



## Acetoxylation and hydration of limonene and $\alpha$ -pinene using cation-exchanged zeolite beta

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### ABSTRACT

Hydration and acetoxylation of limonene and  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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,  $\alpha$ -pinene and  $\beta$ -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  $\alpha$ -pinene to produce  $\alpha$ -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].  $\alpha$ -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  $\alpha$ -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  $\alpha$ -pinene, with good selectivity of 48% for terpineol, although long reaction times and high water/terpene ratios are required to ensure good selectivities for  $\alpha$ -terpineol at high pinene conversions. The acid-catalysed processes of limonene hydration commonly produce large amounts of diols besides terpineols [29]. The mixture of  $\alpha$ - and  $\gamma$ -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  $\alpha$ -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  $\alpha$ -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% Na<sub>2</sub>O, 7.8% Al<sub>2</sub>O<sub>3</sub> and 91% SiO<sub>2</sub>. Limonene,  $\alpha$ -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<sup>-</sup> was no more detected by AgNO<sub>3</sub> 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 La<sup>3+</sup>, Li<sup>+</sup>, Ce<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Sr<sup>2+</sup>, and Zn<sup>2+</sup>. 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 N<sub>2</sub> physisorption measurements at 77.4 K employing the BET method [53] using Micromeritics ASAP 2010 surface area analyzer. The samples were activated under

vacuum ( $1 \times 10^{-2}$  mmHg) at 350 °C for 4 h prior to N<sub>2</sub> adsorption measurements.

Structural analysis of catalysts was done by X-ray diffraction using Philips X'Pert MPD diffractometer with Cu K $\alpha$ 1 ( $\lambda = 1.5405 \text{ \AA}$ ) as a radiation source in  $2\theta$  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<sup>-1</sup> using dry N<sub>2</sub> 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<sup>-1</sup> 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<sup>-1</sup> 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  $\alpha$ -pinene, camphene, limonene,  $\alpha$ -terpinene and tricyclene,  $\alpha$ -terpinyl acetate,  $\alpha$ -terpineol, bornyl acetate and

**Table 1**  
Properties of the catalysts on dry basis.

Catalyst	BET S.A. (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /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

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