



Acetoxylation and hydration of limonene and α -pinene using cation-exchanged zeolite beta

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ABSTRACT

Hydration and acetoxylation of limonene and α -pinene into terpineol and terpinyl acetate in the liquid phase have been studied using transition metal and rare earth ion-exchanged beta zeolite. These catalysts under optimized reaction conditions showed higher activity and selectivity compared to conventionally used acid catalysts such as H_2SO_4 and amberlyst-15. Conversions of 9–26% and 58–82% were obtained for limonene in the presence of glacial and aqueous acetic acid, respectively, and the selectivity for major products α -terpinyl acetate and terpineol were up to 54% and 65%, respectively. Conversion values in the range of 62–100% and 72–100% were obtained for α -pinene in the presence of glacial and aqueous acetic acid, respectively. Virtually no oligomerisation of monoterpenes occurred under studied conditions. From the measured acidity data of these zeolites, it is observed that both hydration and acetoxylation are Brønsted acid-catalysed reactions.

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1. Introduction

Limonene, α -pinene and β -pinene are naturally occurring monoterpenes used as substrates for the production of monoterpenoid flavours and fragrances [1,2]. Acid-catalysed hydration and acetoxylation of terpenes are among the important synthetic routes to valuable terpenic alcohols and esters which find applications in perfumery and pharmaceutical industry [1]. Strong mineral acid such as H_2SO_4 is frequently used for hydration and acetoxylation of terpenes [1]. However, the disposal of spent mineral acids poses a serious environmental problem. Therefore, solid acid catalysts such as zeolites [3–7] and cation exchange resins [8–10] being environmentally benign have been considered for these transformations.

Industrially, the hydration of α -pinene to produce α -terpineol, which is one of the top 30 commonly used flavour compounds [11], is mainly performed using dilute aqueous solutions of sulphuric and phosphoric acid [12]. α -Terpineol can also be obtained by hydration [13–18] or bioconversion [19] of limonene. However, search for higher selectivities and environmentally friendly reaction conditions have resulted in a number of research efforts with an objective to replace the traditional homogeneous processes by heterogeneous ones. In recent years, a reasonable amount of

research work has been done on α -pinene isomerisation, using natural or synthetic zeolites as catalysts [20–25]. Zeolites namely beta [26,27] and USY [27,28] have also been successfully used in the hydration reaction of α -pinene, with good selectivity of 48% for terpineol, although long reaction times and high water/terpene ratios are required to ensure good selectivities for α -terpineol at high pinene conversions. The acid-catalysed processes of limonene hydration commonly produce large amounts of diols besides terpineols [29]. The mixture of α - and γ -terpinyl acetates were obtained from limonene and acetic acid with ferric sulphate as the catalyst [30]. The homogeneous and heterogeneous hydration and acetoxylation of monoterpenes catalysed by heteropoly acid have been reported [31]. In hydration of α -pinene, the application of solid acid catalysts such as cation exchange resins, activated carbon dispersed in polymeric membranes [32] and zeolites [8,26,27,33,34] have also been reported.

Zeolite beta can be synthesized [35–37] with Si/Al values from 10 to >100, and possesses a three-dimensional intersecting channel system, two mutually perpendicular straight channels, each with a cross-section of $7.4 \times 6.5 \text{ \AA}$ running in the *a*- and *b*-directions and a sinusoidal channel of $5.5 \times 5.5 \text{ \AA}$ running parallel to the *c*-direction [38–40]. Due to its high acidity and larger sized pore system this zeolite has been reported to be a potential re-generable catalyst in organic reactions [41–45] catalytic cracking [46], isomerisation [47,48], aromatic alkylation with alkenes [49], isobutane alkylation with *n*-butene [50], and disproportionation of hydrocarbons [51].

The present study describes the liquid phase acetoxylation and acetoxylation/hydration of limonene and α -pinene using

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zeolite beta and its cation-exchanged analogues as catalysts. Cation exchange is known to modify catalytic activity and molecular sieving properties of zeolites [52]. Emphasis is put on achieving high selectivities towards the addition products, terpineol, borneol and their acetates.

2. Experimental

2.1. Materials

Zeolite beta was purchased from Zeocat, Uetikon which had a chemical composition of 1.2% Na₂O, 7.8% Al₂O₃ and 91% SiO₂. Limonene, α -Pinene was purchased from Sigma–Aldrich, USA and all other chemicals used in the present study were AR grade from S.D. Fine Chemicals Ltd., Bombay, India. All chemicals procured were used as such without any purification or any other treatment.

2.2. Catalysts preparation

The commercially obtained beta zeolite denoted as Na-beta was used for preparing H-beta as follows; Na-beta was ammonium exchanged by treating zeolite with 0.1 M ammonium chloride solution in a 1:80 (w/v) ratio at 80 °C for 6 h in an oil bath. Thus treated zeolite was then filtered, and washed with hot distilled water till Cl⁻ was no more detected by AgNO₃ solution. The same procedure was repeated thrice to ensure complete ammonium exchange. Dried ammonium-exchanged zeolite sample was calcined by heating at 550 °C in air for 6 h to produce H-zeolite. The H-beta thus prepared was ion-exchanged with solutions of 11 different metal salts. The different metal salt solutions used were those of La³⁺, Li⁺, Ce³⁺, Co²⁺, Cu²⁺, Ag⁺, Fe²⁺, Mn²⁺, Ni²⁺, Sr²⁺, and Zn²⁺. H-beta was mixed with 0.1 M aqueous solution of each salt separately. The zeolite to salt solution ratio was kept as 1:80 (w/v). The resultant mixture was heated to 80 °C for 6 h and then filtered, washed with distilled water and dried at a temperature below 80 °C in vacuum. The above-described procedure was repeated twice to achieve higher ion exchange of all metal ions. In the case of silver exchange, the above procedure was performed in dark to prevent oxidation of silver ions. The catalysts were designated as M-beta, where M represents the exchanged metal ion.

