



Aerobic epoxidation of olefins over the composite catalysts of Co-ZSM-5(L) with bi-/tridentate Schiff-base ligands

B. Qi, X.-H. Lu, S.-Y. Fang, J. Lei, Y.-L. Dong, D. Zhou, Q.-H. Xia*

Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, & School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China

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ABSTRACT

Three tridentate or bidentate Schiff-base ligands inclusive of salicylaldehyde benzoylhydrazone (L_1), vanillic aldehyde benzoylhydrazone (L_2) and 4-methyl benzaldehyde benzoylhydrazone (L_3), have been designed, synthesized and employed to coordinate with Co^{2+} ions and ion-exchanged Co-ZSM-5 forming several Co-L complexes and Co-ZSM-5(L) composite catalysts. The catalytic epoxidation of several alkenes with dry air has been carried out at 90 °C under atmospheric pressure using Co-L complexes and Co-ZSM-5(L) catalysts (using TBHP in small amounts as the initiator). In contrast, the catalysts Co-ZSM-5(L) shows higher catalytic activity than Co-ZSM-5 itself and Co-L complexes. Among three Co-ZSM-5(L) catalysts, Co-ZSM-5(L_1) exhibits the highest activity for the selective epoxidation of alkenes. Recycling studies show the recyclability of Co-ZSM-5(L_1) as a heterogeneous catalyst, which does not lose the catalytic activity after even eight reuses appreciably. Based on the experiments, one possible reaction mechanism is proposed.

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1. Introduction

The catalytic epoxidation of alkenes to produce epoxides is an important industrial reaction, since epoxides are key building blocks in organic synthesis [1], as well as commercially important intermediates used in the synthesis of chiral pharmaceuticals, pesticides, epoxy paints, agrochemicals, perfume materials and sweeteners [2,3]. Traditionally, epoxides are produced by the chlorohydrin process and the Halcon process [4]; however, a lot of by-products resulted from both processes are environmentally undesirable. Thus, the pursuit for environmentally-benign methods with clean and cheap oxidant has been a challenge in chemical industrial and academic fields. Epoxidation of alkenes using molecular oxygen as the oxidant is in accordance with our desires [5]. However, most epoxidations using O_2 as the oxidant need sacrificial reductants, such as O_2 with H_2 [6–10], O_2 with Zn powder [11] or O_2 with organic alcohols or aldehydes [12–17]. Transition metal complexes, especially cobalt complexes, are well-known catalysts for the selective oxidation of alkenes with O_2 , e.g. cobalt(III) acetylacetonate (acac) for styrene, *tert*-butylethylene, norbornylene and 1,1-dineopentylethylene [18], cobalt(II) complex for terminal olefins with 2-ketones and 2-alcohols [19,20], as well as Co(salen) complexes for alkenes with isobutyratehyde [21]. Also,

aerobic oxidation of α -pinene over Co(II)-complexes without any co-oxidant was studied, where verbenone was the main product [22].

Cobalt-based heterogeneous catalysts applied for the epoxidation of alkenes using O_2 without any co-reductant have attracted much attention. Tang et al. first reported that ion-exchanged Co-faujasite zeolites and Co-MCM-41 could catalyze the epoxidation of styrene with O_2 in the absence of co-reductant [23,24]. Co^{2+} -exchanged faujasite-type zeolites modified by increasing the cobalt content or introducing alkali and alkaline cations were used to catalyze the epoxidation of styrene, α -pinene and cycloalkenes [25–27]. Co-TUD-1 exhibited a high reactivity for the epoxidation of *trans*-stilbene by O_2 , and the selectivity of epoxides was very high [28]. Co(II)Saloph-Y catalyzed the selective oxidation of α -pinene with air to epoxide and D-verbenone with small amounts of azobisisobutyronitrile as the initiator, where the main products were epoxide and verbenone [29]. Additionally, the composite catalyst consisting of *cis*- MoO_2 -Schiff-base complexes and zeolite-Y could efficiently catalyze the epoxidation of alkene with O_2 [30–32].

Our group previously reported that the composite catalyst Co-ZSM-5(L) coordinated with tridentate ligands (e.g. vanillic aldehyde salicylhydrazone) could efficiently catalyze highly selective epoxidation of styrene with dry air in the presence of small amounts of TBHP as the initiator [33]. In the present study, we further extend previous ideas to other tridentate or bidentate Schiff-base ligands, such as three newly designed Schiff-bases salicylaldehyde benzoylhydrazone (L_1), vanillic aldehyde benzoylhydrazone (L_2)

* Corresponding author. Tel.: +86 27 5086 5370; fax: +86 27 5086 5370.

E-mail addresses: xia1965@yahoo.com, xiaqh518@yahoo.com.cn (Q.-H. Xia).

and 4-methyl benzaldehyde benzoylhydrazone (**L**₃), and to the epoxidation of various alkene molecules with air, inclusive of α -pinene, styrene, α -methyl styrene and cyclooctene. Fortunately, some encouraging results have been attained.

2. Experimental

2.1. Materials

The main reagents used in the synthesis of Schiff-base ligands and catalysts were 4-methyl benzaldehyde (99%), salicylaldehyde (99.5%), vanillic aldehyde (99.5%), benzoylhydrazide (99%), cobalt(II) acetate tetrahydrate (Co(Ac)₂·4H₂O, 99.5%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 99.5%), Na-ZSM-5, absolute ethanol (EtOH, 99.5%). The freshly distilled solvents were dimethylacetamide (DMA), dimethylformamide (DMF), dioxane, cyclohexanol and toluene. Other reagents included distilled water, α -pinene (>98%), styrene (>99%), cyclooctene (>99%), α -methyl styrene (>99%), NaClO, NaIO₄, aqueous H₂O₂ (30%), aqueous *tert*-butyl hydroperoxide (TBHP, >65%) and dry air.

