

Highly Selective Epoxidation of α -Pinene and Cinnamyl Chloride with Dry Air over Nanosized Metal Oxides

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Abstract Catalytic epoxidation of α -H-containing olefins with air over nanosized metal oxides under mild conditions has been first reported. Nanosized Co_3O_4 was considerably active for the epoxidation of α -pinene and cinnamyl chloride with air at atmospheric pressure. A substrate α -pinene conversion of 70.75 mol% with an epoxide selectivity of 87.68% was achieved at 363 K over Co_3O_4 . Once Co_3O_4 was further modified with metal oxides or ammonium salts through a simple procedure consisting of ultrasonic agitation, drying and calcination, thus-prepared catalysts presented lower catalytic activity and higher epoxide selectivity than cobalt oxide itself. Over Co_3O_4 modified with surfactants, the conversion of α -pinene was somewhat reduced to 48.86–63.76 mol%, but the epoxide selectivity was increased to 92.12–94.83%. However, the composite oxide $\text{CoO}_x\text{-SnO}_x$ (10:1) catalyzed 48.21 mol% of α -pinene conversion with 85.82% of epoxide selectivity. For the substrate cinnamyl chloride, the best result was 40.76 mol% of conversion and 87.17% of epoxide selectivity achieved by $\text{CoO}_x\text{-ZnO}$ (5:1). It is noteworthy that the use of TBHP in small amounts initiated the reaction efficiently, and the lack of TBHP would lead to a low conversion and selectivity.

Keywords Catalytic epoxidation · Nanosized oxides · α -Pinene · Cinnamyl chloride · Butyl acrylate · Co_3O_4 · $\text{CoO}_x\text{-MO}_x$ · Air

1 Introduction

Catalytic epoxidation of olefins has attracted much attention both in industrial processes and in organic syntheses, as the epoxides are the most useful synthetic intermediates [1] or precursors in the production of fine chemicals and pharmaceuticals [2, 3]. Epoxides can find a large range of applications in pharmaceutical industry as drug intermediates, and in the preparation of epoxy resins, polymers and paints. The commercial manufacturing of epoxides involves chlorohydrins-Halcon process, which is a two-stage process and produces co-products stoichiometrically. However, the chlorohydrins-Halcon process has caused seriously environmental pollution. Therefore, many alternative methodologies have been developed for the epoxidation of alkenes using single oxygen donor reagents, such as NaIO_4 , NaOCl , PhIO , ROOOH and H_2O_2 .

Selective oxidation of hydrocarbons using molecular oxygen as the oxidant has been more attractive and challenging because of low cost and environmentally friendly nature [4]. Catalytic epoxidation with molecular oxygen under mild conditions is a challenging process for researchers [5, 6]. Many catalytic systems with the use of dioxygen, aliphatic aldehyde and various transition metal compounds have been reported [7–10]. Most of which describe the use of homogeneous catalysts, and only a few deal with the applications of heterogeneous catalysts [11–14]. The complexes of transition metal Co, Ti, Mn and Mo were used to catalyze the selective epoxidation of cyclic olefins such as cyclohexene and other alkenes with oxygen [15–18]. Silica-based titanium-containing materials (particularly TS-1 and TS-2) have been widely studied in the liquid-phase selective oxidation reactions using aqueous hydrogen peroxide as the oxidant [19, 20]. Wang et al. [21] employed polymer-anchored $\text{PSt-CH}_2\text{AcAc-Co}$ (II)

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with iso-butyraldehyde as co-reductant in the epoxidation of various cyclic alkenes with molecular oxygen. Raja et al. [22] developed MAIPO-36 (M=Co or Mn) catalyst for the epoxidation of cyclohexene and other alkenes in the presence of sacrificial aldehyde. CoO_x -MCM-41 prepared by the precipitation of cobalt tricarbonyl nitrosyl in decaalin was used in the epoxidation of alkenes by O_2 in the presence of iso-butyraldehyde [23]. Pruss et al. [24] reported that cobalt complexes immobilized on modified HMS could catalyze the epoxidation of alkenes with O_2 . Wang and co-workers described that the single site Co(II) catalysts present in faujasite zeolites or in MCM-41 were active in the aerobic epoxidation of styrene giving higher conversions and lower epoxide selectivities [25].

Nanostructured materials have attracted great interest in recent years due to their particular physical and chemical properties [26]. The properties of these materials mainly depend on their shape, size and structure, which are strongly determined by the synthetic processes. Nanostructured catalysts, such as Fe_2O_3 , Co_3O_4 and mixed Fe-Co oxide have been employed in the hydrocarbon oxidations [27, 28]. In the previous works, we reported the selective epoxidation of styrene with air over Co-ZSM-5 coordinated with ligands and nanosized Co_3O_4 [29, 30], in which the latter showed high up to 96% of the epoxidation selectivity. The present work is first to report the epoxidation of α -H-containing alkenes (like α -pinene and cinnamyl chloride) by air over nanosized metal-oxides under atmospheric pressure, and further to investigate the factors influencing the conversion of substrate and the selectivity to epoxide. Under mild conditions, the best selectivity to epoxide could reach 94.83% superior to the catalysts reported in the literature, which is relatively attractive.