2.3. Catalysts characterization

All prepared catalysts were characterized for surface area, pore volume, pore size distribution, and crystallinity. The surface area and pore volume were determined by N₂ physisorption measurements at 77.4 K employing the BET method [53] using Micromeritics ASAP 2010 surface area analyzer. The samples were activated under

vacuum (1×10^{-2} mmHg) at 350 °C for 4 h prior to N₂ adsorption measurements.

Structural analysis of catalysts was done by X-ray diffraction using Philips X'Pert MPD diffractometer with Cu K α 1 ($\lambda = 1.5405 \text{ \AA}$) as a radiation source in 2θ range from 2° to 60°.

The catalyst morphology was determined by electron microscopy using a scanning electron microscope, Leo 1430VP. The catalyst samples were mounted directly on the holders and covered with sputtered gold and then observed at an accelerating voltage of 10–20 keV.

Diffuse reflectance FT-IR spectra were recorded on a PerkinElmer Spectrum GX FT-IR 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). 'The Selector' collects diffuse reflectance using optically optimized off-axis configuration. Activated samples with pyridine adsorbed on its surface were placed in the micro cup (cell) of EC equipped with a ZnSe window using a special Delrin filling funnel. For DRIFT experiments, catalyst sample was activated at 120 °C for 3 h and then exposed to pyridine vapour. Typically in a vacuum desiccator, 25 ml of dry pyridine and 0.5 g of zeolite samples were kept under vacuum for 24 h. Subsequently, the samples were evacuated (10^{-2} Torr) for 30 min at room temperature to desorb physisorbed pyridine. DRIFT spectra were recorded, initially at room temperature, in the range of 400–4000 cm⁻¹ using dry N₂ as a carrier gas. The sample was then successively heated at a specific temperature in the range of 100–450 °C at the rate of 25 °C min⁻¹ at atmospheric pressure. The sample was held at each temperature for 30 min, thus allowing sufficient time for pyridine desorption before recording spectra. Vapours of desorbed pyridine were collected in dilute HCl solution. For recording the spectra, typically 100 scans were co-added at a resolution of 4 cm⁻¹ with a standard mid-IR DTGS detector and a germanium-coated KBr beam splitter.

2.4. Catalytic activity

Typically, reactants were taken in a 50 ml two-necked round bottom flask fitted with a coiled condenser. Reaction mixture was heated to desired temperature with the reaction temperature being controlled by a PID controller. The magnetic stirring was continuously done for efficient contact between reactant molecule and catalyst surface. Adequate precautions were taken to maintain the reaction temperature and to restrict the vapour loss of products. All catalysts were activated at 450 °C for 4 h prior to their use in catalytic reaction.

Brönsted acidity of all catalysts was measured using model reaction of dehydration of cyclohexanol to cyclohexene. For cyclohexanol dehydration, 0.1 g of the catalyst, 2 ml of cyclohexanol and 1 g of molecular sieve 4 Å were taken in a 50 ml two-necked round bottom flask. Reactions were conducted at 150 °C under continuous stirring for 9 h. The catalysts and molecular sieve 4 Å were activated at 450 °C for 4 h their use in the reaction. Molecular sieve 4 Å was used for in situ adsorption of water generated during dehydration of cyclohexanol.

The reaction products were analyzed by a gas chromatograph (Hewlett–Packard, model 6890 USA) equipped with a Carbowax capillary column 60 m long and 0.25 mm in internal diameter. Nitrogen was used as a carrier gas (flow 0.5 ml/min) with injection port temperature of 250 °C, and column temperature ranging from 70 to 220 °C. Pure α -pinene, camphene, limonene, α -terpinene and tricyclene, α -terpinyl acetate, α -terpineol, bornyl acetate and

Table 1
Properties of the catalysts on dry basis.

Catalyst	BET S.A. (m ² /g)	Micropore volume (cm ³ /g)	Crystallinity (%)
Na-beta	548	0.171	100
Li-beta	543	0.167	70
Cu-beta	534	0.173	91
La-beta	523	0.167	91
Ce-beta	512	0.164	91
Mn-beta	523	0.161	84
Co-beta	534	0.167	86
Zn-beta	534	0.169	85
Sr-beta	518	0.167	77
Ni-beta	546	0.175	64
Fe-beta	528	0.170	91
Ag-beta	513	0.163	76
H-beta	544	0.174	87

