

Epoxidation of cycloalkenes with cobalt(II)-exchanged zeolite X catalysts using molecular oxygen

Krishna Mohan Jinka, Jince Sebastian, Raksh Vir Jasra*

*Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute,
Gijubhai Badheka Marg, Bhavnagar, Gujarat 364002, India*

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Abstract

Catalytic epoxidation of cycloalkenes to corresponding epoxides using molecular oxygen was carried out in presence of cobalt(II) exchanged zeolite X based catalysts. Effect of temperature (353–418 K) and pressure (30–150 psi) was studied to obtain the optimum conditions for the reaction. The best results were obtained at 60 psi pressure and 373 K using NaCoX96 catalyst with cycloalkene conversion and epoxide selectivity for cyclohexene, cycloheptene and *cis*-cyclooctene were obtained in the range 26–47 and 48–100% respectively. Alkali and alkaline earth cationic promoters were introduced into the zeolite catalyst in order to study the effect of basicity of the catalyst on the cycloalkene conversion and epoxide selectivity. Cobalt(II) exchanged zeolites X, NaCoX96, seems to be efficient heterogeneous catalysts for the epoxidation reactions using molecular oxygen. The catalyst was observed to be recyclable as conversion and selectivity were retained even after four catalytic reaction cycles.
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Keywords: Epoxidation; Cycloalkene; Epoxides; Molecular oxygen; NaCoX96 catalyst

1. Introduction

Catalytic partial oxidation of alkenes to produce epoxides is an important industrial reaction because of their use in the synthesis of a wide variety of fine chemicals [1,2] and as flexible intermediates and precursors to many useful chemical products [3–5] as well. Epoxides find a range of applications in pharmaceutical industry as drug intermediates, preparation of epoxy resins, polymers and paints. The commercial manufacturing methods of epoxides are the chlorohydrin process and the Halcon process. Both of these are two-stage processes and stoichiometrically produce co-products. Besides, chlorohydrin process causes serious environmental pollution. Therefore, many alternative methodologies using single oxygen donor reagents such as NaIO₄, NaOCl, PhIO, ROOOH, and H₂O₂ have been reported for the epoxidation of alkenes. Hydrogen peroxide is efficient and attractive epoxidation reagent, particularly due to its low cost and absence of pollution in the post reaction effluents [6–12]. However, using molecular oxygen will be more adequate for syn-

thesis of bulk, fine chemicals and commodity products. Selective oxidation of hydrocarbons using molecular oxygen as an oxidant will be an elegant reaction because of low cost and environmentally friendly nature of the oxidant [13]. Molecular oxygen as an oxidant was reported with various sacrificial reductants like aldehydes or alcohol [14–17], O₂ with Zn powder [18], use of O₂ with H₂ as reductant [19–25]. Some heterogeneous catalyst systems for epoxidation of alkenes are also reported [26,27].

Transition metal complexes of Co, Ti, Mn, Mo, were used as the catalyst, and high selectivity of epoxides of cyclic olefin such as cyclohexene has been reported [28–32]. Among all, cobalt complexes have been extensively used for the epoxidation of various alkene substrates with different oxidants [33–35]. Among microporous metallosilicate molecular sieves, titanium-containing silica-based materials, particularly TS-1 and TS-2, are widely studied in liquid-phase selective oxidation reactions using aqueous hydrogen peroxide as the oxidant [36–40]. Nb-containing mesoporous and macroporous material [41] have also been reported especially for epoxidation of cyclohexene using H₂O₂.

Heterogeneous Fe²⁺ catalysts were studied for epoxidation of cycloalkenes like cyclooctene using molecular oxygen [42]. Cobalt catalysts have been applied for the selective oxidation

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2567562/6970.
E-mail address: rvjasra@csmcri.org (R.V. Jasra).

Table 1
Chemical composition, crystallinity and BET surface area of the catalysts

Catalyst sample	Chemical composition (on dry basis)	Crystallinity (%)	BET surface area (m ² /g)
NaX	Na ₈₈ Al ₈₈ Si ₁₀₄ O ₃₈₄	100	508
NaCoX96	Co _{42.5} Na ₃ Al ₈₈ Si ₁₀₄ O ₃₈₄	72	676
KCoX19	Co _{8.4} Na _{2.2} K ₆₉ Al ₈₈ Si ₁₀₄ O ₃₈₄	93	558
RbCoX22	Co _{9.7} Na _{14.4} Rb _{54.2} Al ₈₈ Si ₁₀₄ O ₃₈₄	88	554
CsCoX20	Co _{8.8} Na _{20.6} Cs _{49.8} Al ₈₈ Si ₁₀₄ O ₃₈₄	83	518
MgCoX22	Co _{9.7} Na _{7.2} Mg _{30.7} Al ₈₈ Si ₁₀₄ O ₃₈₄	92	668
CaCoX19	Co _{8.4} Na ₄ Ca _{33.6} Al ₈₈ Si ₁₀₄ O ₃₈₄	93	567
SrCoX18	Co _{7.9} Na ₅ Sr _{33.6} Al ₈₈ Si ₁₀₄ O ₃₈₄	93	326
BaCoX15	Co _{6.6} Na _{5.6} Ba _{34.6} Al ₈₈ Si ₁₀₄ O ₃₈₄	90	407
CsBaCoX20	Co _{8.8} Na _{9.2} Cs ₂₈ Ba _{16.6} Al ₈₈ Si ₁₀₄ O ₃₈₄	83	432
KSrCoX20	Co _{8.8} Na _{2.4} K ₃₇ Sr _{15.5} Al ₈₈ Si ₁₀₄ O ₃₈₄	90	256