2.2. Synthesis of Schiff-base ligands

Benzoylhydrazide (0.03 mol) was added into a 100-ml round-bottom flask filled with 40 ml of absolute ethanol under stirring, and the resulting mixture was refluxed at 78 °C until the dissolution of benzoylhydrazide. Subsequently, 0.03 mol of salicylaldehyde (or vanillic aldehyde, or 4-methyl benzaldehyde) was slowly dripped into the above solution while stirring, which was refluxed for another 3 h until the completion of reaction. After the solution was cooled down to room temperature, a coarse product could be recovered by filtration, which then underwent further recrystallization with mixed ethanol and distilled water to obtain pure salicylaldehyde benzoylhydrazone crystal (**L**₁) (or vanillic aldehyde benzoylhydrazone (**L**₂), or 4-methyl benzaldehyde benzoylhydrazone (**L**₃)) (Scheme 1).

L₁: yield, 90.2%, M.p.: 171 °C; IR (KBr) (cm⁻¹): 3270, ν (N–H); 1668, ν (C=O); 1617, ν (C=N); 3070, ν (O–H); ¹H-NMR (DMSO-*d*₆) (600 MHz): 12.111 (s, 1H, N–H), 11.298 (s, 1H, Ar–OH), 8.651 (s, 1H, N=C–H), 7.952–6.932 (m, 9H, Ar–H); UV–vis (in ethanol): 288, 299 and 330 nm.

L₂: yield, 88.1%, M.p.: 192 °C; IR (KBr) (cm⁻¹): 3250, ν (N–H); 1655, ν (C=O); 1610, ν (C=N); 3420, ν (O–H); ¹H-NMR (DMSO-*d*₆) (600 MHz): 12.666 (s, 1H, N–H), 9.549 (s, 1H, Ar–OH), 8.346 (s, 1H, N=C–H), 7.906–6.843 (m, 8H, Ar–H), 3.840 (s, 3H, –OCH₃); UV–vis (in ethanol): 240 and 328 nm.

L₃: yield, 86.4%, M.p.: 156 °C; IR (KBr) (cm⁻¹): 3198, ν (N–H); 1650, ν (C=O); 1610, ν (C=N); ¹H-NMR (DMSO-*d*₆) (600 MHz): 11.798 (s, 1H, N–H), 8.425 (s, 1H, N=C–H), 7.918–7.276 (m, 9H, Ar–H), 2.352 (s, 3H, Ar–CH₃); UV–vis (in ethanol): 236 and 310 nm.

2.3. Synthesis of Co-L complexes

Thus-synthesized ligand (0.03 mol) (**L**₁, **L**₂ or **L**₃) was added into a 100-ml round-bottom flask filled with 30 ml of absolute ethanol under stirring, and the mixture was refluxed at 78 °C until the dissolution of the ligand. Then, a solution of 0.03 mol cobalt(II) chloride hexahydrate dissolved in 30 ml absolute ethanol was slowly dripped into the above solution, which was again refluxed for another 2 h until the completion of reaction. After the solution was cooled down to room temperature, a coarse product was recovered by filtration, which was further recrystallized with ethanol to obtain pure Co-L crystals (Co-**L**₁, Co-**L**₂ or Co-**L**₃) (in Scheme 1). The C, H, N contents of Co-L complexes were determined close to the theoretical values, in which Co-**L**₁ is tridentate complex [34] (elemental analysis calcd (%) for C₁₄H₁₀N₂O₂CoCl: C, 50.62; H, 3.03;

Table 1
Physicochemical characterization of Co-zeolite(L) catalysts.

Catalysts	Co-content ^a (wt%)	SiO ₂ /Al ₂ O ₃ ratios ^a	Surface area ^b (m ² /g)
Na-ZSM-5	0	25	406.5
Co-ZSM-5	1.21	25	375.6
Co-ZSM-5(L ₁)	1.16	25	335.2
Co-ZSM-5(L ₂)	1.15	25	329.1
Co-ZSM-5(L ₃)	1.15	25	327.3
Na-Y	0	4.7	821.3
Co-Y	1.30	4.7	720.4
Co-Y(L ₁)	1.24	4.7	665.2
Na-4A	0	2.0	155.7
Co-A	1.12	2.0	120.6
Co-A(L ₁)	1.07	2.0	97.5

^a Results obtained from ICP-AES.

^b Values obtained from N₂-adsorption results.

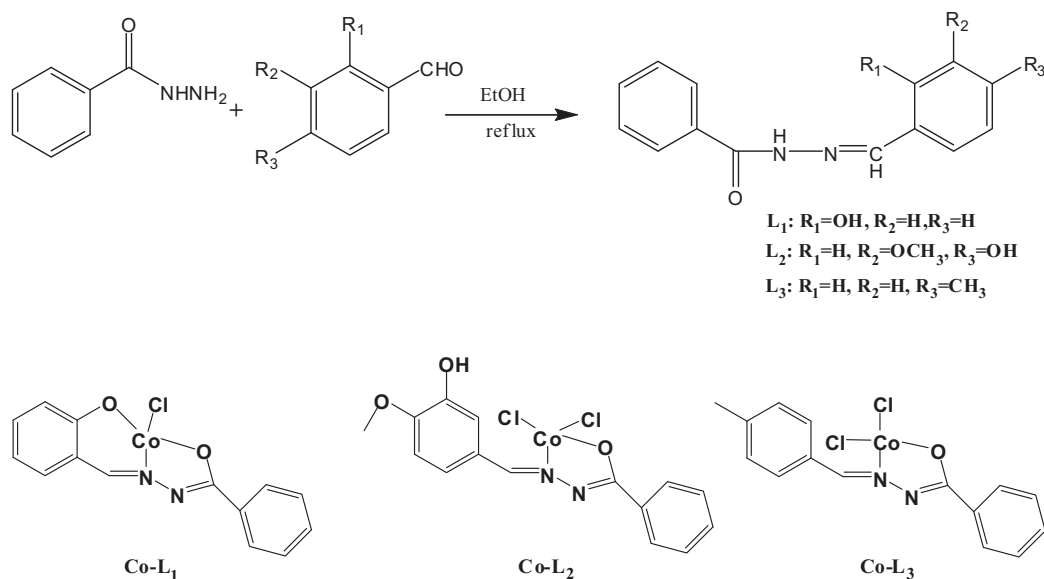
N, 8.43; found: C, 50.57; H, 3.05; N, 8.38); Co-**L**₂ is bidentate complex (elemental analysis calcd (%) for C₁₅H₁₃N₂O₃CoCl₂: C, 45.14; H, 3.28; N, 7.02; found: C, 45.10; H, 3.31; N, 6.98); Co-**L**₃ is bidentate complex (elemental analysis calcd (%) for C₁₅H₁₃N₂OCoCl₂: C, 49.07; H, 3.57; N, 3.81; found: C, 49.10; H, 3.60; N, 3.79).

