Catalytic epoxidation of α-pinene with molecular oxygen using cobalt(II)-exchanged zeolite Y-based heterogeneous catalysts

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Abstract

Cobalt cation-exchanged zeolite Y-based catalysts were studied for epoxidation of α-pinene with molecular oxygen in 20–100 psi pressure range using *N,N*-dimethylformamide (DMF) as a solvent at 373 K. The catalysts characterization with X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) suggests that cobalt introduced into faujasite zeolite exists in Co(II) state and catalyzes the epoxidation of α-pinene with molecular oxygen. The alkali and alkaline earth metal co-exchanged with Co(II) gives higher conversion than Co(II) alone. Effect of temperature and pressure was also studied to determine the optimum conditions for the reaction. The best results were obtained using NaCsCoY20 with 47% α-pinene conversion and 61% epoxide selectivity at 80 psi pressure and 373 K. Solvent was observed to play important role in epoxidation of α-pinene, and best results were observed in *N,N*-dimethylformamide as a solvent. Free radical mechanism has been proposed for the epoxidation of α-pinene.
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Keywords: Epoxidation; α-Pinene; Epoxide; Molecular oxygen; Ion-exchanged zeolites

1. Introduction

Oxifunctionalization of terpenes is of interest since oxygenated products find use in the synthesis of intermediates in fine and specialty chemicals [1]. Catalytic epoxidation with molecular oxygen under mild conditions is a process of challenge for researchers [2,3]. Many catalytic systems for alkenes epoxidation with the use of dioxygen, aliphatic aldehyde and various transition metal compounds have been reported [4–7]. Most of these studies describe the use of homogeneous catalysts and only few papers deal with the application of heterogeneous catalysts [8,9]. Molecular sieves containing metal center in their framework were reported for some epoxidation reactions recently [10–14].

Epoxidation of terpenes to oxygenated products is of interest since these products finds use in the preparation of commercial products [15]. For example, α-pinene is one of the low priced monoterpenes, which gives valuable oxygenated products, like α-pinene epoxide, verbenol and verbenone. Campholenic aldehyde is another major product synthesized by rearrangement of the α-pinene epoxide. In industries, most of the epoxidation processes use conventional oxidizing reagents. However, catalytic route offers a wide variety of different sites for the activation of the cleaner oxidants such as molecular oxygen, hydrogen peroxide, even though molecular oxygen is always a preferable oxidant for epoxidation process. In the literature, there are some studies reported on the catalytic oxidation of terpenes [16–26]. Lajunen have reported homogeneous Co(II) complexes for α-pinene oxidation by molecular oxygen and Joseph et al. have reported zeolite encapsulated ruthenium and cobalt Schiff base complexes for allylic oxidation of α-pinene [16,18]. Guidotti et al. have tested various titanium silicates with different structural features for epoxidation of monoterpenes and van der Waal et al. reported Ti-beta as selective catalyst for epoxidation of bulky alkenes [17,19]. Gusevskaya et al. have reported Pd(II) catalyst for oxidation of monoterpenes [20,22,25,26]. However, still there is a scope to develop efficient catalysts for the epoxidation of α-pinene to achieve commercially viable and environmentally acceptable reaction conditions.

In the present study, Co^{2+} ions-exchanged zeolite Y having various alkali and alkaline earth metal as co-cations were inves-

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tigated as the catalysts for α-pinene epoxidation with molecular oxygen as an oxidant.

2. Experimental

2.1. Materials

Sodium form of zeolite Y (SiO$_2$/Al$_2$O$_3$ = 5.5), Na$_{30}$Al$_{30}$Si$_{162}$O$_{384}$ was procured from Süd-Chemie AG, Germany and cobalt nitrate hexahydrate, potassium chloride, cesium chloride, magnesium chloride hexahydrate, calcium chloride dihydrate, strontium chloride hexahydrate and barium chloride dihydrate from s.d. Fine Chemicals Ltd., Bombay, India and were used as the starting materials for the catalyst preparation. α-Pinene from Sigma–Aldrich Corporation Bombay, India, *N,N*-dimethylformamide (DMF) (99.7%) from Qualigens Fine Chemicals Ltd., Bombay, India and oxygen (99.9%) from Inox Air Products Ltd., Bombay, India were used for the epoxidation studies.

2.2. Preparation of catalysts

Cobalt-exchanged zeolites was prepared by ion exchange of zeolite with 0.1 M aqueous Co(NO$_3$)$_2$·6H$_2$O solution with 1:80 ratio of NaY zeolite to Co(NO$_3$)$_2$·6H$_2$O solution followed by heating at 353 K for 4 h. The resulting solution was filtered and washed with distilled water till it free from unexchanged ions. These washed samples were dried at temperature 373 K for 4 h. This catalyst was designated as NaCoY66. Above procedure was repeated three times and the resultant catalysts obtained after each step of ion exchange were designated as NaCoY80, NaCoY86, and NaCoY93, respectively with the numerical representing the % exchange of Na$^+$ ions with Co^{2+} ions.