2 Experimental

2.1 Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5%), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (99%), ZnCl_2 (99%) were purchased from Tianjin Bodi Chemical Co. CTAB (hexadecyl trimethyl ammonium bromide, >98%), DTAB (dodecyl trimethyl ammonium bromide, >98%), OTAB (octyl trimethyl ammonium bromide, >98%) were purchased from Tianjin Fuchen Chemical Co. The main reagents used in the epoxidations were α -pinene (99.9%, Shanghai), *trans*-cinnamyl chloride (98%, Aldrich) and butyl acrylate (98%, Shanghai), tert-butyl hydrogen peroxide (TBHP, >65%, Shanghai) were directly used as received. The freshly distilled solvents included *N,N'*-dimethylformamide (DMF), *N,N'*-dimethyl acetamide (DMA), toluene, dioxane,

dichloroethane, dibromoethane, acetic acid, acetonitrile, cyclohexanone.

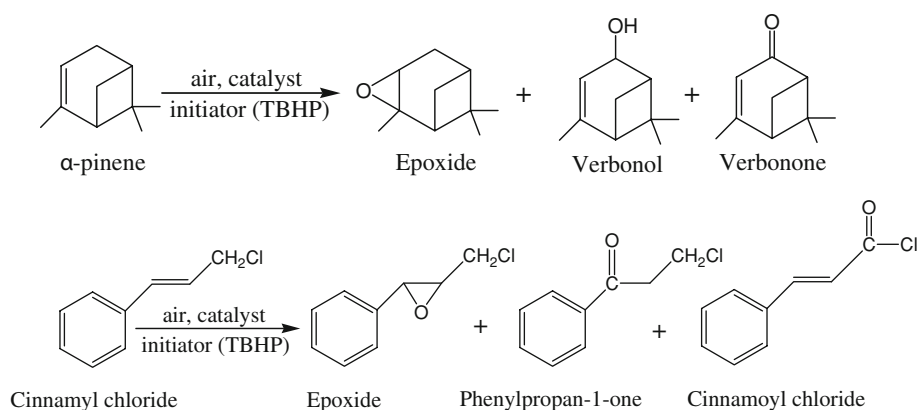
Co_3O_4 nanocrystals were prepared by a precipitation route using cobalt nitrate as the precursor in the presence of surfactant. In a typical synthesis, 124.5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 25.0 mmol of surfactant were dissolved in 750 mL of deionized water (in a 2,000-mL round bottom flask) to give a pink solution. After the pink solution was ultrasonically agitated for 40 min, 249.0 mmol of triethylamine was rapidly added to achieve a blue mixture under vigorous agitation. Then, the blue mixture was stirred at 348 K for 8 h until the color was changed into black. The precipitate was recovered by centrifugation and then dried at 353 K for 24 h, which would undergo a Soxhlet extraction by ethanol for 48 h to remove the stabilizer. The obtained solid was dried at 373 K for 8 h and then calcined at 573 K in flowing air for 2 h. The composite oxide CoO_x - MO_x was prepared by the following procedure. Typically, certain molar ratio of $\text{Co}(\text{NO}_3)_2$ and the other metal salt were mixed and ground for 30 min, which was then placed in a crucible and calcined at desired temperature in an air atmosphere for some time. After that, the black solid was ground into powder and directly used as the catalyst. The molar ratios of CoO_x - SnO_x were 10:1 and 2:1, and those of CoO_x - ZnO were 10:1 and 5:1.

2.2 Characterization of Catalysts

IR spectra were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer; the samples were ground with KBr and pressed into thin wafers. The scanning range was from 4,000 to 400 cm^{-1} , with a resolution of 2 cm^{-1} . UV-vis spectra of samples were recorded on a Shimadzu UV-2550 spectrometer. For the diffuse reflectance mode (solid), the powdered sample was loaded into a holder, and the spectra were collected in the range of 200–800 nm referenced to BaSO_4 . XRD (X-ray diffraction) patterns of solid samples were recorded on a Rigaku D/MAX – IIIIC diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54184$ Å) radiation operating at 30 kV and 25 mA. The scanning range was from $2\theta = 5^\circ$ to 65° with a scanning speed of $2^\circ/\text{min}$. The particle sizes of samples were calculated based on TEM images, which were determined on a Nippon Electronics JEM-100SX transmission electron microscope.

2.3 Catalytic Reactions

The epoxidation of α -H-containing olefins (mainly α -pinene and cinnamyl chloride) with air were carried out in a batch reactor under atmospheric pressure (Scheme 1). In a typical run, 3 mmol of olefins, 10 g of solvent, 0.5 g of 3-Å molecular sieve (MS) and certain quantity of catalyst were added into a 100-mL two-necked flask equipped with

Scheme 1 Reaction routes for the epoxidation of α -pinene and cinnamyl chloride

a cryogenic-liquid condenser and with an air pump. The mixture was vigorously stirred by a magnetic stirrer and heated to the desired temperature. Then dry air with a stable flow rate of 30 mL/min controlled by a flowmeter was introduced into the bottom of reactor by bubbling at atmospheric pressure. After the completion of the reaction, the mixture was cooled down to room temperature and the catalyst was filtered off. The filtrate was quantitatively analyzed by a gas chromatograph (Shimadzu GC-2010) with a DB-1 column (30 m \times 0.25 mm \times 0.25 μ m) and an FID detector using chlorobenzene as the internal standard and hydrogen as carrier gas. The conversion of olefins (mol%) and the selectivity (%) to epoxide were calculated accordingly.