of alkanes [42] but very few reports contributed to the development of heterogeneous catalysts for epoxidation of cycloalkenes with O₂. Wang et al. [43] employed polymer anchored PSt-CH₂AcAc-Co(II) with *iso*-butyraldehyde as co-reductant for epoxidation of various cyclic alkenes with molecular oxygen. Co²⁺ exchanged molecular sieves catalyze the epoxidation of alkenes especially of styrene with O₂ in the absence of a co-reductant giving high conversions and epoxide selectivities [44–46].

In the present study, we report epoxidation reactions of various cycloalkenes with molecular oxygen using Co²⁺-exchanged zeolite X. The effect of temperature, pressure and basicity of zeolite on epoxidation of cycloalkenes was also studied.

2. Experimental

2.1. Materials

Sodium form of zeolite X, Na₈₈Al₈₈Si₁₀₄O₃₈₄ was procured from Zeolites and Allied Products, Bombay, India, which has unit cell dimension of 24.94 Å and BET surface area of 542 m²/g. Cobalt nitrate hexahydrate, potassium chloride, cesium chloride, magnesium chloride hexahydrate, calcium chloride dihydrate, strontium chloride hexahydrate and barium chloride dihydrate were purchased from S.D. Fine Chemicals Ltd., Bombay, India. *N,N*-Dimethylformamide (99.7%) was procured from Qualigens Fine Chemicals Ltd., Bombay, India, oxygen (99.9%) from Inox Air Products Ltd., Bombay, India, were used for the epoxidation studies. All the cycloalkene substrates were obtained from Sigma–Aldrich Corporation, Bangalore, India, and used as such without any further purification.

2.2. Catalyst preparation

The commercially obtained zeolite X which was in sodium form, was ion exchanged with alkali and alkaline earth metal salts using potassium, rubidium, cesium, magnesium, calcium, strontium and barium salt solutions at 353 K separately or in combination so as to replace the sodium ions present in the zeolite system. Cobalt cations were introduced into highly crystalline zeolite X by the cobalt ion exchange from aqueous solution. Typically, the zeolite was treated with 0.05 M aqueous

solution of the cobalt or alkali/alkaline earth metal salts like nitrates or chlorides in the solid/liquid ratio 1:80 at 353 K for 4 h. The residue was filtered, washed with hot distilled water, until the washing was free from nitrate or chloride ions and dried in air at room temperature. Zeolite X samples having different amount of cobalt exchange were prepared by subjecting repeated ion exchange into the commercial zeolite. The extent of cobalt exchange in zeolite X was determined by the complexometric titration of the original solution and filtrate obtained after the ion exchange with EDTA using murexide indicator. The different catalyst numerals in different catalysts (Table 1) indicate the percentage of sodium exchanged with cobalt in the catalyst system.

2.3. Catalyst characterization

X-ray powder diffraction of cobalt-exchanged zeolite X at ambient temperature was carried out using PHILIPS X^{pert} MPD system in 5–65° 2θ range using Cu Kα₁ (λ = 1.54056 Å). The diffraction patterns of the starting materials show that these are highly crystalline showing the reflections in the range 5–35° typically of zeolite X (Fig. 1). There was no major change in the crystalline nature and the zeolite structure was retained even after cation exchange and percentage of crystallinity and composition of the catalysts are given in Table 1.

Surface area of the cobalt-exchanged zeolites was determined from the N₂ adsorption data at 77.35 K. The equilibrium nitrogen adsorption at 77.35 K was measured using Micromeritics ASAP 2010. The samples were activated at 373 K under vacuum (5 × 10⁻³ mmHg) for 12 h before the N₂ sorption measurements. The surface areas of different catalyst samples were determined by applying BET equation and it was observed that large sized cation led to higher decrease in surface area.

Diffuse reflectance spectroscopic (DRS) studies were carried out using Shimadzu UV-3101PC equipped with an integrating sphere. BaSO₄ was used as the reference material. The spectra were recorded at room temperature in the wavelength range of 200–750 nm.