Alkali and alkaline earth metal ion containing catalysts were prepared by taking NaY zeolite and aqueous solution of respective ion source, where the amount of metal ion is equivalent to Na$^+$ in NaY zeolite. Thus, exchanged zeolites were then re-exchanged with concentrated solution of Co (NO$_3$)$_2$·6H$_2$O solution of 50% equivalent Na$^+$ ion in NaY. These catalysts were designated as NaMCoY; here M is K, Cs, Mg, Ca, Sr, and Ba.

Other set of ion-exchanged catalysts were prepared by treating NaY with concentrated solution of Co (NO$_3$)$_2$·6H$_2$O in single step, these catalysts were designated as NaCoY73 NaCoY53, NaCoY40 and NaCoY20, where the numerical indicate percentage exchange of Na$^+$ ion with Co^{2+} ion. The percentage exchange of Co^{2+} was found to be 73%, 53%, 40% and 20% in NaCoY73, NaCoY53, NaCoY40 and NaCoY20, respectively.

Ion exchange was performed by taking zeolite and salt solutions in 1:80 ratio followed by heating at 353 K for 4 h and then filtered, washed with double distilled water until they free from unexchanged ions, all the samples were dried at temperature 373 K for 4 h. The percentage of metal ion was determined by Inductively Coupled Plasma (Perkin Elmer, optical emission spectrometer, Optima 2000 DV).

2.3. Characterization

X-ray powder diffraction measurements of various cobalt-exchanged zeolite NaY at ambient temperature were carried out using *PHILIPS X′pert MPD system* in the 2θ range of 2–70° using Cu Kα (λ = 1.54056 Å).

Surface area and pore size distribution of the various cobalt-exchanged zeolites were determined from the N$_2$ adsorption data at 77 K. The equilibrium nitrogen adsorption at 77 K was measured using a Micromeritics ASAP 2010. The samples were activated at 373 K under vacuum (5 × 10^{-3} mmHg) for 12 h before the N$_2$ sorption measurements. The surface areas of different catalyst samples were determined by applying the BET equation to the measured N$_2$ adsorption data. Micropore volume and external area were determined from *t*-plots of the data [27].

Diffuse reflectance spectroscopic studies were carried out using *Shimadzu UV–3101PC* equipped with an integrating sphere and BaSO$_4$ was used as the reference material. The spectra were recorded at room temperature in the wavelength range of 200–750 nm.

The surface morphological details of catalysts were studied by SEM (Leo 1430) accelerated at 10 keV and 20 keV. The catalyst samples were mounted directly on the holders and covered with sputtered gold and then observed in SEM.

2.4. Catalytic studies

The α-pinene epoxidation experiments were carried out in a 100 ml PARR 4843 autoclave under O$_2$/air pressure. In a typical experiment, reaction mixture containing known amounts of α-pinene, catalyst and *N,N*-dimethylformamide (DMF) as solvent along with dodecane (internal standard), were placed into the autoclave. The autoclave was then pressurized at 80 psi with O$_2$/air and was then brought to the temperature 373 K and kept at this temperature under constant stirring 600 rpm. The reaction mixtures were withdrawn at fixed time intervals. The reaction products were analyzed by gas chromatography (Hewlett Packard, Model 6890) equipped with HP-5 capillary column 30 m long and having 0.25 mm internal diameter. Nitrogen was used as a carrier gas (flow 0.5 ml/min) with injection port temperature of 523 K and programmed ramping of column temperature from 323 K to 453 K. Pure α-pinene, α-pinene epoxide, verbenone and verbenol were used for calibration of gas chromatography response; dodecane was used as internal standard for calculation. The following equations were used for determining the conversion and selectivity of products. The identities of these products were confirmed by GC–MS (Shimadzu GCMS QP 2010).