3 Results and Discussion

3.1 Structural Characteristics of Catalyst Samples

Nanosized metal oxide Co_3O_4 were prepared from nitrates in the presence of surfactants (inclusive of CTAB, DTAB and OTAB) and amines (including triethylamine, tributylamine, triethanolamine and di-*n*-propylamine). Figure 1 shows the FT-IR spectra of Co_3O_4 (calcined at 773 K for 2 h), which underwent modification by triethylamine (traces a, b and c) before extraction of the stabilizer by ethanol. There was no peak observable at 2,915 and 2,848 cm^{-1} of the C–H stretching modes resulting from CTAB and triethylamine, suggesting that surfactant and triethylamine had been totally removed from samples. Two bands appearing at 668 and 579 cm^{-1} could be assigned to the vibrations of Co–O due to Co_3O_4 nanoparticles [31], as evidenced by the color change from blue to black of the mixture after the addition of triethylamine. Distinctly, the presence of CTAB, DTAB, OTAB and triethylamine, tributylamine, triethanolamine, or di-*n*-propylamine stabilized nanoparticles by capping the surface of nanoparticles with organic ligands. The formation of nanoparticles was proposed through a model of inorganic–

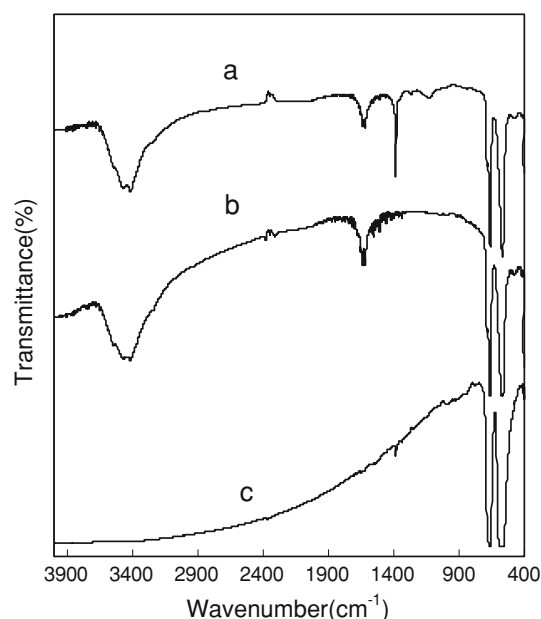


Fig. 1 FT-IR spectra of Co_3O_4 after calcination at 773 K for 2 h. *a* Modified by OTAB; *b* modified by DTAB; *c* modified by CTAB

organic layered particles. This is that the polar surface of metal oxide particles benefited the adsorption of the organic cations generated in situ to form the organic shells on the surface of nanoparticles and to prevent nanoparticles from aggregation through enhancing steric hindrance to overcome van der Waals interactions between the nanoparticles, as proposed by the literature [32, 33]. Figure 2 compares the UV–vis spectra of Co_3O_4 samples, which show evidently different ultraviolet absorbance characteristics. UV–vis spectra of Co_3O_4 samples show absorbance bands at 392, 677 nm for trace-a (modified by OTAB), at 376, 671 nm for trace-b (modified by DTAB), and at 357, 639 nm for trace-c (modified by CTAB), similar to the absorbance bands at 384, 687 nm of trace-d (calcined directly from cobalt nitrate), totally different from those at 259, 263, 282, 305, 313 nm of the corresponding metal salt $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [34].

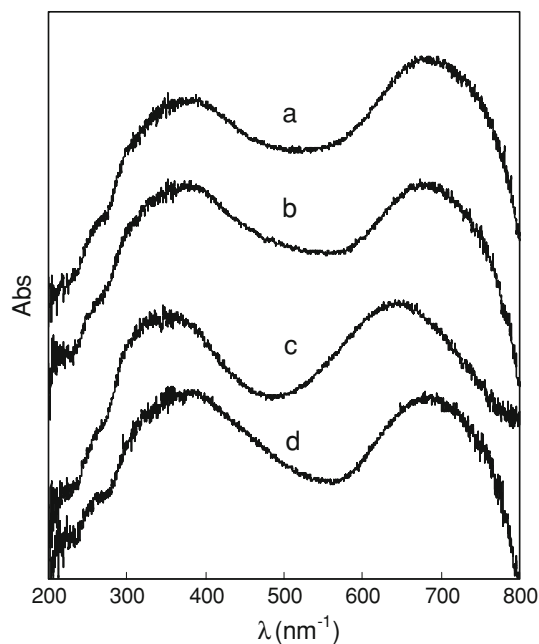


Fig. 2 UV-vis spectra of Co_3O_4 nanocatalysts. *a* Modified by OTAB; *b* modified by DTAB; *c* modified by CTAB; *d* calcined directly from cobalt nitrate

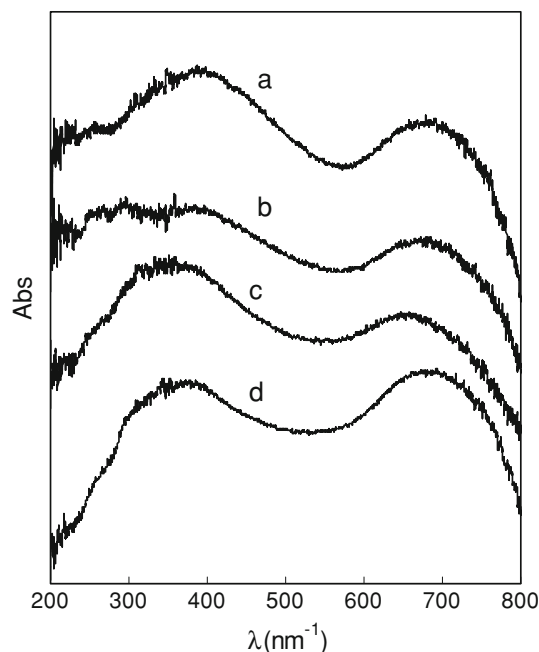


Fig. 3 UV-vis spectra of various composite $\text{Co}_3\text{O}_4\text{-MO}_x$ oxides. *a*—10:1 $\text{CoO}_x\text{-SnO}_x$; *b*—2:1 $\text{CoO}_x\text{-SnO}_x$; *c*—5:1 $\text{CoO}_x\text{-SnO}_x$; *d*— Co_3O_4 , modified by DTAB