2.4. Preparation of zeolite composite catalysts

Initially, ion exchange was carried out at 90 °C for 9–10 h by stirring 5 g of Na-ZSM-5 in an aqueous solution (250 ml) of cobalt(II) acetate tetrahydrate (0.375 g, 1.5 mmol). The solid product was recovered by filtration, washed thoroughly with hot water till all soluble acetate ion species were removed, and then dried in an oven at 120 °C for 5 h. Certain amount of ion-exchanged zeolites were separately added into hot ethanol solution of **L**₁, **L**₂ or **L**₃ (1.5 mmol), and stirred at 78 °C for 10 h to ensure the formation of composites. In order to remove the excessive ligands, the recovered solids that had been washed several times with hot ethanol were again subjected to the Soxhlet extraction in ethanol under refluxing until no free ligand was detected from the extract by the UV–vis spectrum. The resulting zeolite composites coordinated with ligands were in vacuo dried at 80 °C for 24 h and stored in the desiccator for catalytic uses.

2.5. Structural characterizations of ligands and catalysts

Powder X-ray diffraction (XRD) profiles were recorded on a Rigaku D/MAX – IIIC diffractometer with CuK α ($\lambda = 1.54184 \text{ \AA}$) operating at 30 kV and 25 mA. Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer. UV–vis spectra were collected on a Shimadzu UV–vis UV-2550 spectrometer. ¹H-NMR spectra of samples dissolved in DMSO-*d*₆ were measured on a Varian Inova-600 (600 MHz) NMR instrument using 0.03% TMS ((CH₃)₄Si) as an internal standard. Thermogravimetric analysis (TGA) of Co-L and Co-ZSM-5(L) were conducted on a TGA-7 analyzer. Elemental analyses (C, H, N) of Co-complexes were conducted on an Elementar VarioEL-III instrument. The content of Co in the sample was determined by the inductively coupled plasma (ICP) technique. The BET specific surface area was calculated using the BET equation with relative pressure (p/p_0) at 0.05–0.25. Metal-containing complexes and zeolites were determined to contain 16.4 wt% Co for Co-**L**₁, 15.2 wt% Co for Co-**L**₂, 15.7 wt% Co for Co-**L**₃, 1.21 wt% Co for Co-ZSM-5. Co contents, BET surface areas and SiO₂/Al₂O₃ ratios of Co-ZSM-5(L) were also shown in Table 1. The electrochemical measurements were performed on a CHI 660A electrochemical workstation.



Scheme 1. Synthetic routes of Schiff-base ligands and the structure of Co-L complexes.

2.6. Epoxidation of alkenes

In a typical run, the catalyst (10 mg of Co-L or 100 mg of Co-zeolite (L)), 3 mmol of alkene, 10 g of solvent (DMF) and 0.5 mmol of TBHP were mixed in a 50-ml three-necked flask equipped with a cryogenic-liquid condenser and with an air pump under magnetic stirring and heated to desired temperatures. Then dry air with a stable flowrate of 30 ml/min controlled by a flowmeter was introduced by bubbling into the bottom of reactor at atmospheric pressure. Five hours later, the reaction was terminated and the solid catalyst was filtered off. The liquid filtrate was quantitatively analyzed by GC-900A equipped with an FID detector and an SE-30 column (30 m × 0.25 mm × 0.25 μm), where hydrogen was used as carrier gas. GC error for the determination was within ±3%. Chlorobenzene was used as an internal standard to quantify the components. In order to investigate the stability and recyclability of Co-ZSM-5(L₁), the solid catalyst was recovered from the reaction mixture by filtration, washed successively with distilled water and Soxhlet extraction using ethanol under refluxing, dried at 80 °C for 6 h, and reused in the next run.

3. Results and discussion

3.1. Characteristics of catalysts

As revealed by IR spectra of L and Co-L complexes (Supplementary data, Fig. 1(a) and (b) in the supplement), once coordination with cobalt metal, the C=O band of the ligand L at about 1650 cm⁻¹ disappears totally. Instead, characteristic C=N bands emerges at about 1610 cm⁻¹ and 635 cm⁻¹ for Co-L. IR spectra of Co-ZSM-5(L) (Supplementary data, Fig. 1(c) in the supplement) show additional weak infrared signals in the range of 1400–1650 and 2900–3550 cm⁻¹, which can be associated with the ligand molecules coordinated onto the surface of Co-ZSM-5 [33]. This coordination also leads to the emergence of one weak infrared band at 630 cm⁻¹, attributed to the Co-N vibration in Co-ZSM-5(L). XRD patterns of Co-ZSM-5(L) exhibit the maintenance of integrated ZSM-5 frameworks after ion-exchange and coordination treatments.

UV-vis spectra of L and Co-L (Supplementary data, Fig. 2 in the supplement) show several absorbance bands at 225, 235, 312, 418 nm for Co-L₁, at 230, 331 nm for Co-L₂ and at 240, 312 nm for

Co-L₃. Obviously, the absorption at about 315 nm for the Co-L complexes is slightly shifted compared with that for the L complexes, accompanied with the appearance of one band at about 235 nm. Co-ZSM-5 produces two absorption bands with maxima at 246 and 520 nm (Fig. 1), in which the peak at 520 nm may represent Co²⁺ species coordinated octahedrally as [Co(H₂O)₆]²⁺ [35]. However, there are recognizable three bands at 252, 310, 394 nm for Co-ZSM-5(L₁), at 245, 327, 526 nm for Co-ZSM-5(L₂), and at 246, 307, 527 nm for Co-ZSM-5(L₃). For Co-ZSM-5(L), the absorption band at about 520 nm disappears or becomes very weak, suggesting the coordination of the majority of Co²⁺ species with Schiff-base ligands.