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

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

$$\text{TOF} = \frac{\text{No. of moles of } \alpha - \text{pinene oxide formed}}{\text{No. of moles of Co}^{+2} \text{in catalyst} \times \text{reaction time}}.$$
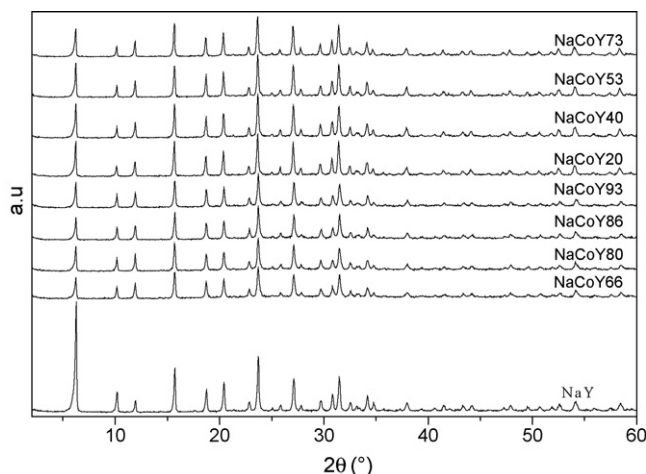
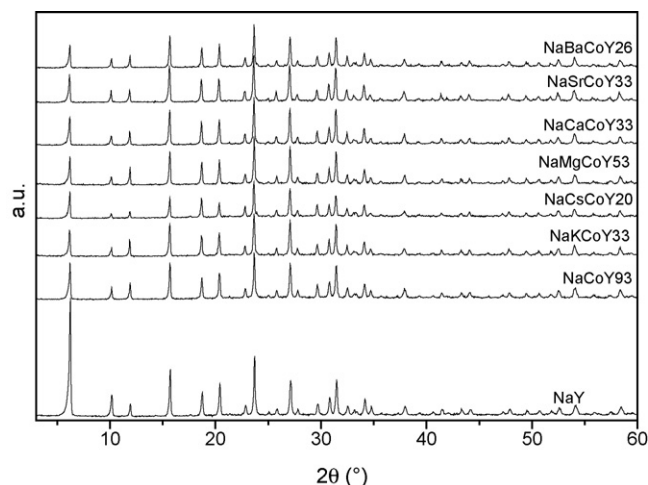Fig. 1. X-ray diffraction pattern of cobalt exchange zeolite NaY.

Fig. 2. X-ray diffraction pattern of alkali and alkaline earth metal ion exchange zeolite NaY.

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction patterns of different ion-exchanged zeolites and starting material are shown in Figs. 1 and 2. These figures confirm that no significant structural variations occurred after ion exchange as compared to the original zeolite. The diffraction patterns of all the catalysts show that they are highly crystalline materials showing the reflections at 2θ values 6.2, 15.7, 18.7, 20.4, 23.7, 27.1, and 31.4, in the range 5–35° typical of zeolite NaY. The percentage crystallinity of ion-exchanged zeolites are estimated with respect to the NaY by comparing the X-ray peak intensities of six major peaks of prepared samples with the intensity of six major peaks of NaY zeolite. Loss in crystallinity is found during ion exchange which is shown in Table 1 [28].

Table 1 shows the surface area values of all the catalyst samples used in the present study. It can be noted that there is no significant change in the surface area of ion-exchanged zeolite. Presence of same type of hysteresis loop in all the catalyst shows that the pores are identical in all zeolites. External surface area was calculated by the t-plot method. The external surface area is the total surface area of all meso and macropores. The external surface area of the pristine and ion-exchanged zeolite confirms that the structural property of the zeolite is retained after ion exchange.

Diffuse reflectance spectroscopy (DRS) detects the d–d transitions of Co^{2+} in the near infrared region and the $O \rightarrow Co^{2+}$ charge transfer transition in the ultraviolet region [29]. Diffuse reflectance spectra of different ion-exchanged zeolites are given in Figs. 3 and 4; in the hydrated pink sample, spectral minima appear around 514 nm in the visible region and 272 nm in the UV region. These absorptions are assigned to the transitions of the octahedral $[Co(H_2O)_6]^{2+}$ complex located in the super cages of the zeolite [29]. The intensity of both the peaks at 514 nm and 272 nm increases correspondingly with the amount of cobalt exchange.

Table 1
Chemical composition and other characteristics of the catalysts used

| Catalyst	Chemical composition (on dry basis)	Micropore area ($cm^2\,g^{-1}$)	% Crystallinity	BET S.A. ($m^2\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	Ext. S.A. ($m^2\,g^{-1}$)
NaY	$Na_{30}Al_{30}Si_{162}O_{384}$	693	100	788	0.345	95
NaCoY66	$Na_{10}Co_{10}Al_{30}Si_{162}O_{384}$	555	88	673	0.251	118
NaCoY80	$Na_6Co_{12}Al_{30}Si_{162}O_{384}$	508	81	622	0.236	114
NaCoY86	$Na_4Co_{13}Al_{30}Si_{162}O_{384}$	523	75	637	0.242	114
NaCoY93	$Na_2Co_{14}Al_{30}Si_{162}O_{384}$	537	71	652	0.249	115
NaCoY20	$Na_{22}Co_3Al_{30}Si_{162}O_{384}$	566	92	639	0.263	73
NaCoY40	$Na_{18}Co_6Al_{30}Si_{162}O_{384}$	567	90	638	0.263	71
NaCoY53	$Na_{14}Co_8Al_{30}Si_{162}O_{384}$	563	91	636	0.261	73
NaCoY73	$Na_8Co_{11}Al_{30}Si_{162}O_{384}$	681	86	769	0.316	88
NaKCoY33	$Na_{10}Co_5K_{10}Al_{30}Si_{162}O_{384}$	639	79	713	0.297	74
NaCsCoY20	$Na_6Co_3Cs_{18}Al_{30}Si_{162}O_{384}$	538	87	601	0.250	63
NaMgCoY53	$Na_8Co_8Mg_3Al_{30}Si_{162}O_{384}$	531	90	625	0.248	90
NaCaCoY33	$Na_{14}Co_5Ca_3Al_{30}Si_{162}O_{384}$	554	94	622	0.257	68
NaSrCoY33	$Na_{10}Co_5Sr_5Al_{30}Si_{162}O_{384}$	565	93	635	0.263	70
NaBaCoY26	$Na_{10}Co_4Ba_6Al_{30}Si_{162}O_{384}$	547	79	617	0.255	68
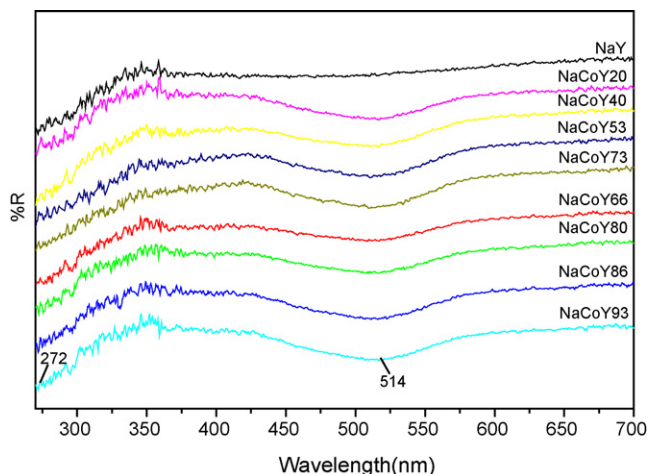
Fig. 3. Diffuse reflectance spectra of various amounts of cobalt ion-exchanged zeolite NaY.

