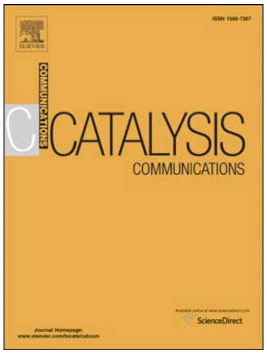

Co^{2+}-exchanged MOR and 5A zeolites as efficient solid catalysts for the epoxidation of styrene with air

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Co^{2+}-exchanged MOR and 5A zeolites as efficient solid catalysts for the epoxidation of styrene with air

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Abstract

Selective oxidation of alkenes with air to corresponding epoxides was performed over simply ion-exchanged Co-MOR and Co-5A. Among all transition metal ions-exchanged M-zeolites, both Co-MOR and Co-5A exhibited the highest activity at 363 K. Appreciably, for the epoxidation of styrene, α-pinene, α-methyl styrene and cyclooctene, Co-MOR obtained higher conversions than Co-5A, in agreement with the difference of pore sizes of both zeolitic materials. Recycling and control tests showed high durability of Co-MOR as heterogeneous catalyst in our catalytic system.

Keywords: Cobalt ion-exchange; Mordenite; 5A, Epoxidation of styrene; Air

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1. Introduction

The catalytic epoxidation of alkenes to produce epoxides is an important industrial reaction in the manufacturing of fine chemicals and pharmaceuticals, since epoxides are key building blocks in organic synthesis [1,2]. Over the past decade, with respect to environmental and economic consideration, the epoxidation of alkenes by H_2O_2 [3,4] or molecular oxygen [5,6] has attracted much attention; however, the epoxidation of alkenes with O_2 was generally carried out in the presence of co-reductants like H_2, alcohols and aldehydes [1,7,8].

Recently, molecular sieve materials as heterogeneous catalysts have been a subject of growing interests in the epoxidation of alkenes. Tang et al. firstly reported that Co^{2+}-exchanged faujasite-type zeolites could catalyze the epoxidation of styrene with O_2 in the absence of co-reductant [9]. Later on, the selective oxidation of alkenes with oxygen/air have achieved encouraging results over other Co-doped porous catalysts, like Co-X [10], Co-Y [11], Co-SBA-15 [12], which, however, could merely obtain a low epoxide selectivity of <70%. Very recently, our group has reported the efficiencies of simply ion-exchanged Co-ZSM-5, Co-Beta, Co-SAPO-34, Co-SAPO-5 with a low Co content (*ca*. 1.2 wt.%) for dissociating triplet ground state of O_2 to epoxidize singlet olefins in the absence of co-reductant with a high selectivity of > 90% [13,14].

It is noteworthy that the above-stated ZSM-5, Beta, SAPO-34 and SAPO-5 were hydrothermally synthesized with organic quaternary ammonium ions or amines as structure-directing agents, which would definitely increase the environmental pollution and the synthesis cost. However, their Co^{2+}-exchanged counterparts could effectively catalyze aerobic epoxidation of alkenes like styrene and α-pinene. This arouses our interest to study the activity of Co^{2+}-exchanged mordenite (MOR) and 5A zeolites, which are cheap and can be simply synthesized without any organic templates. Herein, our new progress firstly shows high activities of Co^{2+}-exchanged MOR and 5A for the selective epoxidation of styrene with dry air, comparable to other Co-zeolites.

2. Experimental

2.1 Preparation of catalysts

Co^{2+} and other transition metal ions were introduced into zeolite by a simple ion-exchange method as described elsewhere [13]. In a typical run, 5.0 g of zeolite was treated with an aqueous solution (250 ml) of metal salts (2.6 mmol) at 363 K overnight. The solid powder was recovered by filtration, washed several times with hot distilled water until no acidic residue was detected, followed by drying at 373 K for 8 h, in which no calcination was required. Fe-MOR, Cr-MOR, Cu-MOR, Ni-MOR, Mn-MOR and Zn-MOR were prepared through the same procedure stated above.