2.4. Catalytic epoxidation reactions

The cobalt ion exchanged zeolites dried at room temperature were used for the catalytic studies with out any further activa-

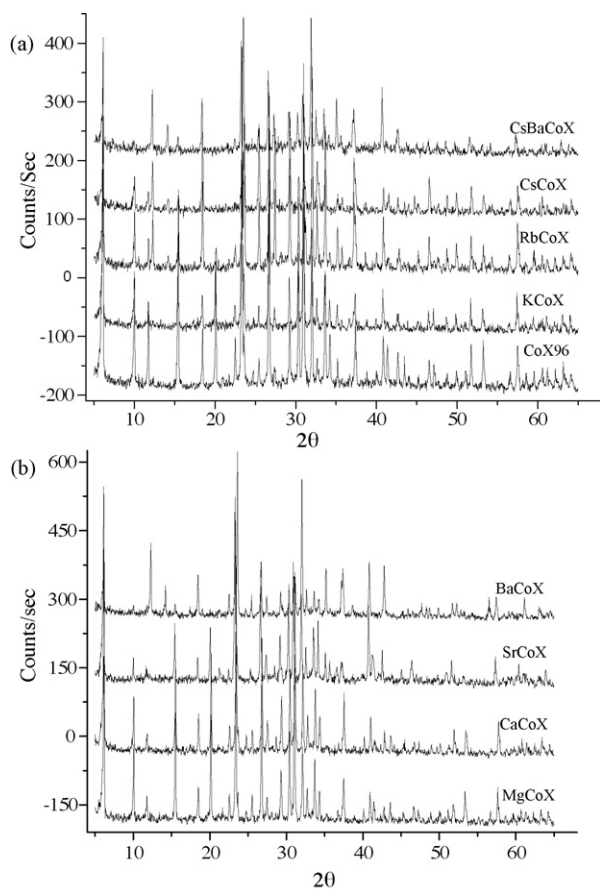


Fig. 1. X-ray powder diffraction patterns of various MCoX catalysts. (a) Alkali metal exchanged CoX catalysts and (b) alkaline earth metal exchanged CoX catalysts.

tion. The catalytic epoxidation reactions with respect to all the cycloalkenes were carried out in PARR 4843 series autoclave reactor at 373 K under O_2 pressure. The reactions were carried out under pressure because under the atmospheric conditions during O_2 purge into the reaction system, vapour loss of substrate was observed. In order to overcome this vapour loss all the reactions were carried out in a closed bench top autoclave reactor system. In a typical experimental procedure, 2 g cycloalkene (CYA) along with 40 ml *N,N*-dimethylformamide (DMF) solvent and 200 mg catalyst and 0.2 g Tridecane as GC internal standard were added to 100 ml SS vessel. A small amount of this mixture was taken out for zero time analysis and then reactor was pressurized to desired pressure with O_2 gas and reactor temperature was maintained at 373 ± 2 K using water circulation. The reaction was started by initiating the stirring process and the reaction mixture was stirred at 600 rpm. After 8 h of reaction, the reaction was stopped followed by cooling the reactor to room temperature. The oxygen gas remained in the reactor was gradually let through the vent provided and the final reaction mixture was collected. Catalyst was separated by centrifuging the reaction mixture and the liquid organic mixture was analysed with a gas chromatograph (Hewlett-Packard Model 6890, USA) having a flame ionisation detector and HP-5 capillary column (30 m length and 0.32 mm diameter, packed

with silica-based supel cosil), programmed oven (temperature range 333–503 K) and N_2 as carrier gas. Calibrations of GC peak areas of cycloalkenes and all the products were carried out using solutions having known amounts of cycloalkene and products, respectively. The products formed in the reactions were also identified using Gas chromatography–Mass spectrometer (Shimadzu GCMS-QP2010, Japan) with GC oven programmed in temperature range 323–503 K and helium as carrier gas and MS in EI mode with 70 eV ion source.

The conversion was calculated on the basis of mole percent of alkenes, the initial mole percent of cycloalkene was divided by initial area percent (CYA peak area from GC) to get the response factor. The unreacted moles of cycloalkene remained in the reaction mixture were calculated by multiplying response factor with the area percentage of the GC peak for CYA obtained after the reaction. The conversion and selectivity were calculated as follows:

$$\text{Conversion (mol\%)} = \frac{(\text{initial mol\%}) - (\text{final mol\%})}{\text{initial mol\%}} \times 100 \quad (1)$$

$$\text{Epoxide selectivity} = \frac{\text{GC peak area of epoxide}}{\sum \text{GC peak area of all products}} \times 100 \quad (2)$$

2.5. Computational details

The density functional calculation for geometry optimization of the cycloalkene structures was done using DMol³ module of Material Studios software (Accelrys software, USA).

2.6. Catalyst regeneration

The spent catalyst was recovered from the reaction mixture by filtration and thoroughly washed with DMF and distilled water, then dried in air at room temperature.

3. Results and discussion

Total sodium ion exchange of zeolite NaX with cobalt ions was attempted by repeated treatment of NaX sample using cobalt salt solution at 353 K. However, 96% of sodium present in the zeolite could only be exchanged. The surface area of the zeolite X samples was observed to increase on cobalt ion exchange. This is due to the decrease in the number of extra framework cations while replacing monovalent sodium ions with divalent cobalt ions as one Co^{2+} ion replaces two Na^+ ions. The crystal structure of cobalt-exchanged zeolite X reported in the literature [47] shows that the Co^{2+} ions prefer site II. After completely occupying the available site II locations, Co^{2+} ions occupy sites I' and III'. The cations sitting in the site I' are not accessible to the oxygen molecules. The cation sitting in site II can interact with the oxygen molecules through the six member ring windows and the cations in site III' can interact directly with oxygen. The distance between Co^{2+} ions in site III' and the framework oxygen atoms are long ($Co-O$ distance 2.30 and 2.27 Å) and these Co^{2+}