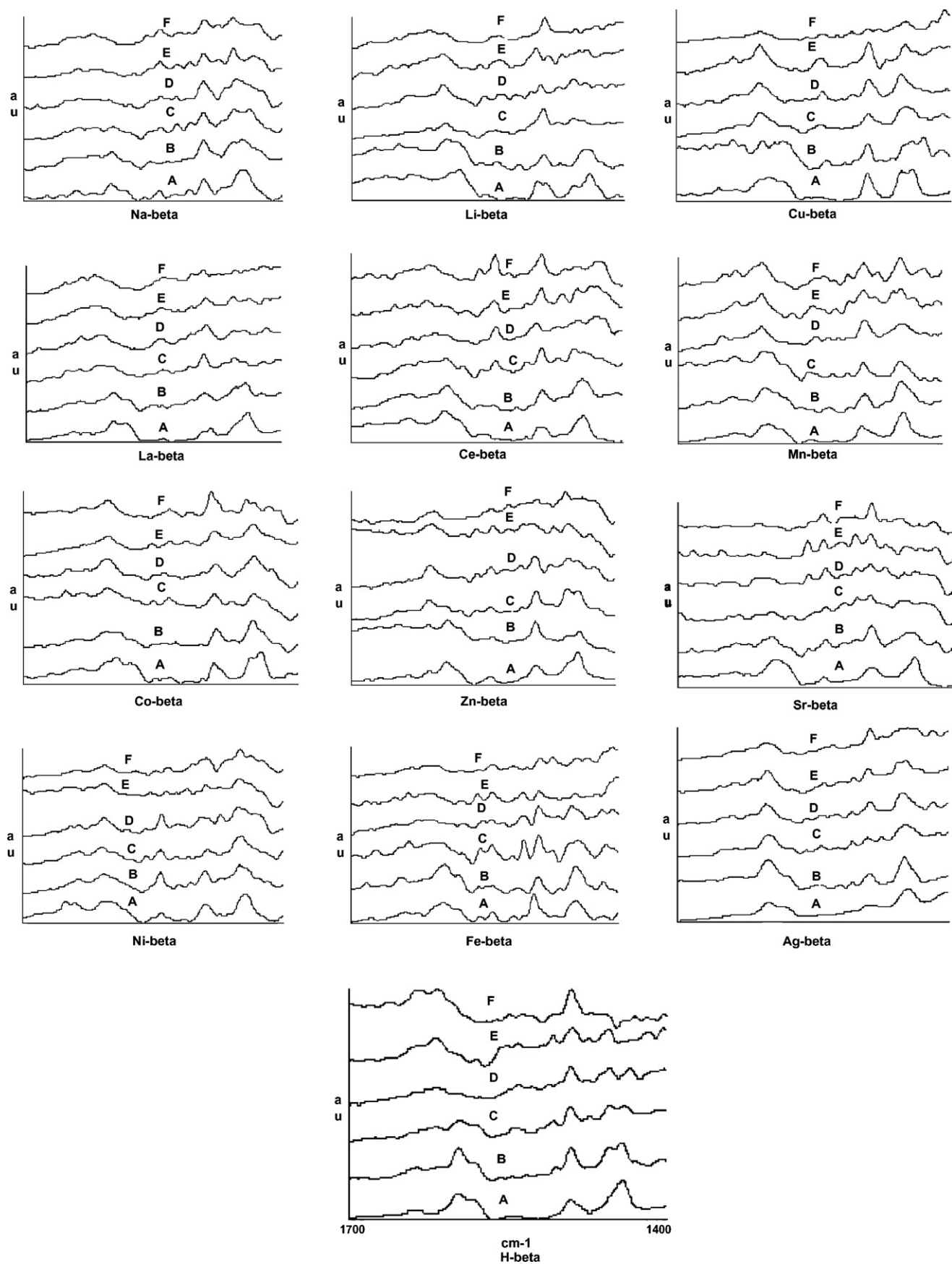


Fig. 1. Pyridine-adsorbed DRIFT IR of ion-exchanged beta zeolites at various temperatures: (A) 100 °C; (B) 200 °C; (C) 300 °C; (D) 350 °C; (E) 400 °C; (F) 450 °C.

borneol were used for calibration of gas chromatography response:

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

$$\text{selectivity of product} = \frac{\text{GC peak area of desired product}}{\sum \text{GC peak area of all products}} \times 100$$

3. Results and discussions

3.1. Catalyst characterization

Table 1 shows the surface area and micropore volume of catalysts studied for acetoxylation/hydration reactions. No significant change in the surface area and micropore volume of zeolite beta after cation exchange. The X-ray diffraction patterns corresponding to Na-zeolite, H-zeolite and ion-exchanged zeolites are shown

in Fig. S1 (supporting information). All the catalysts showed characteristic peaks in 2θ range of 7.5–22.5 corresponding to zeolite beta. The X-ray crystallinity of ion-exchanged beta zeolites were compared with Na-beta using the equation:

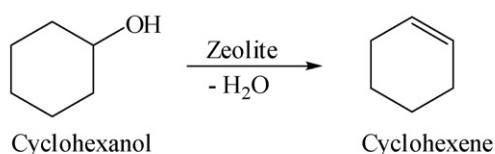
$$\text{crystallinity (\%)} = \left(\frac{\sum I}{\sum I_{\text{Na}}} \right) \times 100$$

where I is the intensity of six major peaks of samples and I_{Na} is the intensity of six major peaks of Na-beta zeolite.