2.2 Charaterization of catalysts

X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/MAX-IIIC diffractometer with Cu *Kα* radiation (λ = 1.54184 Å) operating at 30 kV and 25 mA. Cobalt content in each sample was analyzed on a Shimadzu XRF-1800 spectrometer. The morphology and size of crystals were imaged on a JEOL

JSM-6510A scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) data was acquired on a Thermol ESCALAB-250 system using Al *Kα* monochromatic radiation (1486.6 ev). The BET specific surface area was calculated using the BET equation in the range of relative pressures (p/p_0) between 0.05 and 0.25.

2.3 Catalytic reactions

The epoxidation of alkenes with air was performed in a 50-mL two-necked round-bottom glass flask equipped with a cryogenic-liquid condenser under atmospheric pressure. For reaction and analysis details, please refer to the supporting information.

3. Results and discussion

3.1 Characterization of catalysts

The XRD patterns of ion-exchanged MOR and 5A have been shown in Figure 1. Clearly, the diffraction patterns of Co^{2+}-exchanged MOR and 5A show the characteristics of highly crystalline materials, with typical reflections of MOR and LTA structures. However, the intensity of diffractions of Co-5A within 5–45° shows a slight reduction, as compared to that of the parent 5A, which is probably due to partial removal of Al from the framework of 5A zeolite. The majority of Co species in the Co^{2+}-exchanged samples exists in the form of Co^{2+} cations, as characterized by the appearance of only one peak with the binding energy of *ca*. 782 eV in the X-ray photoelectron spectra, characteristic of Co^{2+}-zeolites [15]. BET surface areas and pore sizes of various zeolites determined by BET analysis are given in Table 1. It can be seen that the ion-exchange treatment has led to a slight decrease in the surface area of catalysts, which is easily understandable because such an ion-exchange can remove partial Al species from the framework of zeolites, and some smaller Na^+ ions have been substituted by larger Co^{2+} ions [13,14,16]. The XRF results have shown that the SiO_2/Al_2O_3 ratios in Co-MOR and Co-5A are increased to 25.2 and 3.0 from 20.6 and 2.0 of Na-MOR and 5A, probably due to partial removal of Al atoms from the frameworks of zeolites by ion-exchange treatment. The Co contents of both Co-MOR and Co-5A are determined to be 1.03 wt% and 0.43 wt%, respectively.

The scanning electron micrographs of catalysts are shown in Figure 2, indicating that the morphologies and particle sizes of catalysts that have undergone the ion-exchange treatment are still similar to those of the parent zeolites.

3.2 Epoxidation of styrene with air over various Co^{2+}-exchanged zeolites

The catalytic activity of various Co^{2+}-exchanged zeolites for the epoxidation of styrene has been compared in Table 2. When $Co(Ac)_2 \cdot 4H_2O$ was used as a homogeneous catalyst, only 12.7 mol% of styrene was converted. When Na-MOR or 5A was used, an extremely low conversion of 3.7 mol% or 9.4 mol% was achieved. In contrast, Co-MOR and Co-5A catalysts presented considerably catalytic activity, remarkably higher than those of Co-4A and Co-13X. Co-MOR catalyzed the oxidation of 94.2 mol% styrene to 90.5% styrene epoxide, 3.7% benzaldehyde, and 5.8% phenylacetaldehyde. Likewise, Co-5A catalytically converted 89.4 mol% styrene to 90.2% styrene epoxide, 4.1% benzaldehyde, and 5.7% phenylacetaldehyde.

3.3 Epoxidation of styrene with air over various M-MOR zeolites

As shown in Figure 3, among various M-MOR catalysts, only Co-MOR could achieve very high styrene conversion of 94.2 mol% and epoxide selectivity of 90.5%. Other M-MOR catalysts exhibited much lower activities, in which all the conversions were < 24.4 mol% (see Table S1). The catalytic activity of different M-MOR catalysts decreased in the following order of Co-MOR (94.2 mol%) > Zn-MOR (24.4 mol%) > Cr-MOR (13.8 mol%) > Cu-MOR (13.5 mol%) > Mn-MOR (12.5 mol%) > Ni-MOR (9.7 mol%) > Fe-MOR (7.8 mol%). The epoxide selectivity presented a different decreasing trend: Co-MOR (90.5%) > Cu-MOR (80.7%) > Fe-MOR (77.9%) > Zn-MOR (73.4%) > Cr-MOR (73.0%) > Ni-MOR (70.6%) > Mn-MOR (70.1%).