TG curves of Co-L and Co-ZSM-5(L) samples contain three-stage weight losses in air (Supplementary data, Fig. 3 in the supplement). Evidently, the first weight loss below 270 °C is assigned to the evaporation of physically adsorbed and intra-zeolite water molecules [36], the second between 270 and 420 °C to the combustion of organic ligand molecules coordinated onto the outer surface of zeolite, and the third ranging from 420 to 750 °C to the oxidative decomposition of organic ligand molecules adsorbed onto the metal sites in the pores. Quantitatively, the total weight-loss

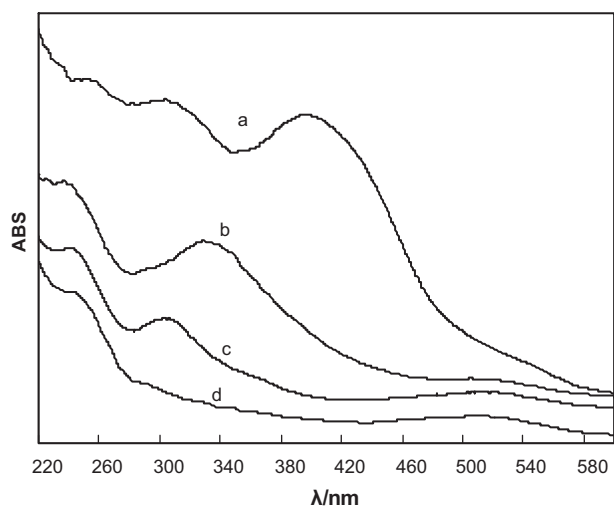


Fig. 1. UV-vis spectra of samples: (a) Co-ZSM-5(L₁), (b) Co-ZSM-5(L₂), (c) Co-ZSM-5(L₃), and (d) Co-ZSM-5.

percentage of Co-ZSM-5(L₁), Co-ZSM-5(L₂) and Co-ZSM-5(L₃) are measured to be about 5.2, 4.4 and 4.0 wt% in the temperature range of 270–750 °C, respectively. It is known that the oxidation of Co²⁺ ions exchanged into Na-ZSM-5 is difficult, because of the strong interaction between Co²⁺ and anionic zeolite ZSM-5 framework [24]. Thus, the Co species introduced into Na-ZSM-5 by ion-exchange method exist mainly in the form of Co(II) state.

3.2. Catalytic epoxidation of α -pinene with dry air

3.2.1. Epoxidation of α -pinene with TBHP + air over different catalysts

The catalytic activity of several Co-L complexes and Co-zeolite(L) catalysts for the epoxidation of α -pinene has been tested in DMF at 90 °C, with air as the oxidant and TBHP as the initiator. Under our experimental conditions, different catalysts with similar Co content show a great difference in the catalytic conversion of α -pinene (Table 2). When no catalyst is added, only 10.9 mol% of α -pinene is converted with 67.4% the epoxide selectivity. Very clearly, Co-ZSM-5(L) catalysts are more active but less selective for the epoxide than the corresponding Co-L complexes. For homogeneous catalysts, the catalytic activity and the epoxide selectivity gradually decrease in the sequence of Co-L₁ > Co-L₂ > Co-L₃ > Co(Ac)₂. For heterogeneous catalysts, the catalytic activity gradually decreases in the order of Co-ZSM-5(L₁) > Co-ZSM-5(L₂) > Co-ZSM-5(L₃) > Co-Y(L₁) > Co-ZSM-5 > Co-A(L₁), slightly different from the descending order of the epoxide selectivity: Co-ZSM-5(L₁) \approx Co-ZSM-5(L₃) > Co-A(L₁) > Co-ZSM-5(L₂) > Co-Y(L₁) > Co-ZSM-5. The catalyst Co-ZSM-5(L₁) show higher catalytic performance than Co-ZSM-5(L₂) and Co-ZSM-5(L₃), since L₁ is tridentate Schiff-base ligand while L₂ and L₃ are bidentate Schiff-base ligands. Fukuda and Katsuki have reported that the Co(salen) complex bearing electron-donating methoxy group at 3-carbons showed better activity than one bearing methyl (hydrogen) group [37]. A similar phenomenon can be observed from our results. Meanwhile, the TON value characterizing the activity of metal ions decreases gradually in the sequence of Co-ZSM-5(L₁) (145.4) > Co-ZSM-5(L₂) (141.1) > Co-ZSM-5(L₃) (137.6) > Co-Y(L₁) (107.8) > Co-A(L₁) (103.0) > Co-ZSM-5 (100.1) > Co-L₁ (74.2) > Co-L₂ (62.8) > Co-L₃ (59.0) > Co(Ac)₂ (19.5).

3.2.2. Effect of various oxidants, solvents and temperature over Co-ZSM-5(L₁)

Table 3 compares the effect of various oxidants on the epoxidation of α -pinene catalyzed by Co-ZSM-5(L₁) under identical conditions. When TBHP is used as the oxidant, the conversion of α -pinene is 31.1 mol% in 5 h, with an epoxide selectivity of 78.8%. Without the addition of TBHP, dry air oxidizes 26.6 mol% of α -pinene at 90 °C, with an epoxide selectivity of 77.4%. Also, singular TBHP (0.5 mmol) as the oxidant, the conversion of α -pinene and the selectivity of epoxide are only 7.6 mol% and 79.7%. However, once TBHP in small amounts is added into the catalytic system, the conversion of α -pinene and the selectivity of epoxide are largely elevated to 95.3 mol% and 88.4%. Compared with air, other oxidants like NaClO, NaIO₄ and H₂O₂ are less efficient for the epoxidation of α -pinene under the present experimental conditions. H₂O₂ converts 12.6 mol% of α -pinene (76.1% the epoxide selectivity), while NaIO₄ achieves only 9.8 mol% of conversion (77.6% the epoxide selectivity); however, NaClO merely oxidizes a trace of α -pinene.