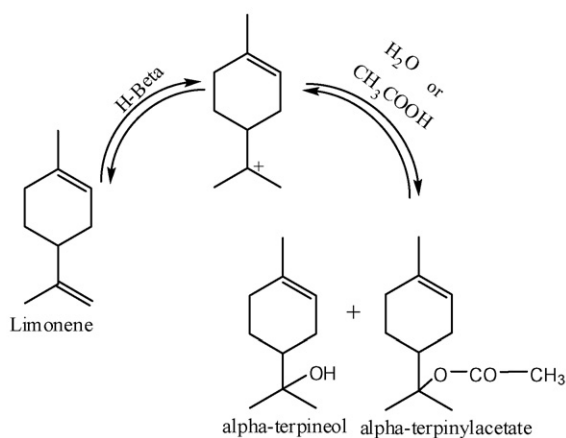
Loss in crystallinity was found in ion-exchanged catalysts as shown in Table 1. It could be due to dealumination in beta zeolite during the cation exchange and calcination processes [54]. H-beta structure is known to be relatively fragile and calcination or steaming above 673 K is reported to cause dealumination with deposition of extra framework aluminum inside the channels [55,56].

The scanning electron micrographs of the ion-exchanged calcined form of zeolites (Fig. S2, supporting information) show that these zeolites are well crystalline. Furthermore, textural properties

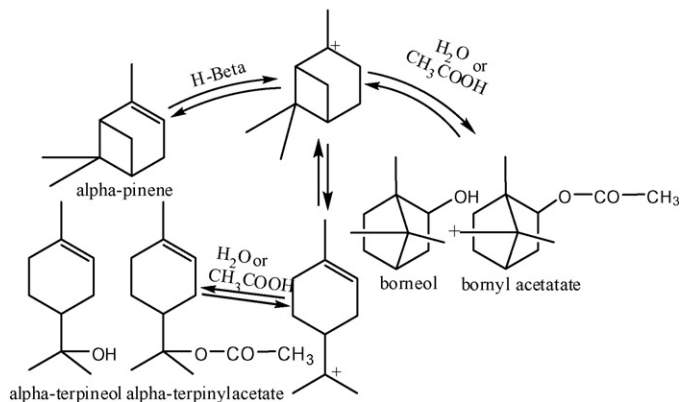
Dehydration of cyclohexanol



Hydration and acetoxylation of limonene



Hydration and acetoxylation of α -pinene



Scheme 1. Hydration and acetoxylation of limonene and α -pinene with acetic acid.

of all catalysts are retained on ion-exchange and were similar to Na-zeolite.

Pyridine interacts differently with solid surface acid sites depending upon the nature of acid sites, i.e., Brønsted or Lewis sites [57] as depicted in Scheme 1 (supporting information). Species I (Lpy) is formed as coordinately bound pyridine through its lone pair of electrons on the nitrogen atom to Lewis acid center, e.g., Al^{3+} cations present on clay mineral surface. Species II (Bpy) is formed as pyridinium ion, with a transfer of H^+ ion from the Brønsted acid site of the minerals to pyridine. Species III (Hpy) is formed as a result of hydrogen bonding between the pyridine nitrogen atom and the $-OH$ groups of minerals. Pyridine vibration bands appear in the IR region of $1400-1700\text{ cm}^{-1}$. The IR bands near 1640 and 1540 cm^{-1} correspond to Bpy (Brønsted pyridine) acid sites. The band at 1540 cm^{-1} attributed to $-NH$ bending of pyridinium ions is characteristic for Bpy acid sites. The IR band at $1450-1455\text{ cm}^{-1}$ is characteristic of Lpy (Lewis pyridine) acid sites and bands near 1440 and 1590 cm^{-1} correspond to Hpy (pyridine hydrogen-bonded) sites [58,59]. A strong band at 1490 cm^{-1} is attributed to pyridine associated with all acid sites, i.e., Lpy + Bpy + Hpy [60,61].

The DRIFT spectra of pyridine-adsorbed ion-exchanged beta zeolites were recorded at various temperatures as shown in Fig. 1. In all samples, a broad peak at $1437-1445\text{ cm}^{-1}$ appearing at lower temperature was attributed to the physical adsorption of pyridine. At lower temperatures, the LPy peak at $1450-1455\text{ cm}^{-1}$ was found to merge with the above peak. However, at higher temperatures, the LPy peak appeared clearly up to a temperature of 400°C in all catalysts. The characteristic peaks of BPy appeared at $1540-1545$ and 1637 cm^{-1} at lower temperature. The peaks appearing at $1540-1545\text{ cm}^{-1}$ were sharper at lower temperatures and started diminishing as the temperature was increased. The peak at 1637 cm^{-1} broadened at higher temperature. The peak at 1490 cm^{-1} attributed to all types of sites disappeared at higher temperatures. The HPy peaks at $1437-1445$ and $1595-1599\text{ cm}^{-1}$ also disappeared after 300°C .

3.2. Reaction studies

The acidic catalyst promotes not only addition of acetic acid or water to limonene and α -pinene but also many side reactions such as skeletal and/or double-bond isomerisation and oligomerisation of substrate molecules. The formation of α -terpineol along with its acetate was detected as the major products of limonene, while monocyclic α -terpineol and bicyclic borneol along with their

acetate were the major products of α -pinene (Scheme 1). The balance between various reaction pathways is very delicate and depends on the reaction conditions. The effect of reaction variables on the catalytic activity and product distribution was studied as described below.