Clearly, cobalt is an effective component for catalyzing the epoxidation of styrene with oxygen, and hence widely used in the field of epoxidation of alkenes with O_2/air [6,9,10,12-14,17-26]. A comparison of our results with the earlier data reported for the epoxidation of styrene is summarized in Table 3, where further shows the excellent catalytic activity of our aerobic epoxidation system using Co^{2+}-exchanged zeolites as the catalysts.

3.4 Effect of solvents and oxidants on the epoxidation of styrene over Co-MOR

The effect of different solvents on the activity of Co-MOR was compared in Table S2. The epoxidation of styrene with air in pyridine could not occur at all. When MIBK, toluene or acetylacetone was used as the solvent, the styrene conversion was low (< 29.0 mol%), and the main product was benzaldehyde (61.1%, 65.6% or 74.0%). Although a high styrene conversion of 95.8 mol% could be achieved in the polar solvent 1,4-Dioxane, the selectivity to epoxide was 48.5%. In contrast, DMF was especially efficient in obtaining both high conversion (94.2 mol%) and good epoxide selectivity (90.5%), probably ascribed to the strong coordination among DMF (solvent), Co^{2+} and O_2 that can promote the activation of O_2 molecules to form an active intermediate, which further reacts with styrene to produce epoxide [6,13,14,23].

It is observed from Table 4 that no any conversion of styrene took place in the presence of NaClO or only inert N_2. When $NaIO_4$ was used, the styrene conversion was very low (13.2 mol%). When only air was bubbled to act as unique oxidant, 10.3 mol% conversion of styrene was achieved. When using H_2O_2 as the oxidant, the conversion of styrene was only 21.4 mol%, mainly ascribed to the rapid decomposition of H_2O_2 into O_2 at 363 K. However, when air was bubbled into the reactor with 0.3 mmol of TBHP or CHP (*ca.* 2 drops) as the initiator, the highest conversion of styrene and selectivity of epoxide were obtained. For the purpose of comparison, even 3 mmol of TBHP (10 times as much as that used as the initiator) was added as the oxidant, but only 20.4 mol% conversion was obtained. Also, we attempted to use H_2O_2 as the initiator; however, only 37.6 mol% of styrene was oxidized. In contrast, the epoxidation could not occur at all when adding TEMPO as the initiator. Obviously, the addition of TBHP or CHP in small amounts is the most beneficial to the catalytic epoxidation of styrene with air.

3.5 Catalytic epoxidation of various alkenes over Co-MOR and Co-5A

The catalytic epoxidation of other alkenes (like α-pinene, α-methyl styrene, and cyclooctene) over Co-MOR and Co-5A is described in Table 5. It is observed that the reactivity of styrene over both Co-MOR and Co-5A was the highest, with a conversion of 89.4−94.2 mol%, and an epoxide selectivity of 90.2−90.5%. Co-MOR could convert almost 100% of α-methyl styrene (with 75.3% selectivity); however, Co-5A converted only 55.8 mol% substrate (96.8% selectivity). The reactivity of α-pinene over Co-MOR and Co-5A was lower than that of styrene, for which 70.8−86.4 mol% α-pinene was oxidized to obtain 81.5−83.6% selectivity. The reactivity of cyclooctene over Co-MOR and Co-5A was the lowest, in which only 28.1−44.2 mol% cyclooctene was converted, but the epoxide selectivity could reach 93.5−96.9%. This can be ascribed to the negative effect of microporous pore sizes of Co-MOR and Co-5A on the diffusion of cyclooctene, which seriously limits the approaching of cyclooctene molecules to catalytic active sites forming the intermediate states.

3.6 Recycling studies

The recycling experiments of Co-MOR and Co-5A catalysts for the epoxidation of styrene were conducted. As observed from Figure 4(a), the reuses of Co-MOR (five times) did not appreciably decrease the conversion of styrene and the selectivity of epoxide, in which all the reactions maintained almost constant levels of the conversion and selectivity of about 94.2 mol% and 90.5%. However, the conversion on Co-5A showed a little reduction in the initial recycle, but remained basically unchanged in the following four recycles with a small fluctuation of 85.8−86.3 mol% conversion and of 89.2−89.5% selectivity.