Table 2
Effect of temperature on epoxidation of cycloalkenes using NaCoX96 catalyst

Entry	Temperature (K)	Cyclohexene		<i>cis</i> -Cyclooctene		1,5-Cyclooctadiene		Cyclododecene	
		C (%)	S (%)	C (%)	S (%)	C (%)	S (%)	C (%)	S (%)
1	358	11	46	8	100	10	100	2	100
2	373	26	48	47	100	11	100	3	100
3	388	19	47	11	100	21	100	3	100
4	403	16	46	13	100	19	100	4	100
5	418	6	47	11	100	17	100	4	100

C (%), Percentage of conversion; S (%), percentage of selectivity (epoxide product). Reaction conditions: CYA, 2 g; IS, 0.2 g; DMF, 40 ml; catalyst, 200 mg; time, 8 h; O₂ pressure \cong 60 psi.

ion are relatively co-ordinately unsaturated compared to Co²⁺ cations present in at site II wherein Co–O distance is 2.129 Å. Therefore, cobalt cations present at site III' is expected to be catalytically more active for the activation of the oxygen molecules compared to cobalt cation present at site II. From PXRD (Fig. 1), it is clear that there was no major change in the crystalline nature and the zeolites structure was retained even after cation exchange and percentage crystallinity and composition of the catalysts are given in Table 1.

3.1. Epoxidation of cycloalkenes (CYA) using molecular oxygen with NaCoX96 catalyst

Co²⁺ exchanged NaCoX96 catalyst was used for epoxidation of cycloalkenes using molecular oxygen as an oxidant with DMF as solvent in a PARR autoclave reactor. The effect of reaction temperature (358–418 K) and pressure (30–150 psi) on the epoxidation of various cycloalkenes was investigated to obtain optimal conditions.

The cycloalkene conversion and epoxide selectivity data obtained for various cycloalkenes keeping the oxygen pressure constant at 60 psi at different temperatures are given in Table 2. It is seen from these data that for cyclohexene, only 11% cyclohexene conversion with 46% epoxide selectivity was observed at 358 K. Cyclohexene conversion was observed to increase to 26% at reaction temperature of 373 K without change in epoxide selectivity value. The variation of reaction temperature from 358 to 418 K did not affect the epoxide selectivity, but the conversion decreased from 26% at 373 K to 6% at 418 K. For *cis*-cyclooctene, the highest conversion (47%) was observed at 373 K which showed decreased values at higher temperatures.

Table 3
Effect of pressure on epoxidation of cycloalkenes using NaCoX96 catalyst

Entry	Pressure (psi)	Cyclohexene		<i>cis</i> -Cyclooctene		1,5-Cyclooctadiene		Cyclododecene	
		C (%)	S (%)	C (%)	S (%)	C (%)	S (%)	C (%)	S (%)
1	30	14	46	10	100	15	100	2	100
2	60	26	48	47	100	11	100	3	100
3	90	17	47	31	100	16	100	3	100
4	120	18	46	20	100	16	100	4	100
5	150	17	47	12	100	17	100	4	100






C (%), Percentage of conversion; S (%), percentage of selectivity (epoxide product). Reaction conditions: CYA, 2 g; IS, 0.2 g; DMF, 40 ml; catalyst, 200 mg; time, 8 h; temperature, 373 K.

There was no effect of temperature on epoxide selectivity in case of *cis*-cyclooctene as well as other higher cycloalkenes studied by us. In the case of 1,5-cyclooctadiene conversions ranging from 10 to 21% were observed in the temperature range of 373–388 K with 100% epoxide selectivity. Cyclododecene did not show significant cycloalkene conversions in the temperature range studied.

The effect of pressure (30–150 psi) on the epoxidation of various cycloalkenes was studied keeping the reaction temperature constant at 373 K using NaCoX96 catalyst and data are summarized in Table 3. In the case of cyclohexene and *cis*-cyclooctene, conversions of about 13 and 8% were obtained with 46 and 100% selectivity of epoxide at 30 psi pressure. As the pressure was increased from 30 to 60 psi, the conversion increased to 26 and 47%, respectively, with selectivity values remaining nearly the same. On further increasing the pressure cycloalkenes conversions decreased without any change in epoxide selectivity.

In Table 4, cyclohexene conversion and percentage selectivities for various reaction products formed during epoxidation at 60 psi and 373 K with NaCoX96 are given. It is seen from the data that conversion up to 26% and selectivity up to 50% for cyclohexeneoxide (*m/z*: 98, 83, 69, 54, 41) is observed. Other products observed include, cyclohexa-2-ene-1-ol (*m/z*: 98, 83, 70, 55, 41) and cyclohexa-2-ene-1-one (*m/z*: 96, 81, 68, 55, 40). With respect to cycloheptene, conversion of 37%, 66% cyclohepteneoxide (*m/z*: 112, 97, 83, 68, 56, 41) selectivity and 34% cyclohepta-2-ene-1-one (*m/z*: 110, 95, 81, 66, 54) were obtained. For *cis*-cyclooctene 47% conversion and 100% epoxide (*m/z*: 126, 111, 97, 83, 67, 55, 41) selectivity was observed. Epoxidation of 1,5-cyclooctadiene yielded 1,2-epoxycycloocta-5-ene (*m/z*: 124, 109, 95, 79, 67, 54, 41), as only product and no diepoxy product was observed. Epoxidation of cyclododecene