The scanning electron micrographs of the ion-exchanged calcined form of zeolites are shown in Fig. 5. It is also understood that morphology of all the catalysts is retained and are similar to NaY zeolite.

3.2. Reaction studies

Epoxidation of α-pinene was carried out with molecular oxygen in a closed reactor. The epoxidation of α-pinene was carried out using as synthesized cobalt-exchanged zeolites as catalysts, with varying reaction parameters like pressure, temperature, time, nature of solvents, catalyst amount, and amount of Co^{2+} ions present in catalysts and presence of alkali & alkaline earth metal ions. The reaction pressure was varied from 20 psi to 100 psi and in the 353–373 K temperature range.

Table 2 shows the results for α-pinene epoxidation at various temperatures with DMF as solvent. It is observed that the epoxidation of α-pinene with molecular was favored at higher temperature, as in the present work, catalyst NaCoY93 at 373 K and 80 psi (O_2 pressure) with DMF as solvent gives
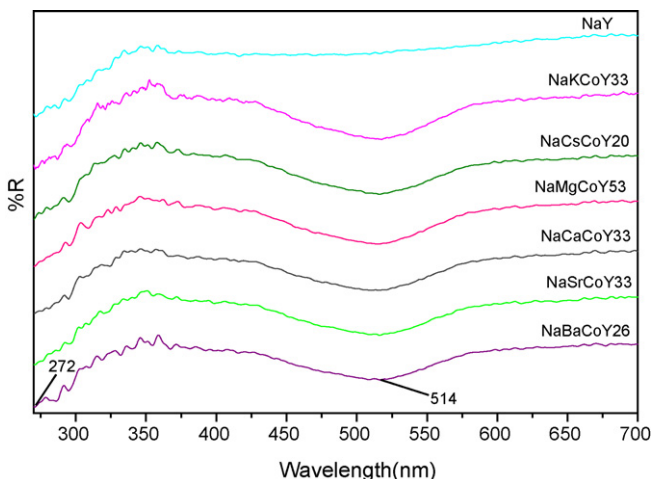

Fig. 4. Diffuse reflectance spectra of alkali and alkaline earth metal-exchanged zeolite NaY.

Table 2
Effect of temperature on α-pinene epoxidation

Run	Temperature (K)	Conversion (%)	Selectivity (%)			
			Epoxide	Verbenol	Verbenone	Trans-carveol
1	373	45	71	10	18	1
2	353	10	82	8	10	–

Reaction conditions: α-pinene, 3 gm; IS, 0.3 g; DMF, 30 ml; NaCoY93 catalyst, 300 mg; O_2, $\cong$80 psi; time, 4 h.

45% α-pinene conversion with 71% epoxide selectivity, while the conversion is observed to decrease from 45% to 10% at lower temperature like 353 K with small increase in selectivity. This decrease in α-pinene conversion at lower temperature like 353 K is attributed to the decrease in activity of molecular oxygen at lower temperature by the active sites Co^{2+} ions in the catalyst.

Table 3 shows the effect of molecular oxygen pressure for α-pinene epoxidation with NaCoY93 as the catalyst at various O_2 pressures and 373 K reaction temperature for 4 h reaction time. The conversions were found to be 45%, 45%, 36%, 30%, 25% at 100 psi, 80 psi, 60 psi, 40 psi, 20 psi, respectively. The results demonstrated the conversion were less at lower O_2 pressure. However, with increase in pressure from 20 psi to 80 psi we found that conversion increased from 25% to 45% with 71% of epoxide selectivity. However, further increase in O_2 pressure from 80 psi to 100 psi did not result in increase in α-pinene conversion, but the epoxide selectivity was found to decrease to 64%.