4. Hydration and acetoxylation of limonene

Hydration and acetoxylation reaction of limonene was carried out at 50°C with aqueous acetic acid and glacial acid. Tables 2 and 3 show the results obtained from hydration and acetoxylation of limonene with cation-exchanged zeolite beta. Product distribution shows that terpinyl acetate and terpineol are the main products. In the presence of acid catalyst, limonene produces carbocation and nucleophile attacks easily on the exocyclic double bond. The reaction is normally complicated by acid-catalysed oligomerisation of limonene. In the present study, only isomerisation of limonene took place together with formation of addition products.

The catalytic activity of ion-exchanged beta zeolites in the presence of glacial acetic acid on limonene showed the following order:

$Cu > Mn > Zn > Ni > H > Co > La > Fe > Li > Ce > Sr > Ag$

In the presence of 10% aqueous acetic acid on limonene, the catalytic activity was in the following order:

$H > Zn > Cu > Ce > Co > Mn \gg La > Sr > Ni > Fe > Li > Ag$

In presence of glacial acetic acid with all catalysts, limonene conversion was in the range of 9–26% maximum conversion of 26% was obtained with Cu-beta while it was minimum 9% with Ag-beta. The product composition showed that two types of products were formed, addition products and isomerised products. α -Terpinyl acetate was the main product with selectivity varying from 41% to 53%.

In aqueous acetic acid conditions, maximum conversion of 59% was obtained with H-beta while it was minimum 28% with Ag-beta. The conversions obtained by Zn-beta 58% and Cu-beta 57% were closer to that obtained with H-beta. For other ion-exchanged zeolites, it varied from 51% to 54%. Product types were similar to those obtained with glacial acetic acid conditions. α -Terpineol was the main product. The maximum selectivity of 65% was obtained with Li-beta while it was minimum 24% with Ag-beta. The remaining catalysts showed selectivity in the range of 43–58%.

The conversions in aqueous condition were always higher than those in glacial acetic acid. In acetic acid solution, in presence of the

Table 2
Reaction of limonene with aqueous acetic acid using ion-exchanged beta zeolite.

Catalysts	Conversion of limonene (%)	Selectivity of products (%)								
		A	B	C	D	E	F	G	H	I
Li-beta	51	1	4	2	3	7	5	65	10	0
Cu-beta	57	2	7	3	3	9	5	57	8	3
La-beta	52	3	8	4	4	11	6	55	6	2
Ce-beta	54	3	7	4	5	11	8	53	7	2
Mn-beta	52	3	7	4	5	11	8	52	6	3
Co-beta	53	2	6	3	4	8	5	58	12	2
Zn-beta	58	3	7	4	5	10	8	51	7	4
Sr-beta	52	3	7	3	5	10	6	57	7	2
Ni-beta	52	4	13	5	6	11	9	43	5	4
Fe-beta	51	4	8	4	6	13	9	46	4	4
Ag-beta	28	8	20	9	11	19	9	24	0	0
H-beta	59	4	10	5	6	11	10	45	4	5

Reaction conditions: Catalyst weight 0.1 g, limonene 2 ml, reaction temperature 50°C , reaction time 24 h, aqueous acetic acid 10 ml. A, α -Phellendrene; B, α -terpinene; C, γ -terpinene; D, *p*-cymene; E, terpinolene; F, other isomers; G, α -terpineol; H, α -terpinyl acetate; I, others addition products.

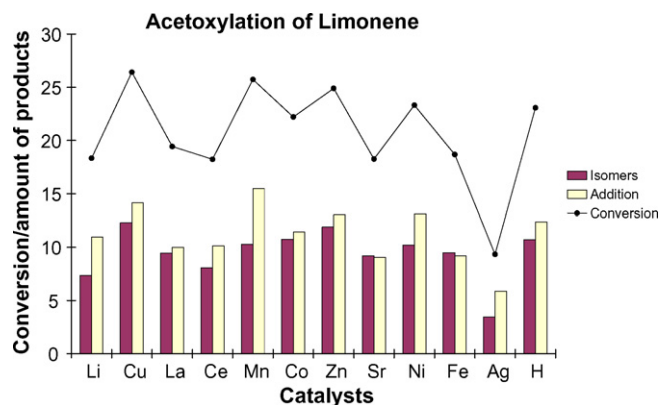


Fig. 2. Isomers addition products and conversion for acetoxylation of limonene. Catalyst weight 0.1 g, limonene 2 ml, reaction temperature 50°C , reaction time 24 h, glacial acetic acid 10 ml.

Table 3
Reaction of limonene with glacial acetic acid using ion-exchanged beta zeolite.