Table 4
Epoxidation of cycloalkenes using molecular oxygen with NaCoX96 catalyst

Entry	Substrate	Conversion (%)	Selectivity (%) (epoxide)	Selectivity (%) 2-ene-1-ol	Others 2-ene-1-one
1		26	48	22	30
2		38	66	–	34
3		47	100	–	–
4		11	100	–	–
5		3	100	–	–

Reaction conditions: CYA, 2 g; DMF, 40 ml; catalyst, 200 mg; O₂ ≅ 60 psi; temperature, 373 K; time, 8 h.

was performed as like all the other substrates with all CoX catalysts but no significant conversions were seen in this case. Only a maximum of nearly 3% conversion of cyclododecene and 100% epoxide (*m/z*: 182, 135, 121, 111, 96, 82, 67, 56, 41) selectivity was observed with NaCoX96 catalyst.

Wang et al. [43] reported high conversions and selectivities using poly(vinylbenzyl) acetylacetonato complex of cobalt as effective and stable catalyst for the epoxidation of cycloalkenes with molecular oxygen at 25 °C and *iso*-butyraldehyde as sacrificial reductant.

3.2. Epoxidation of cycloalkenes using alkali and alkaline earth metal promoted CoX

In our earlier study with styrene [45,46], we have observed that the base promoted CoX catalyst proved effective in enhancing styrene conversion and styrene epoxide selectivity. So epoxidation of cycloalkenes was also studied using different alkali and alkaline earth metal exchanged CoX catalysts. Samantary and Parida [48] has also reported that amine modified TS catalyst to be effective for epoxidation of cyclohexene indicating that the basic character of the catalyst could influence alkene conversion. So, catalytic epoxidation of cycloalkenes using molecular oxygen was carried out under the optimized reaction conditions, i.e., 60 psi O₂ pressure and 373 K with alkali and alkaline earth metal ion exchanged CoX.

During the epoxidation of cyclohexene with alkali and alkaline metal promoted CoX catalysts, there is significant decrease in cyclohexene conversion except for RbCoX21 (entry 3; Table 5) and MgCoX (entry 5; Table 5). However, the selectivity values for epoxide as well as cyclohexa-2-ene-1-ol and cyclohexa-2-ene-1-one did not show variation with alkali/alkaline metal promoted catalysts. Similar decrease in cycloalkene conversion values was observed for *cis*-cyclooctene and 1,5-cyclooctadiene (Table 6) with alkali and alkaline metal

Table 5
Epoxidation of cyclohexene using molecular oxygen

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			Epoxide	2-ene-1-ol	2-ene-1-one
1	NaCoX96	26	48	22	30
2	KCoX19	15	49	24	27
3	RbCoX21	23	49	21	30
4	CsCoX20	12	49	21	30
5	MgCoX22	23	50	24	26
6	CaCoX19	9	47	23	30
7	SrCoX18	9	49	25	26
8	BaCoX15	9	53	22	25
9	CsBaCoX20	16	49	22	29
10	KSrCoX20	12	49	23	28

Reaction conditions: CYA, 2 g; IS, 0.2 g; DMF, 40 ml; catalyst, 200 mg; O₂ ≅ 60 psi; temperature, 373 K; time, 8 h.

Table 6
Epoxidation of *cis*-cyclooctene and 1,5-cyclooctadiene using molecular oxygen

Entry	Catalyst	Conversion (%)	
		<i>cis</i> -Cyclooctene	1,5-Cyclooctadiene
1	NaCoX96	47	11
2	KCoX19	12	6
3	RbCoX21	8	8
4	CsCoX20	6	8
5	MgCoX22	12	6
6	CaCoX19	11	9
7	SrCoX18	6	9
8	BaCoX15	2	7
9	CsBaCoX20	5	12
10	KSrCoX20	4	5

Reaction conditions: CYA, 2 g; IS, 0.2 g; DMF, 40 ml; catalyst, 200 mg; O₂ ≅ 60 psi; temperature, 373 K; time, 8 h.

Table 7
Calculated selective bond angles and cross-sections

Cycloalkene	Height (Å)	Width (Å)	$\angle C1C2C3$ (°)	$\angle C2C3C4$ (°)	$\angle C5C6C7$ (°)	$\angle C6C7C8$ (°)
Cyclohexene	4.303	4.975	123.250	123.250	–	–
Cycloheptene	5.154	5.339	124.691	124.691	–	–
<i>cis</i> -Cyclooctene	5.098	5.414	124.681	126.375	–	–
1,5-Cyclooctadiene	4.756	4.859	122.729	122.79	137.369	137.611

promoted catalysts. The selectivity for respective epoxide was observed to be 100% with NaCoX96 as well as alkali and alkaline metal promoted catalysts.