Table 4 presents the effect of various solvents on the epoxidation of α -pinene with air catalyzed by Co-ZSM-5(L₁), in which the solvents tested include DMF, DMA, dioxane, cyclohexanol and toluene. Under our experimental conditions, the conversion of α -pinene can be arranged in the ascending order of toluene (6.3 mol%) < cyclohexanol (22.0 mol%) < dioxane (22.1 mol%) < DMA (42.8 mol%) < DMF (95.3 mol%), inconsistent

with the rising order of the epoxide selectivity: cyclohexanol (27.8%) < toluene (45.0%) < DMA (64.6%) < dioxane (71.2%) < DMF (88.4%). As shown in Table 4, the solvent plays an important role in the epoxidation reactions, similar to the reports in the literature [24,33]. Additionally, when adding 9 mmol of DMF into the catalytic system using dioxane or toluene as the solvent, the conversion of α -pinene and the selectivity of epoxide merely increased to 20.1–34.3 mol% and 62.4–75.0%, respectively. However, when adding 9 mmol of isobutylaldehyde as the reductant [25], the conversion of α -pinene and the selectivity of epoxide can reach 97.4 mol% and 83.7%. Note that after the completion of reaction the amount of oxo-DMF in the solution was detected by GC to be ca. 0.18–0.30 mmol in optimal experiments, merely corresponding to 1/17–1/10 of α -pinene quantity, i.e. the molar ratios of oxo-DMF/epoxide lie in the range of 0.06–0.11. Thus, the DMF cannot be recognized as a real reductant under the present experimental conditions.

The impact of reaction temperature on the epoxidation of α -pinene over Co-ZSM-5(L₁) in the temperature range 50–100 °C is shown in Supplementary data, Fig. 4 in the supplement. With increasing the reaction temperature from 50 to 90 °C, the conversion of α -pinene and the selectivity of epoxide are increased from 14.2 mol% to 95.3 mol% and from 87.2% to 90.1%, respectively; however, both decrease to 80.0 mol% and 86.0% at 100 °C.

3.3. Catalytic epoxidation of various alkenes with dry air over Co-ZSM-5(L)

Aside from the catalytic epoxidation of α -pinene with dry air as stated above, that of several other alkenes over Co-ZSM-5(L) composites is as well described in Table 5. For the epoxidation of styrene, the catalytic activity of these catalysts gradually decreases in the sequence of Co-ZSM-5(L₁) (93.9 mol%) > Co-ZSM-5(L₂) (92.6 mol%) > Co-ZSM-5(L₃) (83.7 mol%), different from the descending order of the epoxide selectivity: Co-ZSM-5(L₃) (91.7%) \approx Co-ZSM-5(L₂) (91.1%) > Co-ZSM-5(L₁) (89.7%). For α -methyl styrene, almost 100% conversions are attained over Co-ZSM-5(L) (99.7–100 mol%); while the epoxide selectivity shows a descending order of Co-ZSM-5(L₁) (74.1%) > Co-ZSM-5(L₃) (67.9%) > Co-ZSM-5(L₂) (66.1%). For cyclooctene, the epoxide selectivity on Co-ZSM-5(L) catalysts has been 100%, while the substrate conversions are relatively low with about 41.8–43.0 mol%, possibly assigned to the diffusion limitation of larger cyclooctene molecules in small pores of ZSM-5 zeolite and to the difficult activation of these catalysts for cycloalkenes with molecular oxygen [27]. Generally, the activity of three Co-ZSM-5(L) catalysts can be ordered as follows: Co-ZSM-5(L₁) > Co-ZSM-5(L₂) > Co-ZSM-5(L₃), relevant to the difference of electron-donating characteristics of three Schiff-base ligands. A comparison of our results with the earlier data reported for the epoxidation of alkenes is summarized in Table 6, where further shows the excellent catalytic activity of the present aerobic epoxidation system.

3.4. Recycling studies

The catalyst Co-ZSM-5(L₁) is used for recycling studies. It can be observed from Fig. 2, the activity of the catalyst shows an apparent reduction in the former three recycles, but remains basically unaffected in the latter five recycles. The conversion of α -pinene and the epoxide selectivity decrease from 95.3 to 90.6 mol% and from 88.4 to 86.1% in the former three recycles; however, in the latter five recycles both values have maintained more or less constants of ca. 89.0 mol% and 86.0%. ICP analyses of reaction mixture and the used catalysts did detect the leaching of cobalt from Co-ZSM-5(L₁), leading to the reduction of the cobalt content from 1.16 to 1.05 wt%, which could be due to the leaching of soluble Co species trapped in

Table 2
Epoxidation of α -pinene over various catalysts.^a

Catalyst	α -Pinene conversion (mol%)	Selectivity (%)				TON.
		Epoxide	Verbenol	Verbenone	Other	
Blank	10.9	67.4	9.5	18.9	4.2	–
Co(Ac) ₂	20.1	79.9	6.2	11.4	2.5	19.5
Co-ZSM-5	68.3	71.4	7.7	15.6	5.3	100.1
Co-L ₁	68.7	90.3	1.0	5.9	2.8	74.2
Co-ZSM-5(L ₁)	95.3	88.4	2.3	6.7	2.6	145.4
Co-L ₂	53.9	89.5	1.6	6.1	2.8	62.8
Co-ZSM-5(L ₂)	92.4	84.8	4.1	9.5	1.6	141.1
Co-L ₃	52.3	87.8	2.1	7.4	2.7	59.0
Co-ZSM-5(L ₃)	90.2	86.3	3.0	7.7	3.0	137.6
Co-Y(L ₁)	75.5	84.3	3.7	9.8	2.2	107.8
Co-A(L ₁)	62.3	85.1	3.5	8.7	2.7	103.0

^a Reaction conditions: Solvent, DMF(10 g); α -pinene, 3 mmol; catalyst, 0.01 g for homogeneous and 0.1 g for heterogeneous; tempt., 90 °C; time, 5 h; TBHP, 0.5 mmol; air flowrate, 30 ml/min.

Table 3
Effect of various oxidants on the epoxidation of α -pinene.^a

Oxidant	α -Pinene conversion (mol%)	Selectivity (%)			
		Epoxide	Verbenol	Verbenone	Other
Air ^b	26.6	77.4	3.5	13.7	5.4
TBHP ^c	31.1	78.8	6.4	11.5	3.3
Air + TBHP ^d	95.3	88.4	2.3	6.7	2.6
TBHP ^e	7.6	79.7	6.0	11.8	2.5
NaClO ^c	0.7	80.4	0	16.1	3.5
NaIO ₄ ^c	9.8	77.6	3.4	12.7	6.3
H ₂ O ₂ ^c	12.6	76.1	4.1	16.2	3.6

^a Reaction conditions: solvent, DMF(10 g); α -pinene, 3 mmol; catalyst: Co-ZSM-5(L₁), 0.1 g, tempt., 90 °C; time, 5 h.