In order to further verify whether the observed catalysis was truly heterogeneous or not, control experiments were carried out (see Figure 4 (b)). After reactions were initially conducted for 1 h, the styrene conversions were 15.6 mol% over Co-MOR and 10.3 mol% over Co-5A, then solid catalysts were filtered off and the reactions were continued for another 4 h. Finally, the conversions were analyzed by GC to be 19.7 mol% for Co-MOR (with an increment of 4.1 mol%) and 19.2 mol% for Co-5A (with an increment of 8.9 mol%), attributed to the contribution of a small amount of Co^{2+} ions leaching from Co-zeolites and the autoxidation of alkenes by air. This study further revealed the heterogeneity of catalysis occurred over Co-MOR and Co-5A.

4. Conclusions

Various transition metal ions exchanged zeolites were prepared by a simple route, and tested for the aerobic epoxidation of styrene to styrene oxide, in which Co-MOR and Co-5A displayed highly catalytic activities to achieve 89.4–94.2 mol% conversion with the selectivity of > 90%. Solvents, the catalyst amount, the reaction time, the reaction temperature, oxidants and initiators exerted notable impacts on the epoxidation reaction. Recycling studies and control experiments showed the recyclability and stability of Co-MOR and Co-5A as heterogeneous catalysts.

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Captions:

Table 1 Physicochemical characterization of zeolite catalysts. ([a] Result obtained from XRF. [b] Values obtained from N_2-adsorption results.)

Table 2 Epoxidation of styrene with air over various Co^{2+}-exchanged zeolite catalysts and $Co(Ac)_2$. (Reaction conditions: alkene, 3 mmol; DMF, 10 g; catalyst, 0.1 g; initiator (TBHP), 0.3 mmol; time, 5 h; temperature, 363 K; flow rate of air, 40 ml/min.)

Table 3 Comparison of different Co-containing catalysts for the epoxidation of styrene with O_2 or air in the absence of reductant.

Table 4 Effect of various oxidants on the epoxidation of styrene with air over Co-MOR[a]. ([a] Reaction conditions: styrene, 3 mmol; DMF, 10 g; catalyst, 0.1 g; initiator (TBHP), 0.3 mmol; time, 5 h; temperature, 363 K; flow rate of air, 40 ml/min. [b] flowrate of air or N_2, 40 ml/min; [c] 3 mmol; [d] 0.3 mmol; [e] 0.3 mmol.)

Table 5 Catalytic epoxidation of various alkenes over Co-MOR and Co-5A. (Reaction conditions: alkene, 3 mmol; DMF, 10 g; catalyst, 0.1 g; initiator (TBHP), 0.3 mmol; time, 5 h; temperature, 363 K; flow rate of air, 40 ml/min.)

Figure 1 XRD patterns of Co^{2+}-exchanged MOR and 5A zeolites.

Figure 2 SEM images of Co^{2+}-MOR (a), Na-MOR (b), Co-5A (c), and 5A (d) zeolites.

Figure 3 Epoxidation of styrene with air over various transition metal ion-exchanged MOR zeolites. (Reaction conditions: styrene, 3 mmol; DMF, 10 g; catalyst, 0.1 g; initiator (TBHP), 0.3 mmol; time, 5 h; temperature, 363 K; flow rate of air, 40 ml/min.)

Figure 4 (a) Recycling tests of Co-MOR (◆ and ◇) and Co-5A (■ and □) in the epoxidation of styrene (Reaction conditions: DMF, 10 g; styrene, 3 mmol; TBHP, 0.3 mmol; catalyst, 0.1 g; temperature, 363 K; time, 6 h; flowrate of air, 40 ml/min), **(b)** Control experiments of Co-MOR (■&□) and Co-5A (▲&△).