The decrease in the conversions in the case of catalyst having alkali and alkaline earth cation may be attributed to the less cobalt content in the catalyst system or the stereochemistry of the cycloalkene when compared to that of the styrene [46]. In case of styrene the electron withdrawing phenyl group activates the double bond and thus favours the styrene to interact with the active Co^{2+} ions located in supercages leading to higher conversions and epoxide selectivity. As reported by Samantary and Parida [48] where amine modified TiO_2-SiO_2 were used in the epoxidation of cyclohexene, increase in the conversion values only upto 40 mol% amine concentration was observed and beyond which decrease in conversion was obtained. But in our case, there was a gradual decrease in the conversion values as the basicity of the catalyst increased with incorporation of co-cations. The reason for decrease in the conversion may be because of the larger size of the co-cation which might be hindering the reach of the cycloalkene molecule to the active sites.

The order of reactivity of cyclic olefins increases in the order, cyclohexene < cycloheptene < *cis*-cyclooctene. The higher conversion of cyclooctene and cycloheptene compared to cyclohexene indicates that the former alkenes are more easily coordinated to the active $Co(III)$ metal center during epoxidation compared to cyclohexene. These results suggest that the conformation, the bond angle strain and the torsional strain play important roles in governing the epoxidation of the cyclic olefins. We further carried out Dmol³ low energy geometry optimization to find out the selective bond angles and cross-sections of four substrate molecules and as reported by Bhattacharjee and Anderson [49] and the data in Table 7 reveals that all the molecules nearly have a similar type of cross-section but the bond angle associated with the double bond in all the substrates varied accordingly due to different stable conformational arrangements. In case of lower energy geometry optimized structure Fig. 2, in cyclohexene double bonded carbons as well as the allylic carbon are in one plane thus making it possible for the Co^{2+} to attack on either of the positions. But in the case of cycloheptene and *cis*-cyclooctene, the lower energy optimized structures are in a chair confirmation with the double bond in

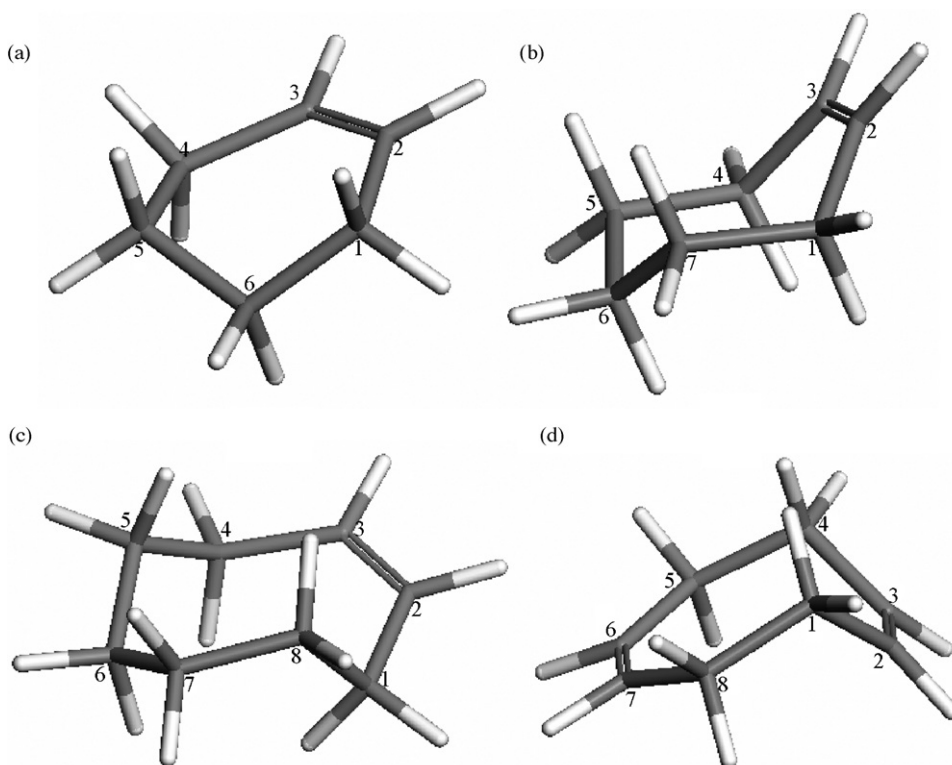


Fig. 2. DMol³ geometry optimized structures of cycloalkenes. (a) Cyclohexene, (b) cycloheptene, (c) *cis*-cyclooctene and (d) 1,5-cyclooctadiene.

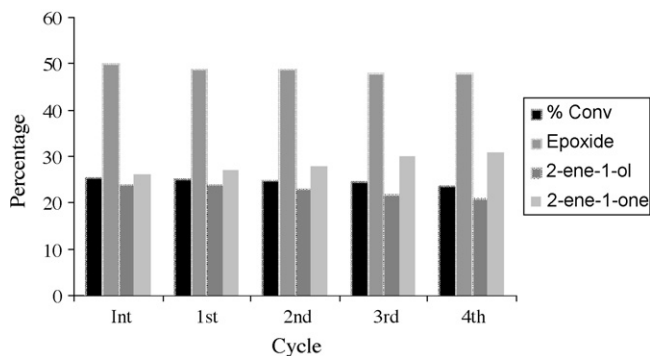


Fig. 3. Reusability of spent catalyst. Reaction conditions: cyclohexene, 2 g; IS, 0.2 g; DMF, 40 ml; $O_2 \cong 60$ psi; temperature, 373 K; time, 8 h; NaCoX96 catalyst, 200 mg.

one plane and all other carbons in another plane. In the case of 1,5-cyclooctadiene, a stable boat conformation is observed with both the double bonds in a different planes. The access of alkene double bond to the active free radical type active oxygen species formed probably due to the activation of O_2 in the Co^{2+} cations present at site III' or II is less hindered in case of cycloheptene and *cis*-cyclooctene, thus leading to higher cycloalkene conversion compared to that for cyclohexene, 1,5-cyclooctadiene and cyclododecene.

