all these samples was observed in the range of 36–86% (Table 5) indicating the existence of the Brönsted acidity in these samples. H- β , Ce- β and La- β showed higher Brönsted acidity as observed from cyclohexanol conversions of 71–86%. The order of the Brönsted acidity is observed as: La- β > Ce- β > H- β > Dy- β > Eu- β > Sm- β = Gd- β > Nd- β > Pr- β . However, the order of conversion of *o*-xylene nitration in acetic anhydride was found to be as Ce- β > Gd- β = Sm- β = Pr- β \geq La- β > H- β > Dy- β > Nd- β > Eu- β . The order of conversion was also observed to be different in dichloroethane solvent (Table 4) than the Brönsted acidity order (Table 5). The lack of direct correlation between *o*-xylene and cyclohexanol conversion shows that the Brönsted acid sites alone are not responsible for the nitration of *o*-xylene in rare earth cation exchanged zeolites. It indicates that in rare earth cation exchanged zeolites both Lewis and Brönsted acid sites are contributing towards nitration of *o*-xylene in both the solvents. However, the extent of the contribution varies with number and strength of Lewis acid sites which will further depend on the location of these cations in zeolite cavities. Location of cations also depends on various factors like temperature and solvent. Therefore, a lack of direct correlation between *o*-xylene conversions and Brönsted acidity of the exchanged zeolites and also different order of catalytic activity in different solvents was observed. It is also reported in the literature that nitration of aromatics occur with the Lewis acids such as lanthanum triflates with good conversion [20].

As the formation of water during the nitration reaction affects the acidity of the zeolite, the use of molecular sieve to absorb the water molecules was studied besides the use of Dean Stark assembly for azeotropic removal of water formed during the nitration reaction. For this, 2 g molecular sieve (4 \AA) was added (i) in the reaction mixture and (ii) in the Dean Stark tube. Addition of molecular sieve in the reaction mixture resulted in the disruption of crystalline structure of molecular sieve due to nitric acid. Since 4 \AA contains Na^+ that may exchange with protons from dissociated HNO_3 resulting into dealumination and

Table 6
Nitration of *o*-xylene with sulfated silica and rare earth cation exchanged zeolites after in situ drying of water

Catalyst	Conversion (wt%)	<i>p</i> -Nitro-xylene (wt%)
SS-3 ^a	54	50
SS-3 ^b	46	32
SS-3 ^c	48	45
La- β ^a	54	63
La- β ^b	45	65
Dy- β ^a	60	61
Dy- β ^b	41	62
Dy- β ^c	56	60

SS-3, sulfated precipitated silica catalyst.

^a Without molecular sieve.

^b With molecular sieve in the reaction mixture.

^c With molecular sieve in the Dean Stark tube.

destruction of high aluminium 4 \AA molecular sieve structure. In both (i) and (ii) cases, the conversion values with sulfated silica (SS-3) as well as with exchanged zeolites (La- β and Dy- β) were observed to decrease, however, without any characteristic effect on *p*-selectivity with exchanged zeolites, as shown in Table 6. Smith et al. [4] also found no significant effect on the conversion and selectivity for the nitration of toluene with the use of molecular sieve.

To study the re-usability of the catalyst, the reaction was carried out with re-used and thermally regenerated catalysts (Dy- β , Ce- β and La- β). The re-used catalyst (after washing with acetone and dried at 120°C for 12 h) showed a sharp decrease in the activity and selectivity of the catalysts. However, after thermal regeneration, (heating at 550°C for 6 h) activity and the selectivity of the catalyst improved and were found to be within 10% of the values for the fresh catalysts (Table 7). The blockage of acidic sites due to the adsorption of the nitro-product on the external surface of the catalyst is responsible for the deactivation. During the activation at 550°C oxidation of the adsorbed species occurs leading to regeneration of catalytic sites for the reaction. The nature of adsorbed species on the catalyst sites was ascertained from FT-IR spectra of the used Dy- β catalyst after nitration reaction in acetic anhydride solvent. The IR bands

Table 7
Nitration of *o*-xylene with fresh, reused and regenerated rare earth cation exchanged zeolites

Catalyst	Conversion (wt%)		<i>p</i> -Nitro-xylene (wt%)	
	AC ₂ O	DCE	AC ₂ O	DCE
La- β ^a	76	54	57	63
La- β ^b	41	36	53	56
La- β ^c	72	48	55	56
Ce- β ^a	86	–	58	–
Ce- β ^b	53	–	49	–
Ce- β ^c	78	–	56	–
Dy- β ^a	–	60	–	61
Dy- β ^b	–	46	–	55
Dy- β ^c	–	56	–	55

^a Fresh catalyst.

^b Reused catalyst.

^c Regenerated catalyst.