The preparation of composite oxide catalysts $\text{CoO}_x\text{-MO}_x$ was quite straightforward, requiring only a simple calcination procedure instead of very complicated synthesis and modification. FT-IR spectra of 10:1 $\text{CoO}_x\text{-SnO}_x$ and 2:1 $\text{CoO}_x\text{-SnO}_x$ samples showed characteristic twin bands at 668 and 579 cm^{-1} , assigned to the vibrations of Co–O bands. The weak band emerging at about 600 cm^{-1} in the IR spectra of traces *a* and *b* can be assigned to the vibration of Sn–O bands. The IR absorption bands near 668 and 579 cm^{-1} observed from traces *c* and *d* are also ascribable to Co–O bands. The weak band emerging at about 400 cm^{-1} is assigned to the Zn–O vibration. UV-vis spectra of composite oxides $\text{CoO}_x\text{-MO}_x$ (containing SnO_x and ZnO, shown in Fig. 3) possess considerably different ultraviolet absorbance characteristics from pure Co_3O_4 , which may indicate the interaction between cobalt oxide and other metal oxide by calcination. For example, there are recognizable four bands at 264, 269, 346, 655 nm for 10:1 $\text{CoO}_x\text{-SnO}_x$, four bands at 272, 293, 375, 675 nm for 2:1 $\text{CoO}_x\text{-SnO}_x$, three bands at 286, 363, 681 nm for 5:1 $\text{CoO}_x\text{-ZnO}$; while four bands of Co_3O_4 emerge at 263, 313, 354, 698 nm.

Figure 4 summarizes XRD patterns of the calcined catalysts Co_3O_4 and $\text{CoO}_x\text{-MO}_x$ prepared by our methods. Observable eight peaks at $2\theta = 19.16, 31.46, 37.08, 39.02, 45.48, 56.06, 59.74,$ and 65.76 for three samples can be assigned to the cubic structure of Co_3O_4 phase with an $Fd\bar{3}m$ space group as compared to a data file of JCPDS-43-1003, which gives eight peaks at $2\theta = 36.88, 65.28, 59.38,$

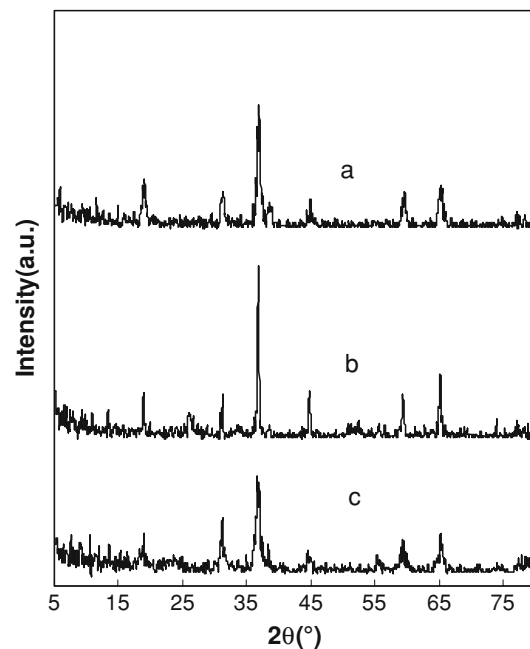


Fig. 4 XRD patterns of the calcined catalysts Co_3O_4 (*a*—modified by DTAB) and $\text{CoO}_x\text{-MO}_x$ (*b*—10:1 $\text{CoO}_x\text{-SnO}_x$; *c*—10:1 $\text{CoO}_x\text{-ZnO}$)

$31.38, 44.88, 19.08, 38.58,$ and 55.78 . The cell constant $a = 0.8082$ is very near to the published data for Co_3O_4 crystal ($a = 0.8084$). It can be clearly observed from Fig. 4

that $\text{CoO}_x\text{-MO}_x$ merely displays several weak X-ray diffractions, such as $2\theta = 19.16, 31.46, 37.08, 39.02, 45.48, 56.06, 59.74,$ and 65.76 , indicating that cobalt species in these composite oxides exist mostly in the form of Co_3O_4 .

The particle sizes of Co_3O_4 (a—) and $\text{CoO}_x\text{-MO}_x$ (b—10:1 $\text{CoO}_x\text{-SnO}_x$ and c—10:1 $\text{CoO}_x\text{-ZnO}$) calculated from the (311) plane using the Sherrer equations [35] were 33, 24, and 19 nm, respectively. TEM analysis has revealed evidences that the particles exhibit platelet morphologies with minor particle agglomeration and a relatively narrow particle size distribution. One can observe one-dimensional arrays of Co_3O_4 nanoparticles (calcined at 623 K at a heating rate of $1^\circ\text{C}/\text{min}$) interconnected along the original directions of the nitrate nanorods. The average particle size is about 40 nm (in the range of 12.5–50 nm diameter with nanostructures of uniform morphology), consistent with the XRD result and the calculation from the Sherrer equation. Once the calcination temperature was reduced to 573 K, some non-oxide impurities were still present. TEM determinations showed nanosized particles of some samples in Fig. 5, e.g. *ca.* 20 nm for Co_3O_4 (modified by DTAB and calcined at 573 K for 8 h), 15 nm for Co_3O_4 (modified by OTAB and calcined at 573 K for 2 h), 10–150 nm for 10:1 $\text{CoO}_x\text{-SnO}_x$ (calcined at 823 K for 4 h) and *ca.* 15 nm for 10:1 $\text{CoO}_x\text{-ZnO}$ (calcined at 573 K for 2 h), respectively.