3.3. Recycling of the spent catalysts

NaCoX96 catalyst was used for reusability studies in regard to cyclohexene epoxidation. The catalyst recovered from the reaction mixture by filtering or by centrifuging, and the recovered catalyst was washed with DMF and then with distilled water to remove all of the organic phases adsorbed on the catalyst and dried at room temperature. The conversion and selectivity obtained are given in Fig. 3. As seen from the data, the catalytic activity of the catalysts remained unaffected after four reaction cycles. The analysis of the liquid phase separated from the reaction mixture did not show the presence of cobalt cations in solution, indicating the absence of leaching of the cobalt metal ions during the catalytic reaction citing that the cobalt(II) cations present in the zeolite had a strong interaction with the zeolite framework.

3.4. Reaction mechanism

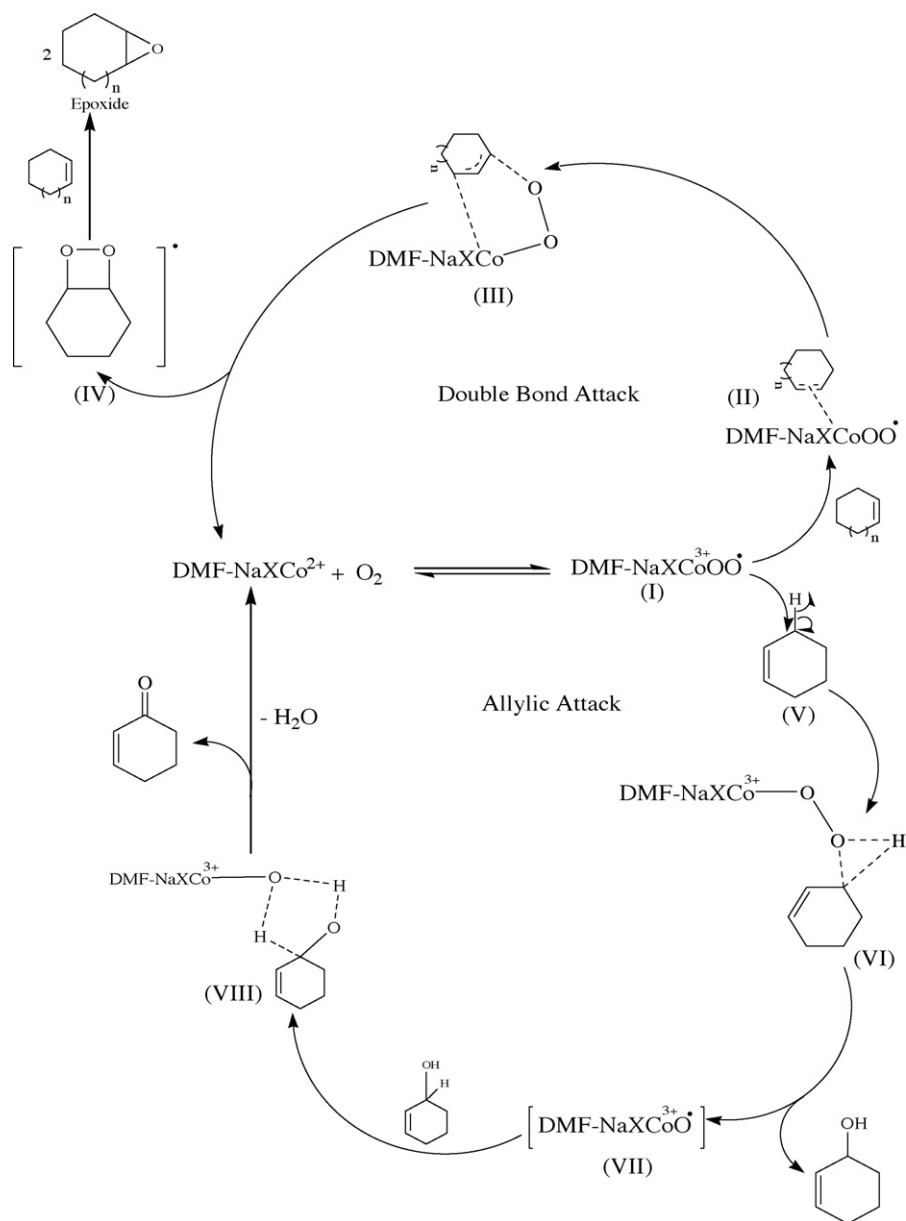
To study the reaction pathway and also the active species formed in the reaction a separate experiment was carried out using a free radical scavenger hydroquinone (50 mg) using NaCoX96 catalyst under same reaction conditions as mentioned in Table 3. The results showed no epoxide or any side product formation in case of cyclohexene and *cis*-cyclooctene confirming free radical mechanism. The free-radical-type active oxygen species are formed due to activation of O_2 in the Co^{2+} cations present at site III' or II. Basing on the present experimental study and earlier reported study [46,49–51] a tentative reaction mechanism for cycloalkene epoxidation has been proposed. The reaction is proposed to proceed as shown in Scheme 1 and is discussed below.