Table 1

Catalyst	Co content[a] (wt%)	SiO_2/Al_2O_3[a] ratios	Surface area[b] (m^2/g)	Pore size (Å)
Na-MOR	0	20.6	249.3	6.6
Co-MOR	1.03	25.2	235.6	6.7
5A	0	2.0	485.0	~5
Co-5A	0.43	3.0	396.3	~5
Na-4A	0	2.0	155.7	~4
Co-4A	1.14	3.0	120.6	~4
13X	0	2.3	862.4	10
Co-13X	1.21	4.0	750.4	10

Table 2

Catalyst	Conv. (mol%)	Sele. (%)		
		Epoxide	Benzaldehyde	Phenylacetaldehyde
Na-MOR	3.7	70.1	29.9	0
Co-MOR	94.2	90.5	3.7	5.8
5A	9.4	75.7	24.5	0
Co-5A	89.4	90.2	4.1	5.7
Co-4A	53.5	83.5	13.1	3.4
Co-13X	40.3	83.1	14.7	2.3
$Co(Ac)_2$	12.7	57.0	41.6	1.4

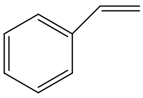
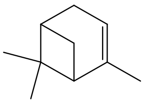
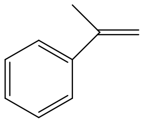
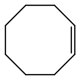
Table 3

Catalyst	Reaction condition		Conv. (mol%)	Sele. (%)	Ref.
	Tempt. (K)	Oxidant			
$CoOx/SiO_2$	363	air	85.7	86.0	6
Co^{2+}-NaX	373	O_2	44.0	60.0	9
Co-MCM-41	373	O_2	45.0	62.0	9
Co-X	373	O_2	45.0	65.0	10
CaCoX, SrCoX, BaCoX	373	O_2	>99	85.0	10
Co-SBA-15-20-5.2	373	O_2	92.4	63.2	12
Co-ZSM-5	363	air	88.4	90.1	13
Co-Beta	363	air	92.4	91.7	13
Co-SAPO-34	363	air	91.9	90.5	14
Co-SAPO-5	363	air	92.0	89.5	14
$[Co(Bzo_2[14]aneN_4)]^{2+}$-NaY	373	O_2	42.1	86.6	17
Co-SBA-15_{20}	373	O_2	94.1	65.5	18
S-8CoYZr	393	O_2	62.0	82.0	19
NaCsCoY20	373	O_2 (5.5 bar)	47.0	61.0	11
Co-Al LDH	373	O_2	97.0	83.0	20
Co-SSZ-S-5	373	O_2	47.5	78.3	21
Ag-Co-SiO_2	373	air	52.0	81.0	22
Co-ZSM-5(L_2)	363	air	90.5	91.1	23
Co-ZSM-5(L_2)	363	air	93.9	89.7	24
CoAlPO-36	323	air (30 bar)	46.0	34.0	25
Co/TS-1	373	O_2	94.5	74.3	26
Co-MOR	363	air	94.2	90.5	this study
Co-5A	363	air	89.4	90.2	this study

Table 4

Oxidant	Conv. (mol%)	Sele. (%)		
		Epoxide	Benzaldehyde	Phenylacetaldehyde
None	0	—	—	—
Air[b]	10.3	66.7	33.3	0
N_2[b]	0	—	—	—
NaClO[c]	0	—	—	—
$NaIO_4$[c]	13.2	79.0	21.0	0
TBHP[c]	20.4	79.7	20.3	0
H_2O_2[c]	21.4	69.4	27.8	2.8
TBHP[d]	11.0	83.9	11.9	4.2
CHP[d]	15.8	85.1	10.5	4.4
Air[b]+TEMPO[e]	0	—	—	—
Air[b]+H_2O_2[e]	37.6	78.5	17.5	4.0
Air[b]+CHP[e]	94.3	90.9	1.5	7.6
Air[b]+TBHP[e]	94.2	90.5	3.7	5.8

Table 5

Catalyst	Alkene	Conv. (mol%)	Sele. (%)
Co-MOR		94.2	90.5
Co-5A		89.4	90.2
Co-MOR		86.4	81.5
Co-5A		70.8	83.6
Co-MOR		100	75.3
Co-5A		55.8	96.8
Co-MOR		44.2	96.9
Co-5A		28.1	93.5