The results from Table 3 show the conversion of α-pinene is high at higher pressure. This may be due to the lower rate of α-pinene epoxidation at lower pressure. As pressure increases the α-pinene epoxidation rate also increases due to presence of more concentration of oxygen in reaction media these results also supported by Henry's law which states that, at a given temperature, the amount of gas dissolved in a solute is directly proportional to the pressure of the gas above the substance. The solubility of a gas depends directly on the gas pressure. The number of molecules leaving the gas phase to enter the solution equals the number of gas molecules leaving the solution. If the temperature stays constant increasing the pressure will increase the amount of dissolved gas.

Table 3
Effect of pressure on α-pinene epoxidation

Run	Pressure (psi)	Conversion (%)	Selectivity (%)			
			Epoxide	Verbenol	Verbenone	Trans-carveol
1	100	45	64	16	18	2
2	80	45	71	10	18	1
3	60	36	71	10	18	1
4	40	30	71	10	18	1
5	20	25	71	10	18	1

Reaction conditions: α-pinene, 3 gm; IS, 0.3 g; DMF, 30 ml; NaCoY93 catalyst, 300 mg; temperature, 373 K; time, 4 h.
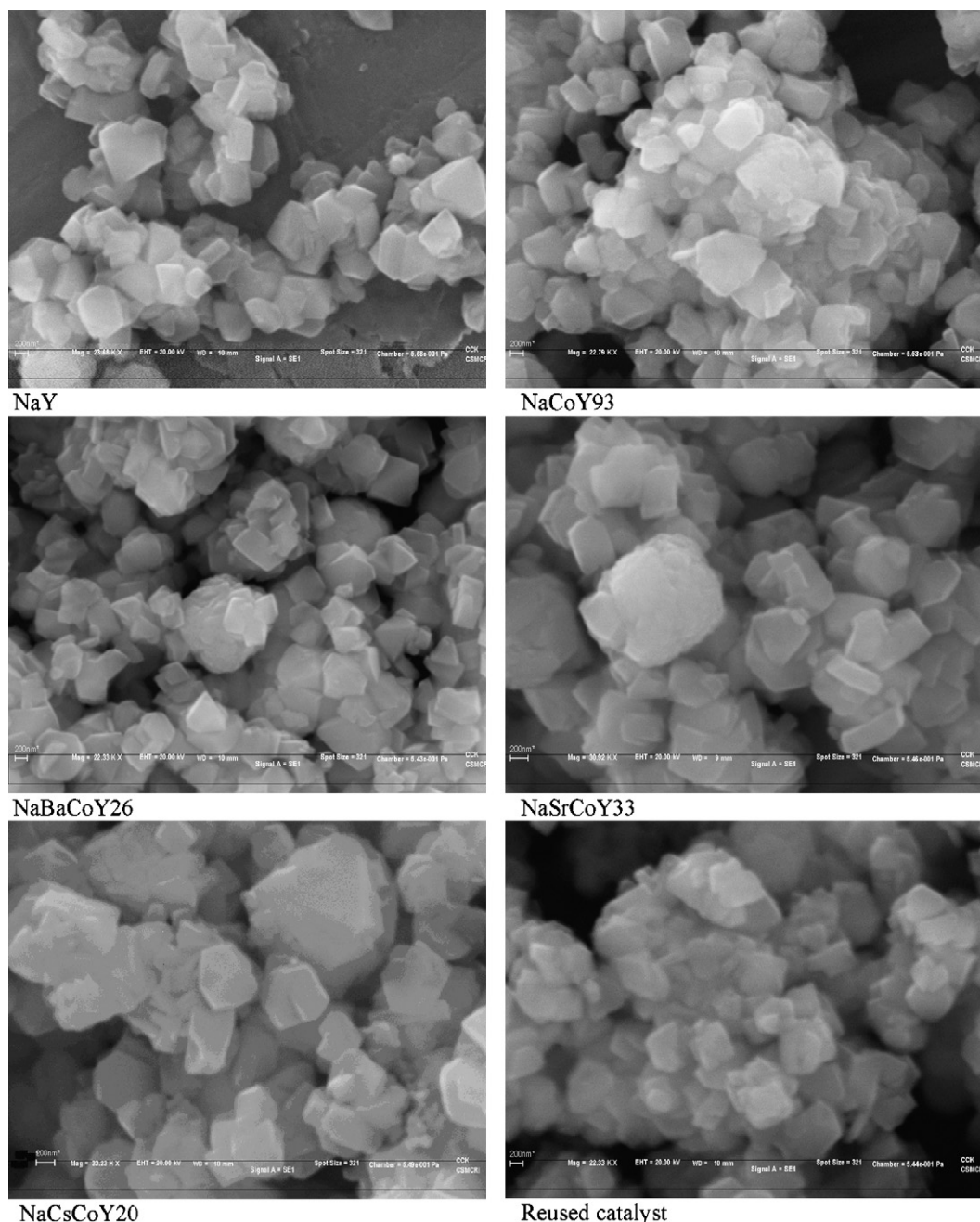
Fig. 5. Scanning electron microscopic images of catalysts.