Catalysts	Conversion of limonene (%)	Selectivity of products (%)							
		A	B	C	D	E	F	G	H
Li-beta	18	3	11	5	4	2	10	50	0
Cu-beta	26	3	14	6	3	17	10	41	2
La-beta	19	3	11	5	3	13	10	41	0
Ce-beta	18	3	12	5	5	15	11	45	0
Mn-beta	26	3	7	5	8	15	10	48	2
Co-beta	22	3	12	5	4	14	10	40	2
Zn-beta	25	3	13	6	5	17	8	42	2
Sr-beta	18	3	12	5	5	12	9	41	0
Ni-beta	23	3	13	6	5	14	10	44	2
Fe-beta	19	3	10	5	7	13	9	41	0
Ag-beta	9	0	11	5	8	13	10	53	0
H-beta	23	3	14	6	3	16	10	42	2

Reaction conditions: Catalyst weight 0.1 g, limonene 2 ml, reaction temperature 50 °C, reaction time 24 h, glacial acetic acid 10 ml. A, α -Phellendrene; B, α -terpinene; C, γ -terpinene; D, *p*-cymene; E, terpinolene; F, α -terpineol; G, α -terpinyl acetate; H, others addition products.

catalysts acetic acid easily adds to the exocyclic double bond of the limonene yielding α -terpinyl acetate. In addition, α -terpineol was also formed, as acetic acid always contains water which is a more efficient nucleophile than the acetic acid. In aqueous acetic acid, hydration was very fast, and therefore α -terpineol was the major product in the reaction.

Fig. S3 (supporting information) depicts the amount of total addition products of both the reactions. It can be understood that the addition products were always higher in aqueous conditions than in glacial acetic acid conditions. However, almost similar amounts of addition products were obtained with Ag-beta catalyst with conversions at their minimum.

Another side reaction that occurred under acetoxylation or hydration condition is the isomerisation of exocyclic double bond of the limonene yielding terpinolene, α -terpinene, γ -terpinene as the main products. The acid-catalysed isomerisation of limonene was fast and reversible; therefore, products such as terpinolene, α -terpinene, γ -terpinene can be recycled together with the unconverted limonene [62]. In glacial acetic acid and aqueous acetic acid, α -terpinene and terpinolene were the major products. The product selectivities in the former were in the range of 7–14% and 2–17%, respectively, while in the latter it ranged from 4% to 20% and 7% to 19%. The formation of *p*-cymene was also observed for the reaction.

Figs. 2 and 3 concisely show the conversion of limonene and the total amount of isomerised and addition products for the all catalysts. The conversion levels and the amount of the addition products

were always higher in aqueous acetic acid than the glacial acetic acid.

5. Hydration and acetoxylation of α -pinene

Tables 4 and 5 show the results of hydration and acetoxylation of α -pinene with cation-exchanged beta zeolite. The product distri-

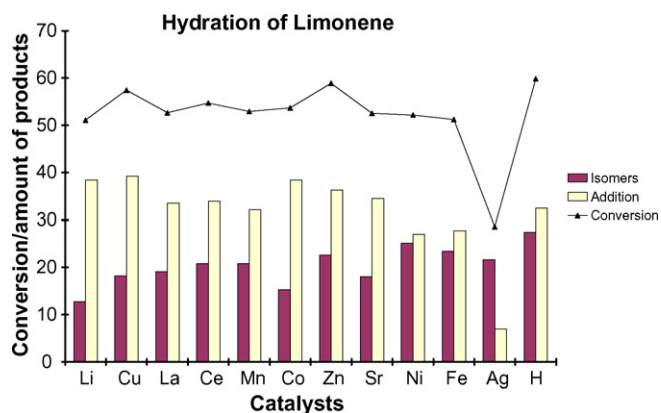


Fig. 3. Isomers addition products and conversion for hydration of limonene. Catalyst weight 0.1 g, limonene 2 ml, reaction temperature 50 °C, reaction time 24 h, aqueous acetic acid 10 ml.

Table 4
Reaction of α -pinene with glacial acetic acid using ion-exchanged beta zeolite.

Catalysts	Conversion of α -pinene (%)	Selectivity of products (%)												
		A	B	C	D	E	F	G	H	I	J	K	L	M
Li-beta	70	12	3	6	28	4	4	7	6	12	2	12	0	5
Cu-beta	100	10	1	16	19	6	2	10	5	12	2	3	1	14
La-beta	86	12	2	7	26	4	4	8	7	12	3	6	1	7
Ce-beta	87	13	2	6	27	4	7	8	8	13	1	4	1	7
Mn-beta	91	12	2	7	28	5	6	8	7	12	2	4	1	8
Co-beta	89	13	2	6	27	4	7	7	7	11	2	6	0	7
Zn-beta	95	12	1	7	27	4	7	8	6	12	2	4	1	9
Sr-beta	79	12	2	7	30	4	6	7	8	12	2	4	0	6
Ni-beta	94	13	2	8	26	4	6	8	5	12	3	5	1	9
Fe-beta	81	14	2	5	29	3	7	7	7	14	1	2	1	7
Ag-beta	62	10	3	7	34	4	4	8	10	11	1	3	0	3
H-beta	93	13	2	7	27	4	8	8	6	14	2	2	1	8

Reaction conditions: Catalyst weight 0.1 g, α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, glacial acetic acid 10 ml. A, Camphene; B, α -phellendrene; C, α -terpinene; D, limonene; E, γ -terpinene; F, *p*-cymene; G, terpinolene; H, others isomers; I, bornyl acetate; J, α -terpineol; K, α -terpinyl acetate; L, borneol; M, others addition products.