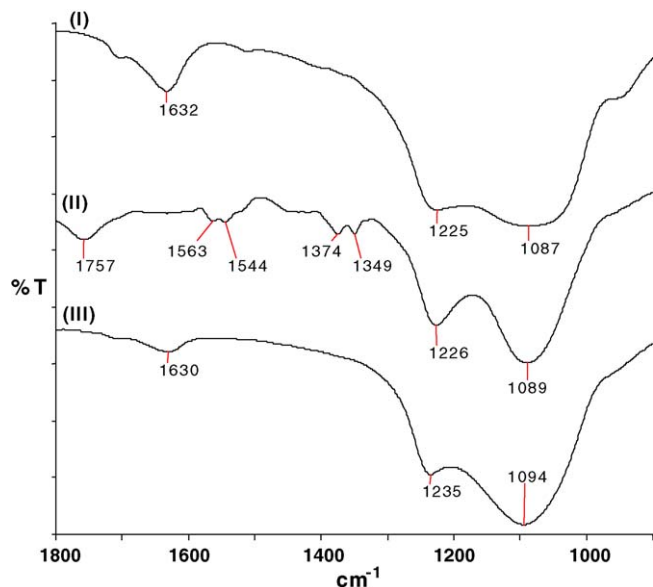


Fig. 3. FT-IR spectra of (I) fresh, (II) used and (III) regenerated catalyst.

(Fig. 3) at 1563, 1544 and 1374, 1349 cm^{-1} are due to asymmetric and symmetric vibrations of nitro-product, respectively [33]. The intense band at 1757 cm^{-1} shows the presence of acetic acid [33] formed during the reaction. FT-IR spectrum, after activation at 550 $^{\circ}\text{C}$ for 6 h, is similar to fresh catalyst indicating the regeneration of the catalyst (Fig. 3). XRD spectra of used catalyst showed a significant decrease of one of the characteristic peak at $7.40\ 2\theta$, which is recovered after regeneration (Fig. 4).

The above study reflects that easily re-generable and strong solid acid is required for nitration reaction, as the water and nitric acid may deactivate the acid sites and also disintegrate the crystalline structure of the catalyst during the reaction. Therefore, zeolite H- β and rare earth exchanged zeolite- β catalysts

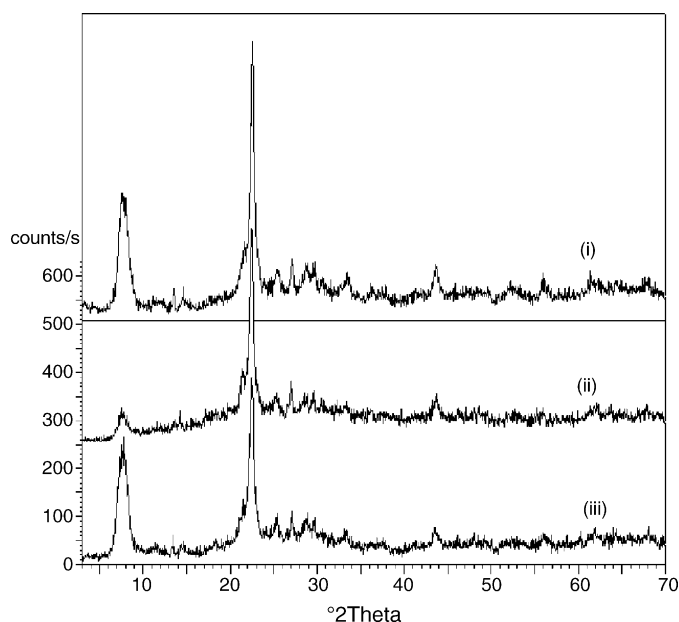


Fig. 4. XRD pattern of (i) fresh, (ii) used and (iii) regenerated catalyst.

are found to be good solid catalysts for the nitration of *o*-xylene in acetic anhydride as well as in 1,2-dichloroethane solvent.

4. Conclusions

H- β and rare earth exchanged zeolite- β are efficient solid acid catalysts for the liquid phase nitration of *o*-xylene with HNO_3 both in acetic anhydride and 1,2-dichloroethane solvent. Nitration with HNO_3 and acetic anhydride via acetyl nitrate as nitrating species is efficient and preferable rather than reaction in 1,2-dichloroethane solvent. Among the lanthanides studied, Ce- β gave maximum conversion 86% with 58% *para* selectivity in acetic anhydride. The catalyst can be easily recovered and regenerated thus providing economic and environmentally friendly method for nitration reaction.

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. C.K. Chandrakanth for analytical support.