However, it is observed that at 100 psi pressure there is decrease in epoxide selectivity this may be due to the instability of α-pinene epoxide at high pressure and temperature, ring opening isomerization of α-pinene epoxide gives the thermodynamically more stable secondary products like *trans*-carveol.

The reaction time also plays very important role in the reaction as shown in Table 4. It observed that increase in reaction time from 4 h to 12 h increases the α-pinene conversion from 45 to 54%. On further increase in reaction time from 12 to 20 h, the constant conversion of α-pinene was observed with slight decrease in epoxide selectivity. This could be due to the conversion of epoxide into isomeric products. It is well known that epoxides are unstable and converts into more stable secondary

products at higher temperatures with increase in reaction time. The selectivity for the epoxide was 71% in 4 h and decreases to 60% in 20 h reaction time.

To further understand the effect of amount of cobalt ion in the catalyst on conversion of α-pinene and epoxide selectivity, the reaction was studied by varying the amount of Co^{2+} ion in the catalysts. This was first done with samples prepared repeated cycle exchange of cobalt(II) up to four cycles as explained in Section 2.

The results of α-pinene conversion with various catalyst are summarized in Table 5, it was observed that on increasing amount of cobalt ion in the catalyst, the conversion of α-pinene and epoxide selectivity increases, the conversion of α-pinene

Table 4
Effect of reaction time on α-pinene epoxidation

Run	Time (h)	Conversion (%)	Selectivity (%)			
			Epoxide	Verbenol	Verbenone	*Trans-*carveol
1	8	47	69	9	19	3
2	12	54	69	9	19	3
3	16	54	64	9	19	8
4	20	54	60	9	19	12

Reaction conditions: α-pinene, 3 gm; IS, 0.3 g; DMF, 30 ml; NaCoY93 catalyst, 300 mg; O_2, ≅80 psi; temperature, 373 K.

was found to 32%, 33%, 40% and 45% for the catalyst CoY66, CoY80, CoY86 and NaCoY93 with epoxide selectivity 66%, 68%, 69% and 71%, respectively.

It was reported that the repeated exchange of metal ion in the zeolite could decrease the crystallinity of the zeolite. Therefore, the catalysts having varied Co^{2+} content were also prepared by a single step exchange of cobalt ion by taking different amount of cobalt ion in solution. Catalyst NaCoY20, NaCoY40, NaCoY53 and NaCoY73 were prepared which were prepared by ion exchange using 25%, 50%, 75% and 100% of cobalt ion solution equivalent to sodium ion in the NaY zeolite, respectively.

Table 5 shows the results for these catalysts for α-pinene conversion. It was again found that the higher amount of cobalt ion favours the conversion. The 31%, 34%, 37% and 40% conversion of α-pinene were for the catalyst NaCoY20, NaCoY40, NaCoY53 and NaCoY73, respectively. The selectivity of epox-

ide for all the catalyst were in the range of 63–66% and other products verbenol and verbenone were in the range of 11–13% and 18–20%, respectively. The reusability of the NaCoY73 catalyst was evaluated for this study. After completion of the reaction, the reaction mixture was centrifuged and the organic layer was filtered out and the solid catalyst were washed 2–3 times with double distilled water followed by washing with DMF and dried at 373 K for 4 h.

The reproducibility of the conversion was observed 37% and 32% after first and second cycled, respectively (Table 5, entries 9 and 10) with no decrease in selectivity. The decrease in the conversion was expected due to blockage of some active sites after reaction. However, the selectivities for products were found unchanged with recycled catalysts.

To study the effect of alkali and alkaline earth metal with cobalt ion on epoxidation of α-pinene we further carry out the reaction in the presence of co-cation along with Co^{2+} ion in zeolite NaY therefore, cobalt-exchanged zeolite catalysts were prepared with alkali and alkaline earth metal ions. The alkali metals K and Cs while alkaline earth metal Mg, Ca, Sr, and Ba were selected for the study. It can be understood from the results that there was an enhancement in conversion of α-pinene and conversions were in the range of 34–48% and the selectivity for epoxide were 60–62% as shown in Table 6. This is in good agreement with reported work [30] that the presence of some amount of alkali and alkaline earth metal ion with cobalt ion can enhance the conversion of olefin to epoxide in the presence of DMF as a solvent and molecular oxygen as an oxidant. As we observed that the formation of *trans-*carveol is