Table 5
Reaction of α -pinene with aqueous acetic acid using ion-exchanged beta zeolite.

Catalysts	Conversion of α -pinene (%)	Selectivity of products (%)												
		A	B	C	D	E	F	G	H	I	J	K	L	M
Li-beta	82	7	1	5	21	3	4	7	7	6	21	9	4	6
Cu-beta	95	7	1	11	20	5	1	8	7	5	17	5	4	7
La-beta	87	7	2	11	26	5	2	9	8	6	12	4	4	5
Ce-beta	89	7	3	10	25	5	3	9	9	6	11	4	4	5
Mn-beta	87	8	2	6	27	5	5	9	9	6	12	4	4	5
Co-beta	93	7	2	11	21	5	1	8	8	6	16	6	4	6
Zn-beta	93	8	2	7	24	4	5	8	7	6	15	4	4	6
Sr-beta	85	7	2	7	27	4	4	8	9	6	13	4	4	5
Ni-beta	90	8	3	8	27	4	5	8	9	6	10	3	4	5
Fe-beta	90	7	2	7	27	4	5	8	8	7	12	3	4	5
Ag-beta	72	6	3	7	33	4	3	10	10	5	9	3	2	5
H-beta	96	9	2	8	23	4	6	8	8	7	12	3	5	6

Reaction conditions: Catalyst weight 0.1 g, α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, aqueous acetic acid 10 ml. A, Camphene; B, α -phellendrene; C, α -terpinene; D, limonene; E, γ -terpinene; F, p-cymene; G, terpinolene; H, others isomers; I, bornyl acetate; J, α -terpineol; K, α -terpinyl acetate; L, borneol; M, others addition products.

butation in both the cases showed that more isomerisation products were formed than addition products.

The catalytic activity of ion-exchanged beta zeolites in the presence of glacial acetic acid on α -pinene showed the following order:

Cu > Zn > Ni > H > Mn > Co > Ce > La > Fe > Sr > Li > Ag

Similarly in the presence of 10% aqueous acetic acid, the catalytic activity showed the following order:

H > Cu > Co > Zn > Ce > Ni > Fe > Mn > La > Sr > Li > Ag.

In the presence of glacial acetic acid with all the catalysts, α -pinene conversion was in the range of 62–100%; maximum conversion of 100% was obtained with Cu-beta while it was minimum (62%) with Ag-beta. In aqueous acetic acid conditions, maximum conversion of 96% was obtained with H-beta while it was minimum (72%) with Ag-beta. For other ion-exchanged zeolites, it varied from 82% to 95%.

In the presence of glacial acetic acid, the formation of bicyclic addition product dominated and bornyl acetate was the major product. However, with aqueous acetic acid, monocyclic alcohol, α -terpineol, was always a major product among the addition products. In the presence of glacial acetic acid, the isomerised products were in the range of 68–81% and addition products were in the range of 19–32%. However, with 10% aqueous acetic acid isomerised prod-

ucts were less. In the presence of acid catalyst, α -pinene rapidly formed carbonium ion, which rearranges to form the isomerised products. The capture of nucleophile by the carbonium ion produced addition products. The addition of nucleophile occurred very slowly by solvation of hydrocarbon products, rather than rearrangement of carbonium ion intermediate [3,63]. The formation of borneol and α -terpineol in hydration of α -pinene in the presence of aqueous acetone and acidic zeolites has been explained by van der Waal et al. [26].

Fig. 4 shows the amount of total addition product formed in both the reactions with all catalysts. It is understood that greater amounts of addition products were formed in aqueous conditions than in the glacial acetic acid conditions.

Henson et al. reported that beta zeolite proved more active for the methoxylation of α -pinene with the formation of addition product α -terpinyl ether in good yield. Figs. 5 and 6 represent the conversion and total amount of isomerised and addition products for all catalysts. It can be observed from the figures that conversion levels and the amount of the addition products were always high in aqueous acetic acid as compared to that in glacial acetic acid.

The data on acidity of ion-exchanged beta zeolites was as determined by cyclohexanol dehydration to cyclohexene. The conversion seems to be high for metal ion-exchanged beta catalyst. However, trend in the acidity of the catalyst is observed even from the data

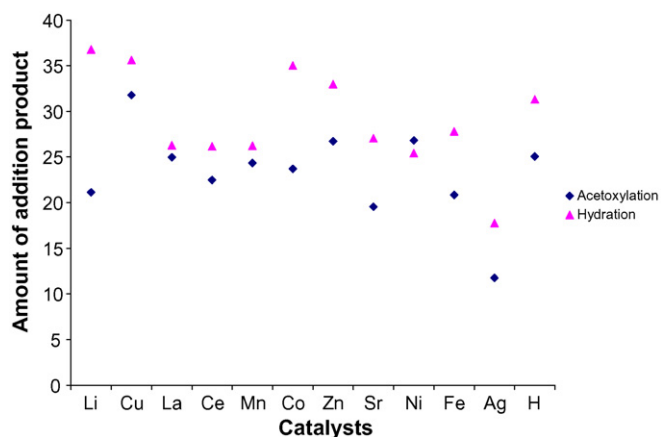


Fig. 4. Total addition products of catalysts for hydration and acetoxylation of α -pinene. Catalyst weight 0.1 g, α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, glacial/aqueous acetic acid 10 ml.