References

- [1] G.A. Olah, R. Malhotra, S.C. Narang, Nitration: Methods and Mechanisms, VCH, New York, 1989.
- [2] R.G. Coombes, D.G.H. Crout, J.G. Hoggett, R.B. Moodie, K. Schofield, J. Chem. Soc. B (1970) 347.
- [3] B.M. Choudary, M. Sateesh, M.L. Kantam, K.K. Rao, K.V. Ramprasad, K.V. Raghavan, J.A.R.P. Sarma, Chem. Commun. (2000) 25.
- [4] K. Smith, A. Musson, G.A. DeBoos, J. Org. Chem. 63 (1998) 8448.
- [5] S.N. Nagy, J. Phys. Org. Chem. 7 (1994) 385.
- [6] (a) T. Esakkidurai, K. Pitchumani, J. Mol. Catal. A: Chem. 185 (2000) 305; (b) T. Esakkidurai, M. Kumarraja, K. Pitchumani, Proc. Ind. Acad. Sci. (Chem. Sci.) 115 (2003) 113.
- [7] S. Bernasconi, G. Pringruber, A. Kogelbauer, R. Prins, J. Catal. 219 (2003) 231.
- [8] M.L. Kantam, B.M. Choudary, N.S. Kumar, K.V. Ramprasad, J. Mol. Catal. A: Chem. 229 (2005) 67.
- [9] K. Smith, Bull. Soc. Chim. Fr. 272 (1989).
- [10] M. Haouas, S. Bernasconi, A. Kogelbauer, R. Prins, Phys. Chem. Chem. Phys. 3 (2001) 5067.
- [11] A. Kogelbauer, D. Vassena, R. Prins, J.N. Armor, Catal. Today 55 (2000) 151.
- [12] J.M. Riego, Z. Sedin, J.M. Zaldivar, N.C. Marziano, C. Tortato, Tetrahedron Lett. 37 (1996) 513.
- [13] P. Laszlo, P. Penntreau, J. Org. Chem. 52 (1987) 2407.
- [14] A. Cornelis, P. Laszlo, P. Penntreau, J. Org. Chem. 48 (1983) 4771.
- [15] B. Gigante, A.O. Prazeres, M.J. Marcelo-Curto, A. Cornelis, P. Laszlo, J. Org. Chem. 60 (1995) 3445.
- [16] S. Samajdar, F.F. Becker, B.K. Banik, ARKIVOC (Part viii) (2001) 27.
- [17] B.M. Choudary, M.R. Sarma, K.V. Kumar, J. Mol. Catal. A: Chem. 87 (1994) 33.
- [18] O.L. Wright, J. Teipel, D. Thoennes, J. Org. Chem. 30 (1965) 1301.
- [19] G.A. Olah, R. Malhotra, S.C. Narang, J. Org. Chem. 43 (1978) 4628.
- [20] (a) F.J. Waller, A.G.M. Barret, D.C. Braddock, D. Ramprasad, Chem. Commun. (1997) 613; (b) M. Shi, S.-C. Cui, J. Fluorine Chem. 113 (2002) 207; (c) A. Kawada, S. Takeda, K. Yamashita, H. Abe, T. Harayama, Chem. Pharma. Bull. 50 (2002) 1060;

- (d) T.N.P. -Vogt, K. Deleersnyder, K. Binnemans, J. Alloys Compd. 374 (2004) 46.
- [21] (a) G.A. Olah, S.J. Kuhn, S.H. Flood, J.C. Evans, J. Am. Chem. Soc. 84 (1962) 3687;
(b) G.A. Olah, S.J. Kuhn, J. Am. Chem. Soc. 84 (1962) 3684.
- [22] S. Uemura, A. Toshimitsu, M. Okano, J. Chem. Soc., Perkin Trans. 1 (1978) 1076.
- [23] R.G. Coombes, L.W. Russell, J. Chem. Soc., Perkin Trans. 2 (1974) 830.
- [24] S. Dinctürk, J.H. Ridd, J. Chem. Soc., Perkin Trans. 2 (1982) 961.
- [25] J.M. Smith, H. Liu, D.E. Resasco, Stud. Surf. Sci. Catal. 111 (1997) 199.
- [26] D.B. Akolekar, G. Lemay, A. Sayari, S. Kaliaguine, Res. Chem. Intermed. 21 (1995) 7.
- [27] R.P. Claridge, N.L. Lancaster, R.W. Millar, R.B. Moodie, J.P.B. Sandall, J. Chem. Soc., Perkin Trans. 2 (1999) 1815.
- [28] A.J. Hill, R.W. Millar, J.P.B. Sandall, Org. Biomol. Chem. 2 (2004) 90.
- [29] J.W. Morzycki, Z. Lotowski, M. Stepniowska, A. Gryszkiewicz, A.Z. Wilczewska, Tetrahedron 53 (1997) 16161.
- [30] K.K. Laali, V.J. Gettwert, J. Org. Chem. 66 (2001) 35.
- [31] M.K. Mishra, B. Tyagi, R.V. Jasra, J. Mol. Catal. A: Chem. 223 (2004) 61.
- [32] J.W. Ward, in: J.A. Rabo (Ed.), Zeolite Chemistry and Catalysis, ACS Monograph 171, American Chemical Society, Washington, USA, 1976, p. 118 (Chapter 3).
- [33] G. Socrates, Infrared Characteristic Group Frequencies, John Wiley, New York.