Table 5
Effect of metal-ion amount in catalyst on α-pinene epoxidation

| Run	Catalyst	Conversion (%)	Selectivity (%)				TOF (h^{-1})
			Epoxide	Verbenol	Verbenone	*Trans-*carveol	
1	NaCoY66	32	66	12	16	6	7.2
2	NaCoY80	33	68	11	17	4	6.2
3	NaCoY86	40	69	10	18	3	7.0
4	NaCoY93	45	71	10	18	1	7.3
5	NaCoY73	40	66	12	19	3	8.2
6	NaCoY53	37	64	12	19	5	10.4
7	NaCoY40	34	64	12	19	5	12.7
8	NaCoY20	31	63	12	19	6	17.4
9	NaCoY73r1	37	66	12	19	3	7.6
10	NaCoY73r2	32	66	12	19	3	6.6

Reaction conditions: α-pinene, 3 g; IS, 0.3 g; DMF, 30 ml; catalyst, 300 mg; O_2, ≅80 psi; temperature, 373 K; time 4 h.

Table 6
Effect of co-cations in catalyst on α-pinene epoxidation

Run	Catalyst	Conversion (%)	Selectivity (%)				TOF (h^{-1})
			Epoxide	Verbenol	Verbenone	*Trans-*carveol	
1	NaKCoY33	34	62	12	19	7	17.0
2	NaCsCoY20	47	61	12	20	7	49.1
3	NaMgCoY53	43	61	12	19	8	12.5
4	NaCaCoY33	40	62	12	18	8	17.5
5	NaSrCoY33	41	60	11	19	10	18.0
6	NaBaCoY26	48	62	12	18	8	23.9

Reaction conditions: α-pinene, 3 gm; IS, 0.3 g; DMF, 30 ml; catalyst, 300 mg; O_2, ≅80 psi; temperature, 373 K; time 4 h.

more in the catalyst containing low cobalt ion and it increases with increase in basic character of the catalyst. This may be due to the NaY having high aluminum content and surface area is most active for ring opening of olefin epoxides as reported in the literature. The reactivity order towards epoxidation of α-pinene on various catalysts in the present study was observed as follows

NaCsCoY20 > NaBaCoY26 > NaMgCoY53

  > NaSrCoY33 > NaCaCoY33 > NaKCoY33.
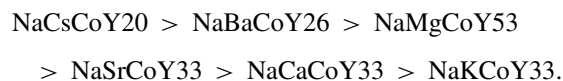
In the present study, the normal AR grade DMF as solvent and complete dry DMF as solvent gave similar results for conversion and selectivity. From this, it can be understood that

the conversion and selectivity for the reaction are unaffected by the presence of trace amount of water in the solvent. Thus, α-pinene epoxidation can be performed in solvents available as such without the care for drying them.

To study the effect of various solvent on α-pinene conversion and selectivity, dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMA) and ethylacetate (Etacet) were taken for the study. It was found that DMSO, DMA and Etacet grossly inhibited the conversion of α-pinene, while DMF demonstrated a conversion of 45% with 71% epoxide selectivity in 4 h reaction time with 80 psi O_2 pressure, hence could be well agreeable choice for this reaction. This is in good agreement with the work of Sebastian et al. [30].
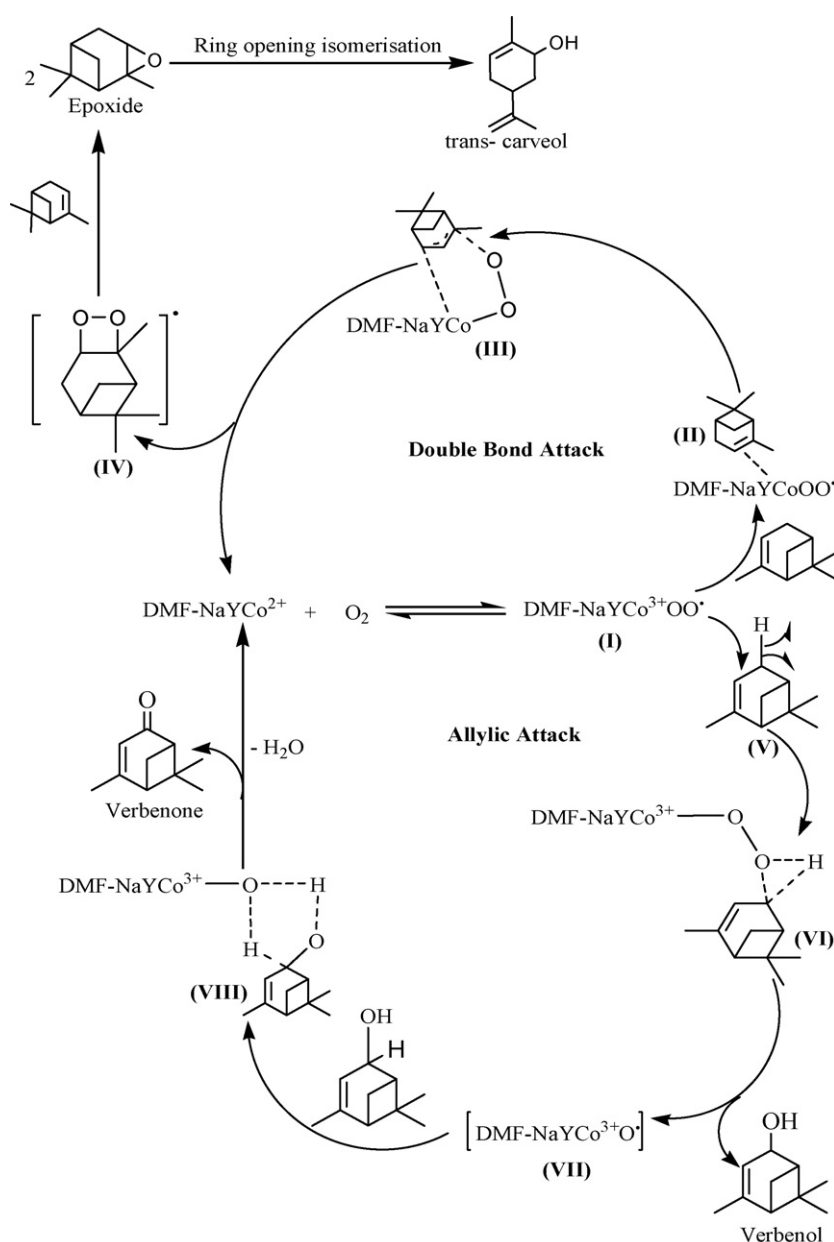
Scheme 1. Tentative reaction mechanism for epoxidation of α-pinene with molecular oxygen catalyzed by cobalt containing zeolite.