^b Air flowrate, 30 ml/min.

^c Oxidant, 3 mmol.

^d Air flowrate, 30 ml/min; TBHP, 0.5 mmol.

^e Oxidant, 0.5 mmol.

Table 4
Effect of various solvents on the epoxidation of α -pinene.^a

Solvent	α -pinene Conversion (mol%)	Selectivity (%)			
		Epoxide	Verbenol	Verbenone	Others
DMF	95.3	88.4	2.3	6.7	2.6
DMA	42.8	64.6	6.4	19.5	9.5
Dioxane	22.1	71.2	14.1	12.1	2.6
Dioxane + DMF ^b	34.3	75.0	8.4	15.2	1.3
Dioxane + IBA ^c	97.4	83.7	2.7	10.6	3.0
Cyclohexanol	22.0	27.8	6.0	60.1	6.1
Toluene	6.3	45.0	17.6	32.2	5.2
Toluene + DMF ^b	20.1	62.4	14.6	18.1	4.8

^a Reaction conditions: solvent, 10 g; α -pinene, 3 mmol; TBHP, 0.5 mmol; catalyst, Co-ZSM-5(L₁) 0.1 g; tempt., 90 °C; time, 5 h; flowrate of air, 30 ml/min.

^b 9 mmol of DMF.

^c 9 mmol of isobutylaldehyde(IBA) as the reductant (IBA/alkene = 3 molar ratio).

Table 5
Epoxidation of various alkenes over Co-ZSM-5(L) composite catalysts.^a

Run	Alkene	Catalyst	Alkene Conv. (%)	Selectivity (%)			
				Epoxide	A	B	Others
1	α -Pinene ^b	Co-ZSM-5(L ₁)	95.3 ^b	88.4	2.3	6.7	2.6
2		Co-ZSM-5(L ₂)	92.4	84.8	4.1	9.5	1.6
3		Co-ZSM-5(L ₃)	90.2	86.3	3.0	7.7	3.0
4	Styrene ^c	Co-ZSM-5(L ₁)	93.9 ^c	89.7	5.7	3.6	1.0
5		Co-ZSM-5(L ₂)	92.6	91.1	5.1	3.2	0.6
6		Co-ZSM-5(L ₃)	83.7	91.7	4.8	2.7	0.8
7	α -Methyl styrene ^d	Co-ZSM-5(L ₁)	100 ^d	74.1	16.5	9.4	0
8		Co-ZSM-5(L ₂)	99.7	67.9	22.9	9.2	0
9		Co-ZSM-5(L ₃)	100	66.1	23.9	10.0	0
10	Cyclooctene ^e	Co-ZSM-5(L ₁)	43.0	100	0	0	0
11		Co-ZSM-5(L ₂)	41.9	100	0	0	0
12		Co-ZSM-5(L ₃)	41.8	100	0	0	0

^a Reaction conditions: solvent, DMF(10 g); alkene, 3 mmol; TBHP, 0.5 mmol; catalyst, 0.1 g; tempt., 90 °C; time, 5 h; flowrate of air (30 ml/min).

^b A = verbenol, B = verbenone.

^c A = benzaldehyde, B = phenylacetaldehyde and benzoic acid as others.

^d A = phenylacetaldehyde, B = acetophenone.

^e Tempt., 125 °C.

Table 6

Comparison of different Co-containing catalysts for the epoxidation of alkene.

Catalyst	Subs ^a	Reaction condition			Conv. (%)	Sele. (%)	Ref.
		Tempt. (°C)	Oxidant	P (atm)			
NaCoY93	I	100	O ₂	5.4	45	71	26
Co ₃ O ₄ ^b	I	90	Air, 30 ml min ⁻¹	1	63.8	92.1	42
BaCoX15	II	100	O ₂ , 6–8 ml min ⁻¹	1	100	83	25
Co ²⁺ -X	II	100	O ₂ , 3 ml min ⁻¹	1	45	65	23
Co-MCM-41	II	100	O ₂ , 3 ml min ⁻¹	1	45	62	24
Co-ZSM-5(L ₂) ^b	II	90	Air, 30 ml min ⁻¹	1	91.8	90.1	33
NaCoX96	III	100	O ₂	4	47	100	27
Co-ZSM-5(L ₁) ^b	I	90	Air, 30 ml min ⁻¹	1	95.3	88.4	Present work
Co-ZSM-5(L ₁) ^b	II	90	Air, 30 ml min ⁻¹	1	93.9	89.7	Present work
Co-ZSM-5(L ₁) ^b	III	125	Air, 30 ml min ⁻¹	1	43.0	100	Present work

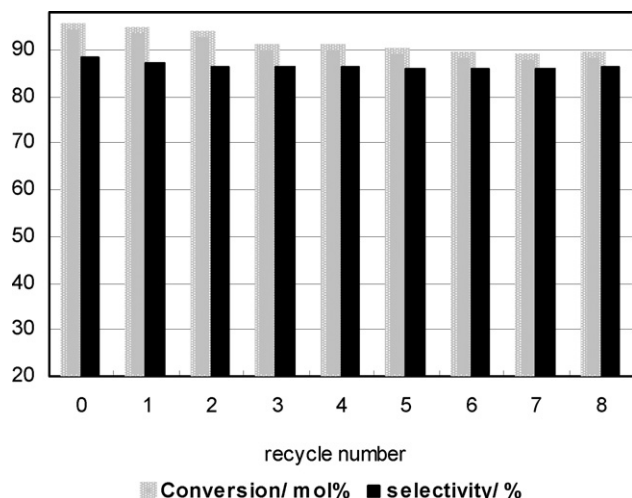
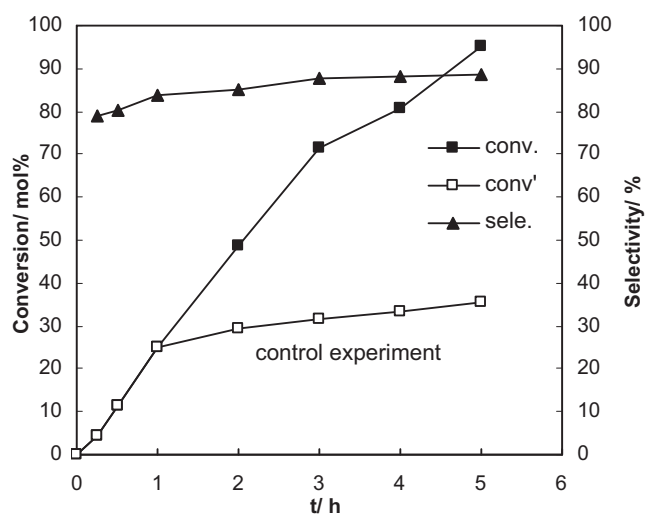
^a I = α -pinene, II = styrene, III = cyclooctene.^b TBHP as the initiator.

the pores of ZSM-5. For the latter five recycles, no further leaching of cobalt was detected.