3.2 Catalytic Epoxidation of α -Pinene and Cinnamyl Chloride with Air

3.2.1 Catalytic Activity of Nanosized Co_3O_4 Catalysts

Table 1 compares the catalytic activities of nanosized Co_3O_4 catalysts modified with different surfactants in the epoxidation of α -pinene with air. Obviously, nanosized Co_3O_4 modified by OTAB obtained the highest conversion of α -pinene (63.76 mol%) and higher selectivity of epoxide (92.12%). However, when no TBHP was added, the conversion and the selectivity of epoxide would be reduced to 20.86 mol% and 69.17%. TBHP played a key role in enhancing the epoxidation activity and selectivity (Table 1); however, when no air was introduced into the reaction (adding 0.7 mmol TBHP), the conversion was largely reduced to 12.07 mol% with an epoxide selectivity of 90.76%. It is noteworthy that the use of TBHP in small amounts initiated the reaction efficiently, and the lack of TBHP or air would lead to a low conversion and selectivity. The catalytic activity (based on the conversion) of all the nanosized Co_3O_4 samples gradually decreased in the following sequence of 63.76 mol% (modified by OTAB) > 61.71 mol% (modified by CTAB) > 48.86 mol% (modified by DTAB). Very interestingly, Co_3O_4 modified by DTAB showed the best epoxide selectivity of 94.83%, although it converted only 48.86 mol% of α -pinene under identical conditions. Based on the results in Fig. 5 and

Fig. 5 TEM images of the calcined catalysts Co_3O_4 and $\text{CoO}_x\text{-MO}_x$ (a—modified by DTAB; b—modified by OTAB) and $\text{CoO}_x\text{-MO}_x$ (c—10:1 $\text{CoO}_x\text{-SnO}_x$; d—10:1 $\text{CoO}_x\text{-ZnO}$)

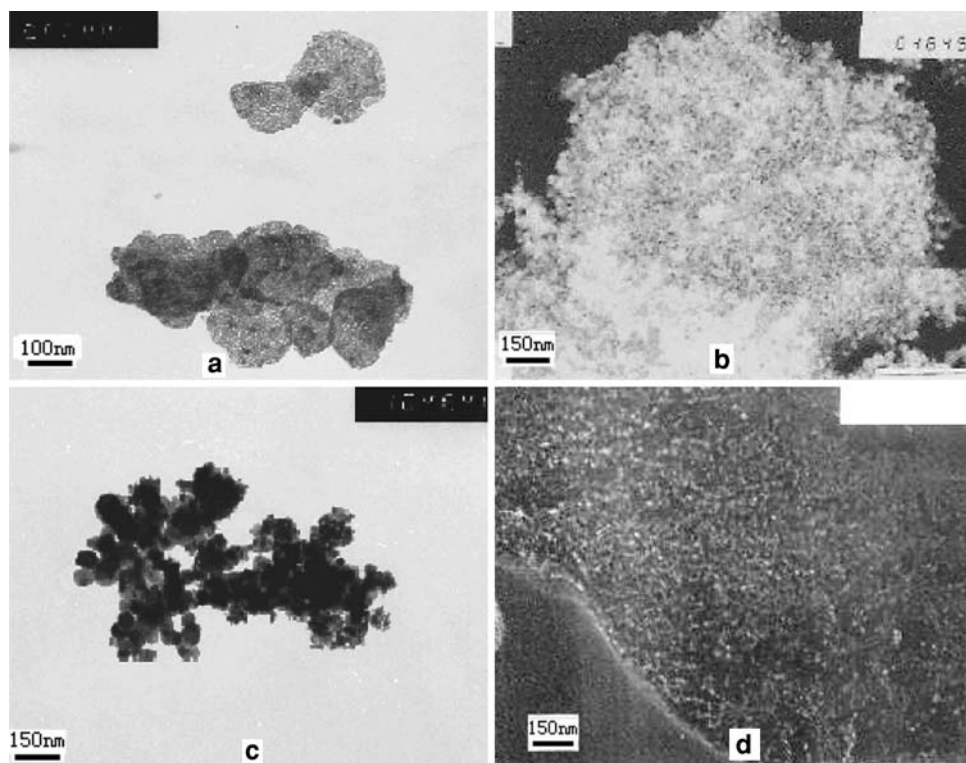


Table 1 Epoxidation of α -pinene with air on Co_3O_4 modified by different surfactants

Entry	Surfactant	α -Pinene conversion (mol%)	Selectivity (%)		
			Epoxide	Verbenol	Verbenone
1	CTAB	61.71	83.01	6.94	10.05
2	DTAB	48.86	94.83	2.84	2.33
3 ^a	OTAB	20.86	69.17	18.53	12.30
4 ^b	OTAB	12.07	90.76	3.82	5.42
5	OTAB	63.76	92.12	3.55	4.33

Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg; TBHP: 0.1 g; 3 Å MS: 0.5 g; temperature: 363 K; time: 5 h; flow rate of air: 30 mL/min

^a Not any TBHP

^b Not any air (only TBHP)

Table 1, it is obvious that the reactivity and epoxidation selectivity of α -pinene catalyzed by the nanosized Co_3O_4 catalysts (modified with different surfactants) could be determined by the particle size and the type of surfactants used in the preparation.