3.3. Reaction mechanism

To study the reaction pathway and also the active species formed in the reaction a separate experiment was carried out using a free radical scavenger hydroquinone (50 mg) using NaCoY93 catalyst under same reaction conditions as mentioned in Table 6. The result showed no epoxide or any side product formation in presence of hydroquinone confirming that formation of free-radical-type active oxygen species occurs in epoxidation of α-pinene, probably due to activation of O_2 in the Co^{2+} cations present at site III' or II and proving that it is a free radical mechanism. Based on this experimental study and as reported earlier [30–34], a tentative reaction mechanism has been proposed as shown in Scheme 1. The reaction proceeds through two pathways one is a double bond attack where the DMF-NaYCo^{2+} interacts with oxygen to form an active superoxo species (**I**) observed from the UV–vis DRS spectra by Sebastian et al. [30] as well reported by Tang et al. [31,32] and Liang et al. [33]. It is evident that Co^{2+} ions present in zeolites are in tetrahedral coordination in the presence of DMF. We believe that Co(II)NaY-DMF present in the zeolite supercage gets coordinated to molecular oxygen to form DMF-NaYCo(III)OO$^\bullet$ (**I**) superoxo complex which results into oxidative addition to the C–C double bond of α-pinene molecule to give an intermediate (**II**). The intermediate (**II**) undergoes migratory insertion to give cyclic peroxide radical (**IV**) through intermediate (**III**) and regenerates DMF-NaYCo (**II**). Cyclic peroxide radical (**IV**) can further react with another molecule of α-pinene to give epoxide.

Similarly in the second path way species (**I**) attacks the allylic position of the α-pinene resulting the formation of species (**V**) which results in the formation of verbenol product through intermediate (**VI**). The attack of the in situ formed intermediate DMF-NaYCoO$^\bullet$ (**VII**), further on the verbenol through (**VIII**) which further under goes epoxidation to form a verbenone with removal of water [34]. Further the effect of alkali and alkaline earth co-cations on the reaction mechanism is yet to be understood.

3.4. Rate constant

The rate constant at optimized reaction conditions (α-Pinene 5.0 gm, catalyst NaCoY93 500 mg, temperature 373 K, O_2 pressure 80 psi, DMF 50 ml) in the present study for α-pinene epoxidation reaction is as follow

Rate constant $(k) = 6.7 \times 10^{-4}$.

4. Conclusions

Cobalt-exchanged zeolite Y has been used for α-pinene epoxidation. Most of the microporous catalysts for the epoxidation reactions were based on framework active site location. Present work explains the effective epoxidation with extra frame work cation using molecular oxygen as an oxidant. The effect of different variables like solvent, temperature and catalyst amount on epoxidation reaction has been explained. Epoxidation of α-

pinene was found to favor at high temperature (373 K) and high pressure (80 psi).

DMF was found to be the only suitable solvent for this study. It was found that an increase in Co^{2+} ion concentration increases conversion of α-pinene, addition of alkali and alkaline earth metal ions in zeolite enhances the activity of reaction. Cesium was found to yield maximum conversion up to 47%. It was found that epoxide was converted into other products as the conversion level and time increases. The reaction mechanism was found to be free radical reaction. In contrast, Cobalt-exchanged zeolites were excellent catalysts for epoxidation of α-pinene in presence of molecular oxygen.

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