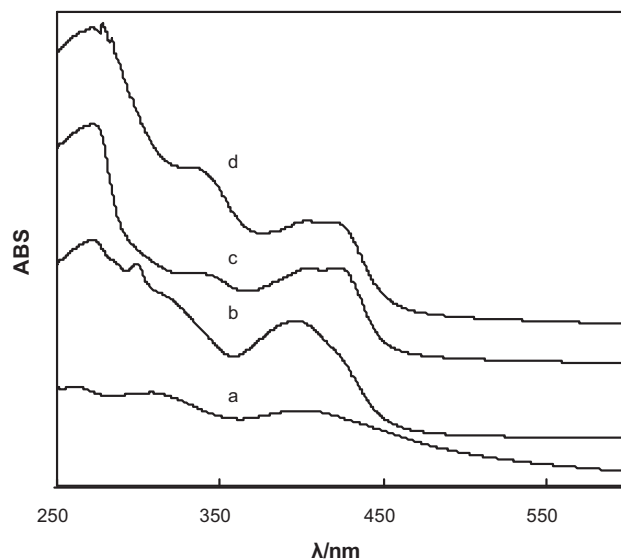
In order to further verify whether the observed catalysis is truly heterogeneous or not, the following control experiment is carried out according to the method described by articles [38]. We investigate the effect of reaction time on the epoxidation of α -pinene over Co-ZSM-5(L₁) at 90 °C, as illustrated in Fig. 3. Clearly, the conversion of α -pinene is stepwise increased from 4.5 mol% in 15 min to 95.3% in 5 h. When the reaction is initially run for 1 h, the obtained conversion is 25.1 mol%. Subsequently, the solid catalyst is filtered off from the reaction mixture, and the reaction is continued with the resulting filtrate for another 4 h. Finally, the conversion is determined to be only 36.5 mol% with a low increment of 11.4 mol% (attributed to the contribution of trace amount of Co²⁺ ions leaching from Co-ZSM-5(L₁) and the autooxidation of α -pinene by air). This result testifies the heterogeneity of the composite catalyst Co-ZSM-5(L₁).

3.5. Possible reaction mechanism

In the present work, the Co-L₁ complex is used to study the catalytic epoxidation mechanism of α -pinene, in which the reaction mixture is monitored by UV–vis spectrum as shown in Fig. 4. The Co-L₁ complex in DMF shows three strong bands centered at 275, 302 and 402 nm, appreciably different from weak signals in C₂H₅OH, indicating the occurrence of the coordination between Co(II) ions and DMF molecules [24,25]. The introduction of air into the Co-L₁ complex in DMF solution results in four clear bands at 277, 334, 402 and 420 nm, which could be attributed to the

**Fig. 2.** Recycling studies of Co-ZSM-5(L₁) catalyst.**Fig. 3.** Control experiment on the epoxidation of α -pinene. α -Pinene, 3 mmol; DMF, 10 g; Co-ZSM-5(L₁), 0.1 g; TBHP, 0.5 mmol; flowrate of air, 30 ml/min; tempt., 90 °C.

interaction of Co-L₁ complex, DMF and molecular oxygen. This probably means that molecular oxygen is activated by Co²⁺ cations to form Co(II)-(O₂⁻) or Co(III)-(O₂⁻), as revealed by the literature [25,39–42]. However, the addition of α -pinene into the above

**Fig. 4.** UV–vis spectra of mixtures: (a) Co-L₁ (in ethanol), (b) Co-L₁ + DMF, (c) Co-L₁ + DMF + air, and (d) Co-L₁ + DMF + air + α -pinene.

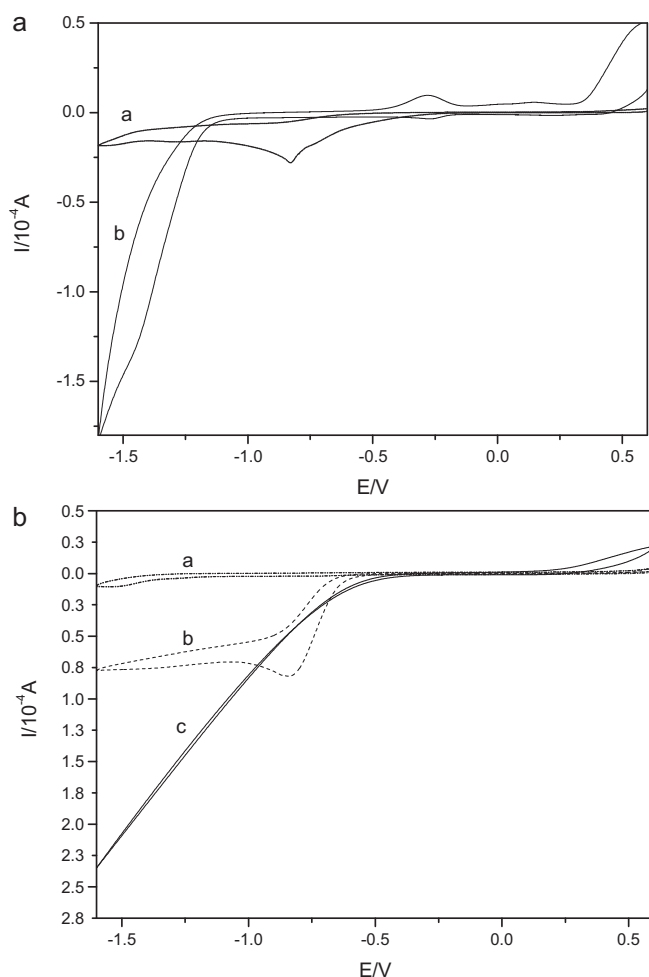
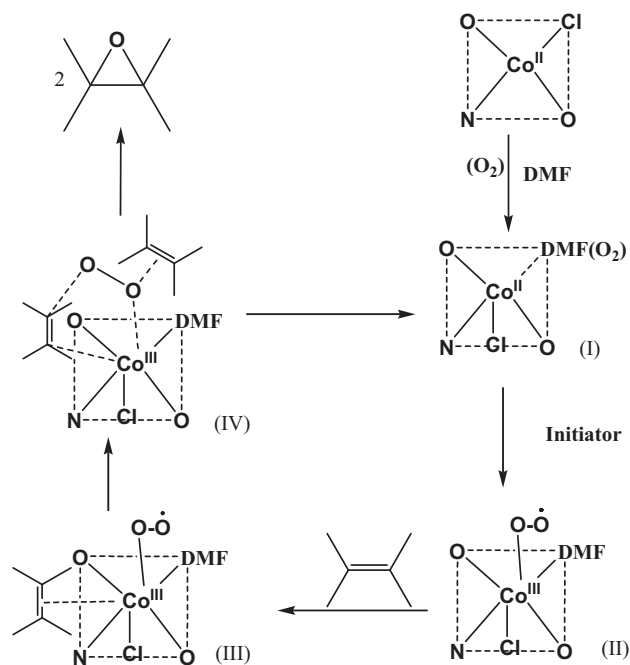