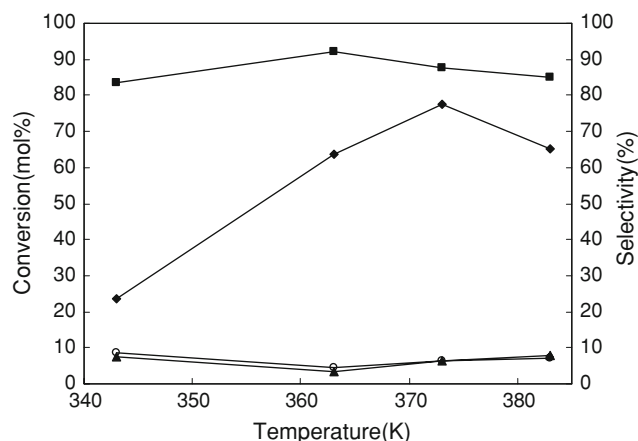
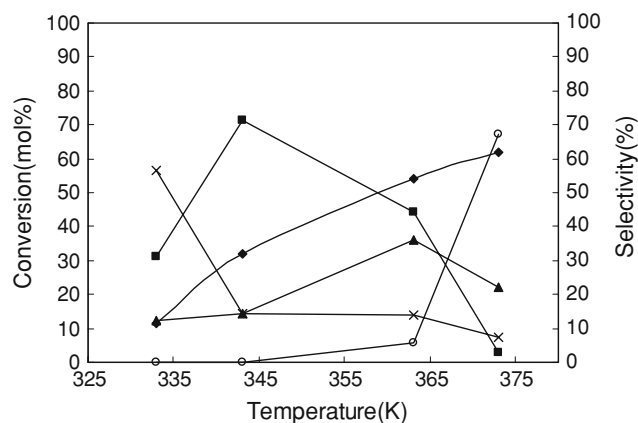
Table 2 shows the epoxidation of cinnamyl chloride with air on Co_3O_4 (modified by DTAB), where the calcination temperature exerted an obvious impact on the catalytic performance of Co_3O_4 . Apparently, the catalytic activity (based on the conversion) of Co_3O_4 samples seriously depended on the calcination temperature regardless of time, which showed a reduction of 52.11 mol% (573 K, 2 h) \approx 50.92 mol% (573 K, 8 h) > 39.02 mol% (673 K, 2 h) > 38.01 mol% (823 K, 2 h). However, the epoxidation selectivity of Co_3O_4 samples displayed a reversal sequence of 87.16% (823 K, 2 h) > 63.05% (673 K, 2 h) > 62.62% (573 K, 2 h) > 60.03% (573 K, 8 h). Lower calcination temperature was beneficial to the activity of the catalyst but not to the epoxidation selectivity.

The impact of reaction temperature on the epoxidation of α -pinene and of cinnamyl chloride over Co_3O_4 (modified by OTAB) is shown in Figs. 6 and 7. Distinctly, the conversions of α -pinene and cinnamyl chloride exhibited an increase with the reaction temperature from 333 to 373 K.

Table 2 Epoxidation of cinnamyl chloride with air on Co_3O_4 (modified by DTAB)

Entry	Calcination program	Cinnamyl chloride conversion (mol%)	Selectivity (%)		
			Epoxide	1-One	Acyl chloride
1	573 K, 2 h	52.11	62.62	31.81	5.56
2	573 K, 8 h	50.91	60.03	19.03	20.94
3	673 K, 2 h	39.02	63.05	36.31	0.64
4	823 K, 2 h	38.01	87.16	10.53	2.32

Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg; TBHP: 0.1 g; 3 Å MS: 0.5 g; time: 5 h; temperature: 363 K; flow rate of air: 30 mL/min

**Fig. 6** Effect of reaction temperature on the epoxidation of α -pinene with air over Co_3O_4 (modified by OTAB and calcined at 673 K for 2 h): (◆) α -pinene conversion, (■) epoxide selectivity, (●) Verbenol selectivity, (▲) Verbenone selectivity. Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg; TBHP: 0.1 g; 3-Å MS: 0.5 g; time: 5 h; flow rate of air: 30 mL/min**Fig. 7** Effect of reaction temperature on the epoxidation of cinnamyl chloride with air over Co_3O_4 (modified by OTAB and calcined at 823 K for 4 h): (◆) cinnamyl chloride conversion, (■) epoxide selectivity, (▲) 1-one selectivity, (×) acyl chloride selectivity. Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg; TBHP: 0.1 g; 3-Å MS: 0.5 g; time: 5 h; flow rate of air: 30 mL/min

When the reaction temperature was lower than 363 K, both α -pinene and cinnamyl chloride achieved low conversions. The conversion of α -pinene was 23.78 mol% at 343 K, rapidly rose to 63.76 mol% at 363 K, then to 77.62 mol% at 373 K, but reduced to 65.18 mol% with a continuous increase to 383 K. The epoxide selectivity of α -pinene first increased from 83.57% at 343 K to the maximum of 92.12% at 363 K, and then slightly reduced to 87.53% at 373 K. The epoxidation of cinnamyl chloride displayed the similar regularity with temperature. For example, below 343 K 32.15 mol% of the cinnamyl chloride was converted with an epoxide selectivity of 71.17%. With the increase in the reaction temperature, the conversion of cinnamyl

chloride increased quickly to 54.06 mol% at 363 K and then slowly to 61.72 mol% at 373 K; however, the epoxide selectivity first increased from 31.02% at 333 K to the maximum of 71.17% at 343 K, and then decreased quickly to about 44.39% at 363 K and to 2.97% at 373 K. This shows that the high temperature did not favor the formation of epoxides under the present experimental conditions.