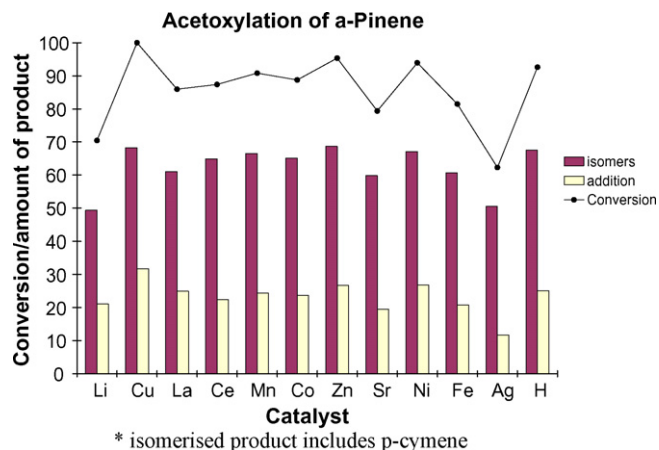


Fig. 5. Isomers addition products and conversion for acetoxylation of α -pinene. Catalyst weight 0.1 g, α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, glacial acetic acid 10 ml.

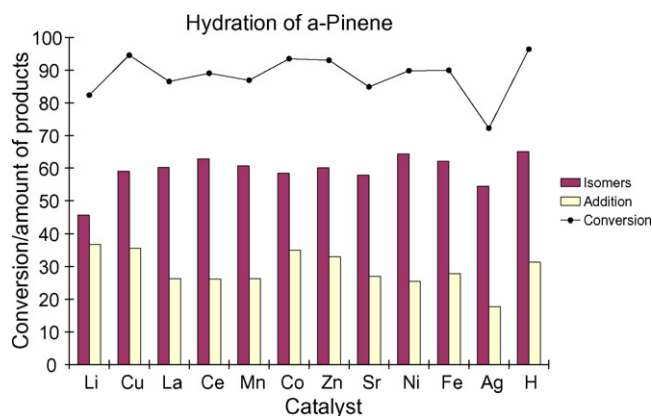


Fig. 6. Isomers addition products and conversion for hydration of α -pinene. Catalyst weight 0.1 g, α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, aqueous acetic acid 10 ml.

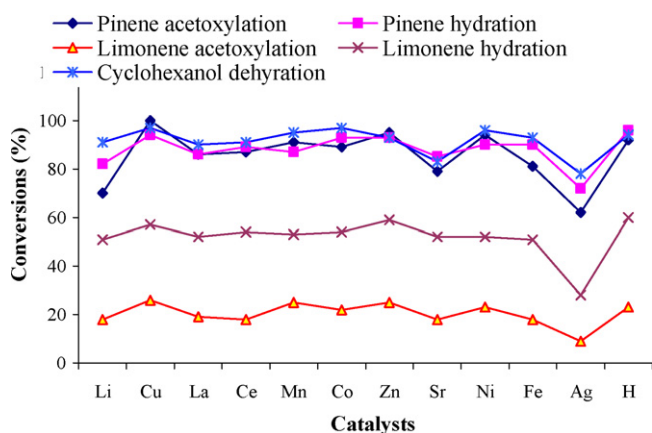


Fig. 7. Comparison of cyclohexanol dehydration with acetoxylation and hydration of α -pinene and limonene. Catalyst weight 0.1 g, limonene/ α -pinene 2 ml, reaction temperature 50 °C, reaction time 24 h, glacial/aqueous acetic acid 10 ml.

Table 6S shows the following order:

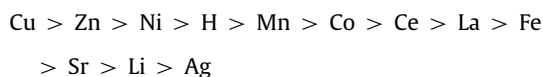


Fig. 7 represents the comparison of cyclohexanol dehydration with hydration and acetoxylation of limonene and α -pinene. The results obtained confirmed that the conversion trend were in agreement with the order of the acidity. These results show that these reactions were catalysed mainly by Brönsted acid. β -Zeolite samples possess both Brönsted and Lewis acid sites as observed from FT-IR spectra of pyridine-adsorbed samples.

6. Conclusions

The present study describes the modification of the beta zeolites by ion-exchange with metal cations such as silver, lanthanum, cerium, iron, cobalt, manganese, nickel, copper, zinc and strontium. The pyridine-adsorbed IR data showed the presence of Brönsted and Lewis acid sites in catalysts. These modified beta zeolites are used for hydration and acetoxylation of α -pinene and limonene. Conversion levels were 9–26% and 58–82% for limonene in the presence of glacial and aqueous acetic acid, respectively, and the selectivity for major products α -terpinyl acetate and terpineol were up to 54% and 65%, respectively. Conversion levels were 62–100% and 72–100% for α -pinene in the presence of glacial and aqueous

acetic acid, respectively. Isomerisation and addition reactions were found simultaneously in the system and bornyl acetate and α -terpineol were the major products among addition products for glacial and aqueous acetic acid, respectively. In the conversion of both limonene and α -pinene the aqueous acetic acid conditions are more favourable. The study shows the potential of ion-exchange beta zeolites for Brönsted acid-catalysed monoterpene transformation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.09.017.

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