It has been shown [44,46] that Co(II) ions present in zeolite X are in tetrahedral coordination in the presence of DMF. UV–vis DRS spectra reported by us [46] as well reported by Tang et al. [44] show that Co(II)NaX–DMF present in the zeolite supercage gets coordinated to molecular oxygen to form DMF–NaXCo(III)OO• (I) superoxo complex which results into oxidative addition to the C–C double bond of cycloalkene molecule to give an intermediate (II). The intermediate (II) undergoes migratory insertion to give cyclic radical (IV) through intermediate (III) and regenerates DMF–NaXCo(II). Cyclic radical (IV) can further react with another molecule of cycloalkene to give epoxide.

In another possibility, DMF–NaXCo(III)OO• (I) superoxo complex can attack the allylic position of the cycloalkene resulting in the formation of species (V) which results in the formation of 2-ene-1-ol product through intermediate (VI). The in situ formed intermediate DMF–NaXCoO• (VII) can further oxidize alcohol through (VIII) to form a ketone, i.e., 2-ene-1-one with removal of water.

Alkene epoxidation has also been reported to occur through hydro peroxides (ROOH) in the literature [52]. In such case, cycloalkene reacts with hydroperoxide to give cyclohexene-hydroperoxide which is decomposed by Co^{2+}/Co^{3+} to give cyclohexen-2-ol and $Co-O\bullet$ species to initiate the radical chain. The latter species then can react with olefin to give epoxide or with 2-ene-1-ol to form 2-ene-1-one. However, the formation of hydro peroxides (ROOH) is remote as we have not used hydrogen peroxide or co-reductant like *iso*-butraldehyde. But, there are some reports [53–55] on the formation of hydroperoxide with auto air oxidation of alkenes. If that happens, epoxide formation through hydroperoxide route is possible. However, the formation of 2-ene-1-ol and/or 2-ene-1-one compounds must be observed if epoxide forms by this route. However, in the present study, during oxidation of higher cyclic alkenes namely, *cis*-cyclooctene, 1,5-cyclooctadiene and cyclododecane, 2-ene-1-ol and/or 2-ene-1-one products were not observed. Epoxide formation occurred with 100% selectivity. These observations cannot be explained by above route and thereby ruling out on this mechanism in the present case. The observed absence of 2-ene-1-ol and/or 2-ene-1-one products for higher cycloalkenes can be explained in terms of the proposed mechanism involving allylic attack by DMF–NaXCo(III)OO• (I) superoxo complex which is less probable with higher cycloalkenes which have sterically hindered allylic hydrogen's. Cyclohexene and cycloheptene molecules possess chair conformation. Besides, in cyclohexene, double bonded carbons as well as the allylic carbon are in the same plane. However, *cis*-cyclooctene 1,5-cyclooctadiene are in boat conformation and the C–C double bonds and the allylic carbons are in different planes. In view of this, *cis*-cyclooctene 1,5-cyclooctadiene are likely to have more steric hindrance towards allylic attack by DMF–NaXCo(III)OO• (I) superoxo complex resulting into absence of 2-ene-1-ol and/or 2-ene-1-one products.

Further in our support we have carried out the kinetic profile of the reaction till 24 h in a time gap of 4 h each and it clearly shows that there is no change in the selectivities of the products (Table 8), which means that further ring opening of the epoxide



Scheme 1. Tentative reaction mechanism for epoxidation of cycloalkenes.

leading to side products was not observed. Selectivities of the products are almost the same through out suggesting that both the epoxidation step via double bond attack and the allylic oxidation step go side by side with the help of the active species (I).

Table 8
Effect of time on conversion and selectivity in case of cyclohexene epoxidation

Entry	Time (h)	Conversion (%)	Selectivity (%)		
			Epoxide	2-ene-1-ol	2-ene-1-one
1	4	8	48	22	30
2	8	25	49	24	27
3	12	25	48	24	28
4	16	26	49	21	30
5	20	27	50	24	26
6	24	30	47	23	30

Reaction conditions: CYA, 2 g; IS, 0.2 g; DMF, 40 ml; NaCoX96 catalyst, 200 mg; $O_2 \cong 60$ psi; temperature, 373 K.

4. Conclusions

Thus, the cobalt exchanged and alkali and alkaline metal earth cationic promoted CoX catalysts catalytic activity with respect to epoxidation of cycloalkenes have been studied. The NaCoX96 catalyst has been efficient catalyst for epoxidation of cyclohexene and *cis*-cyclooctene, using molecular oxygen under pressure in autoclave reactor. Effect of temperature and pressure are also studied and 373 K and 60 psi were found to be the optimum reaction conditions. A tentative reaction mechanism has

been drawn and the energy optimization studies helped to understand the reaction system basing on the stereochemistry of the cycloalkene.

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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.2007.04.029.

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