It is well known that the choice of suitable solvent can play a critical role on the activity and selectivity in the liquid-phase oxidations of hydrocarbons. Various solvents have been tested for the epoxidation of α -pinene by air over Co_3O_4 at 353 K. The solvents chosen included DMF, DMA, toluene, dioxane, dichloroethane, dibromoethane, acetic acid, acetonitrile and cyclohexanone, with an increase order of dielectric constants: dioxane (2.21) < toluene(2.37) < acetic acid(6.15) < dibromoethane(9.72) < dichloroethane (10.4) < cyclohexanone (18.3) < acetonitrile (37.5) < DMF (37.6) < DMA (37.78).

It can be observed from Table 3 that Co_3O_4 catalyst could catalyze the occurrence of α -pinene oxidation with air in all solvents, regardless of the solvent polarity. Under identical conditions, nanosized Co_3O_4 showed the best activity with an epoxide selectivity of 83.50% in DMF, while the use of DMA (an analogue of DMF) resulted in a higher conversion of 49.41 mol% but a lower epoxide selectivity of 69.47%. Although high conversion (*ca.* 64.63 mol%) of α -pinene could be obtained over Co_3O_4 when cyclohexanone was used as the solvent, the selectivity of epoxide was low only 61.19%. Interestingly, using dibromoethane and acetic acid as the solvents did not yield any epoxide but the main product verbenone with the

selectivity of 89.44% and 86.31%, respectively. The investigation on this phenomenon is ongoing.

As the reaction temperature was risen from 353 to 363 K, 70.76 mol% of α -pinene conversion and 87.68% of epoxide selectivity could be achieved in the DMF solution, notably higher than 55.86 mol% of conversion and 74.99% of epoxide selectivity in DMA. The excellent activity and selectivity of catalyst Co_3O_4 could be due to the strong interaction of the DMF molecule with the active site, which further enhanced the desorption of products from the active sites, i.e. the affinity of DMF to O_2 and the cobalt oxide might promote the separation of α -pinene epoxide from the catalytic sites to avoid the occurrence of deep oxidation, as has been revealed by previous studies [29, 36].

3.3 Catalytic activity of Composite Oxides $\text{CoO}_x\text{-MO}_x$

When no TBHP was added, only 9.72 mol % of α -pinene could be converted into the epoxide (77.79% of selectivity) at 363 K by 10:1 $\text{CoO}_x\text{-ZnO}$ catalyst. Once TBHP was used as the initiator, the conversion of α -pinene was notably increased to 35.73 mol% with an epoxide selectivity of 85.03%. Table 4 presents the effect of different $\text{CoO}_x\text{-MO}_x$ catalysts on the epoxidation of α -pinene, in which the reactions were conducted at 363 K using DMF as the solvent and TBHP as the initiator. Very clearly, 10:1 $\text{CoO}_x\text{-SnO}_x$ nanocatalyst displayed the best the catalytic activity for the epoxidation reaction of α -pinene. Under our experimental conditions, 10:1 $\text{CoO}_x\text{-SnO}_x$ catalyst achieved the conversion of α -pinene (48.21 mol%) and the selectivity of epoxide (85.82%), while 10:1 $\text{CoO}_x\text{-ZnO}$ catalyst achieved 32.93 mol% of the conversion and 83.37% of the epoxide selectivity, showing the difference of catalytic activity of various composite metal-oxide catalysts. The catalytic activity of $\text{CoO}_x\text{-MO}_x$ catalysts gradually decreased in the sequence of 10:1 $\text{CoO}_x\text{-SnO}_x > 2:1 \text{CoO}_x\text{-SnO}_x > 5:1 \text{CoO}_x\text{-ZnO} > 10:1 \text{CoO}_x\text{-ZnO}$, implying that the addition of

Table 3 The epoxidation of α -pinene with air on Co_3O_4 in different solvents

Entry	Solvent	α -Pinene conversion (mol%)	Selectivity (%)		
			Epoxide	Verbenol	Verbenone
1	DMF	37.18	83.51	8.31	8.18
2	DMF(363 K)	70.75	87.68	3.56	8.77
3	DMA	49.41	69.47	8.26	22.27
4	DMA(363 K)	55.86	74.99	7.15	17.85
5	Toluene	15.53	48.75	17.93	33.31
6	Dioxane	29.51	65.19	10.19	24.63
7	Acetonitrile	22.45	39.08	13.79	47.13
8	Cyclohexanone	64.63	61.19	9.51	29.30
9	Dichloroethane	19.85	49.83	16.89	33.28
10	Dibromoethane	54.25	0.00	10.56	89.44
11	Acetic acid	51.08	0.00	13.69	86.31

Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg; TBHP: 0.1 g; 3 Å MS: 0.5 g; temperature: 353 K (entry 2 and 4 are 363 K); time: 5 h; flow rate of air: 30 mL/min

Table 4 Epoxidation of α -pinene with air on $\text{CoO}_x\text{-MO}_x$

Entry	Catalyst	α -Pinene conversion (mol%)	Selectivity (%)		
			Epoxide	Verbenol	Verbenone
1	10:1 $\text{CoO}_x\text{-SnO}_x$	48.21	85.82	5.6	8.58
2	2:1 $\text{CoO}_x\text{-SnO}_x$	46.01	80.07	8.08	11.85
3	10:1 $\text{CoO}_x\text{-ZnO}$	32.93	83.37	7.92	8.72
4	5:1 $\text{CoO}_x\text{-ZnO}$	35.73	85.03	6.6	8.38
5	5:1 $\text{CoO}_x\text{-ZnO}^*$	9.72	77.79	16.43	5.78

Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg (entry 1 and 2 calcined at 823 K for 4 h; entry 3 and 4 calcined at 673 K for 4 h); entry 5: not any TBHP; 3 Å MS: 0.5 g; temperature: 363 K; time: 5 h; flow rate of air: 30 mL/min

Table 5 Epoxidation of cinnamyl chloride with air on various catalysts

Entry	Calcination program	Cinnamyl chloride conversion (mol%)	Selectivity (%)		
			Epoxide	1-One	Acyl chloride
1	Co ₃ O ₄	50.26	60.28	20.16	13.73
2	10:1 CoO _x -ZnO	46.53	81.37	17.68	0.95
3	5:1 CoO _x -ZnO	40.76	87.17	11.45	1.37
4	10:1 CoO _x -SnO _x	22.25	58.62	29.26	12.12
5	ZnO	17.12	37.93	46.78	15.29

Substrate: 3 mmol; solvent: 10 g; catalyst: 30 mg (metal oxides 1 and 2 calcined at 573 K for 2 h, metal oxides 3 and 4 calcined at 673 K for 4 h); TBHP: 0.1 g; 3 Å MS: 0.5 g; time: 5 h; temperature: 363 K; flow rate of air: 30 mL/min

basic ZnO was unbeneficial to the epoxidation of α -pinene with air. Additionally, based on the Fig. 5, the reactivity and epoxidation selectivity of α -pinene could be associated with the particle size and composition of the catalyst, which led to different catalytic performances. The size of CoO_x-MO_x catalysts decreased in the sequence of 10:1 CoO_x-SnO_x > 2:1 CoO_x-SnO_x > 5:1 CoO_x-ZnO > 10:1 CoO_x-ZnO, in good agreement with the change of their activities.

Table 5 presents the effect of different CoO_x-MO_x catalysts on the epoxidation of cinnamyl chloride with air. As the comparison, the Co₃O₄ catalyst was prepared through a direct calcination of Co(NO₃)₂ · 6H₂O at 573 K for 2 h. About 50.26 mol% conversion of cinnamyl chloride was obtained over 30 mg of Co₃O₄, but the selectivity of epoxide was only 60.28%. As shown in Table 5, the catalytic activity of CoO_x-MO_x catalysts gradually decreased in the order of Co₃O₄ (50.26 mol% of conversion) > 10:1 CoO_x-ZnO (46.53 mol%) > 5:1 CoO_x-ZnO (40.76 mol%) > 10:1 CoO_x-SnO_x (22.25 mol%) > ZnO (17.12 mol%). However, the selectivity of epoxide exhibited an entirely different descending order of 5:1 CoO_x-ZnO (87.17%) > 10:1 CoO_x-ZnO (81.37%) > Co₃O₄ (60.28%) > 10:1 CoO_x-SnO_x (58.62%) > ZnO (37.93%). The 5:1 CoO_x-ZnO and 10:1 CoO_x-ZnO nanocatalysts were favorable to the epoxidation of cinnamyl chloride, likely because the insertion of ZnO into the domain of Co₃O₄ diluted and modified the catalytic active sites to reduce the possibility of the deep oxidations. Different from the case of α -pinene, the reactivity and epoxidation selectivity of cinnamyl chloride could not be correlated with the variation of nanoparticle sizes. The deep investigations are ongoing.

Note that for the epoxidation of butyl acrylate the result was totally different from above those. Whatever the catalyst was, the conversion of butyl acrylate was always not more than 10 mol% in the range of the reaction temperature from 343 to 383 K, but only an epoxide (butyl acrylate oxide with 100% of selectivity) was yielded.

4 Conclusions

The present work has first described a novel finding in the epoxidation of α -H containing olefins with air catalyzed by nanosized metal oxides under mild conditions. Several transition metal-containing nanosized samples, such as Co₃O₄, CoO_x-SnO_x and CoO_x-ZnO, were prepared by different routes, followed by drying and calcination. Structural characterizations by IR, UV, XRD and TEM have revealed the successful preparation of nanosized Co₃O₄ and composite CoO_x-MO_x oxides. Cobalt oxide (Co₃O₄) prepared from cobalt nitrate was considerably active for the epoxidation of α -pinene and cinnamyl chloride with air, in which 70.75 mol% of α -pinene conversion with an epoxide selectivity of 87.68% was achieved at 363 K over 30 mg of Co₃O₄, superior to the catalysts reported in the literature. Over the catalyst Co₃O₄ modified with OTAB, a high epoxide selectivity up to 92.12% was achieved with a conversion of 63.76 mol% α -pinene at 363 K within 5 h. The catalytic activity of CoO_x-MO_x catalysts on the epoxidation of α -pinene with air gradually decreased in the sequence of 10:1 CoO_x-SnO_x > 2:1 CoO_x-SnO_x > 5:1 CoO_x-ZnO > 10:1 CoO_x-ZnO. However, for the epoxidation of cinnamyl chloride with air the catalytic activity of CoO_x-MO_x exhibited a descending order of Co₃O₄ (50.26 mol% of conversion) > 10:1 CoO_x-ZnO (46.53 mol%) > 5:1 CoO_x-ZnO (40.76 mol%) > 10:1 CoO_x-SnO_x (22.25 mol%) > ZnO (17.12 mol%), entirely different from the change of epoxide selectivity of 5:1 CoO_x-ZnO (87.17%) > 10:1 CoO_x-ZnO (81.37%) > Co₃O₄ (60.28%) > 10:1 CoO_x-SnO_x (58.62%) > ZnO (37.93%).

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