Fig. 5. (A) Cyclic voltammetry of Co-L₁ in (TEAP in DMF) solution (0.1 M): (a) in N₂ atmosphere; (b) in O₂ atmosphere, potential sweep rate of 0.1 V/s. (B) Cyclic voltammetry of mixtures: (a) 0.1 M (TEAP in DMF) solution in N₂ atmosphere; (b) 0.1 M (TEAP in DMF) solution in O₂ atmosphere; (c) 0.1 M (TEAP in ethanol) solution in O₂ atmosphere, potential sweep rate of 0.1 V/s.

solution does not obviously change the wavelengths of observable absorption peaks.

To study the redox behavior of Co species in the Co-complex (Co-L₁), cyclic voltammetry (CV) analysis is conducted in an unstirred solution (0.1 M TEAP in DMF) at a potential sweep rate of 10 mV/s, where the range of potential is from 0.6 to -1.6 V vs. Pt. As shown in Fig. 5(A), one reversible redox peak emerges at -0.27 V, corresponding to the transfer of Co(II)/Co(III) oxidation states. This reversible change between Co oxidation states is important for the catalytic oxidation of hydrocarbons involving molecular oxygen [40]. Once air is introduced into the mixture consisting of Co-L₁ complex and 0.1 M (TEAP in DMF) solution, the redox peak at -0.27 V disappears and one new peak emerges at -0.85 V, which can be attributed to the reduction from coordinative state Co-L₁-DMF-O₂ to Co-L₁-DMF-O-O⁻.

Also, we study the interaction between DMF and molecular oxygen using cyclic voltammetry analysis (Fig. 5(B)). Apparently, there is no any peak when N₂ is introduced into 0.1 M (TEAP in DMF) solution. However, once air is bubbled into 0.1 M (TEAP in DMF) solution, one reduction peak appears at -0.81 V, attributable to the reduction from coordinative state DMF-O₂ to DMF-O-O⁻. It is noteworthy that the replacement of DMF by ethanol results in the disappearance of aforesaid reduction peak. These results are in agreement with the earlier observations on the interaction of DMF



Scheme 2. Possible reaction mechanism for the epoxidation of alkene.

with O₂ by the UV spectrum [33], appreciably revealing the initial point of activation of molecular O₂ under the present experimental conditions.

Although the mechanism for the catalytic epoxidation of alkenes with aerobic oxygen using Co-ZSM-5(L) is not understood very well, the possible synergic coordination of DMF and O₂ molecules to Co(II) sites on Co-ZSM-5(L) or Co-L has been observed by the UV-vis spectra (Fig. 4). Based on above UV-vis spectra and CV analyses as well as the results reported earlier [23–27], one possible reaction mechanism has been postulated in Scheme 2. Firstly, the Co-L₁ complex interacts with DMF and molecular oxygen to form a species (I), where O₂ is adsorbed onto the surface of (I). Then, O₂ is activated synergically by Co²⁺ complex and TBHP to form active peroxy species (II), and Co²⁺ is oxidized to Co³⁺ simultaneously. Finally, alkene molecules consecutively interact and coordinate with (II) to form cyclic intermediate (IV), which subsequently releases epoxide molecules, accompanied with that species (IV) is reduced to species (I), to end one reaction circulation.

4. Conclusions

Three tridentate or bidentate Schiff-base ligands inclusive of salicylaldehyde benzoylhydrazone (L₁), vanillic aldehyde benzoylhydrazone (L₂) and 4-methyl benzaldehyde benzoylhydrazone (L₃) have been synthesized and employed to coordinate with Co²⁺ ions and ion-exchanged Co-ZSM-5. The composite catalysts Co-ZSM-5(L) were readily prepared by simply reacting Co-ZSM-5 and Schiff-base ligands in hot ethanol. The structures of Schiff-base ligands have been characterized by IR spectra, TG, elemental analysis, ¹H-NMR and UV-vis spectroscopy. Co-ZSM-5(L) exhibits a high activity for the epoxidation of several alkenes with air under atmospheric pressure (using TBHP in small amounts as the initiator). Especially, Co-ZSM-5(L₁) shows the highest activity for the selective epoxidation of alkenes: 95.3 mol% the conversion and 88.4% the epoxide selectivity for α -pinene, 93.9 mol% and 89.7% for styrene, 100 mol% and 74.1% for α -methyl styrene and 43.0 mol% and 100% for cyclooctene. These catalysts are highly reusable heterogeneous

ones, e.g. Co-ZSM-5(L₁) does not lose the catalytic activity after eight reuses appreciably.

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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.2010.10.021.

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