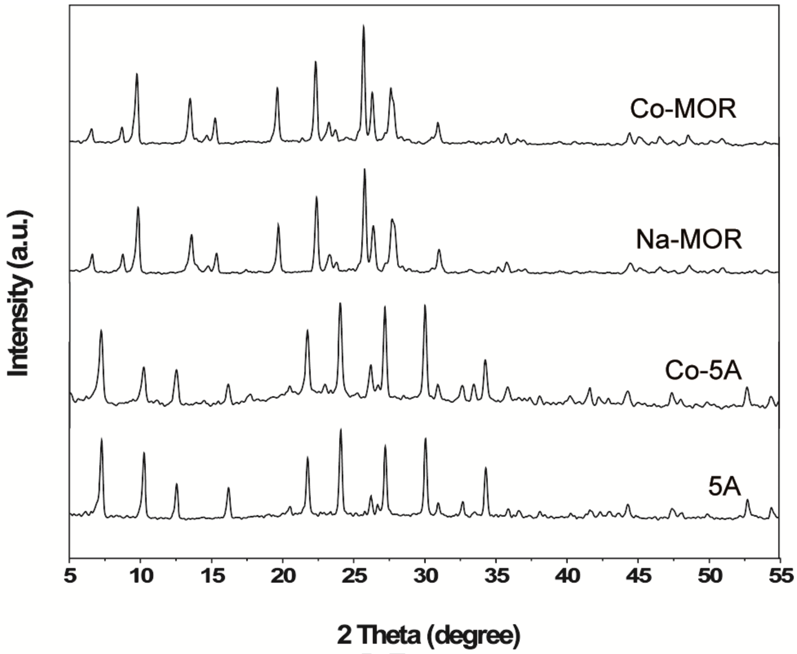


Figure 1

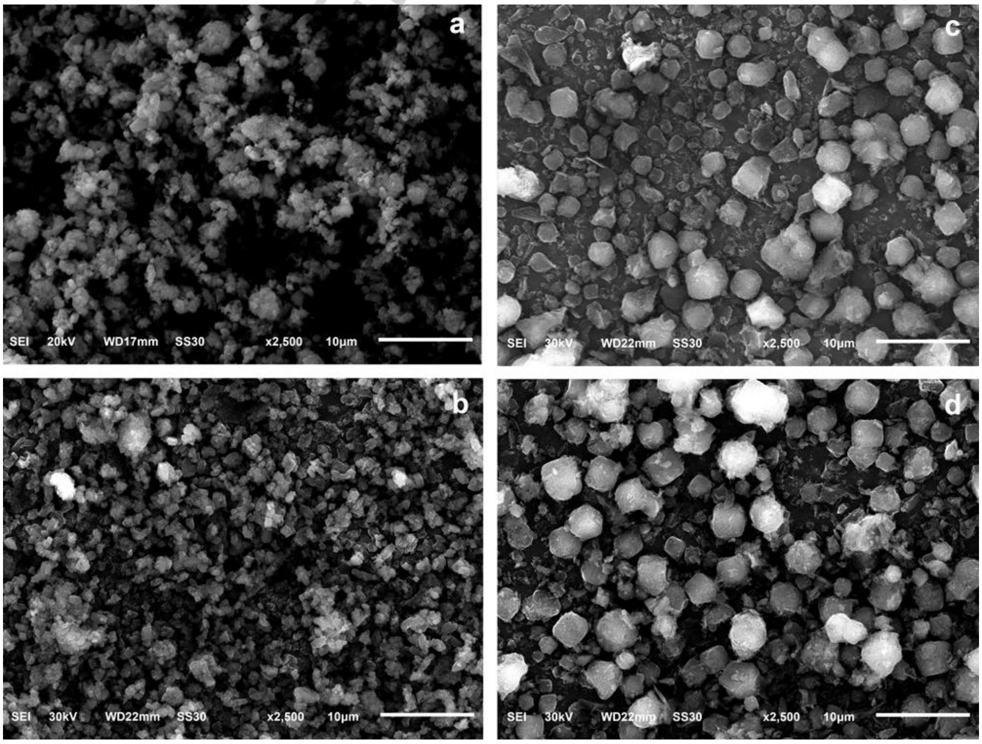


Figure 2

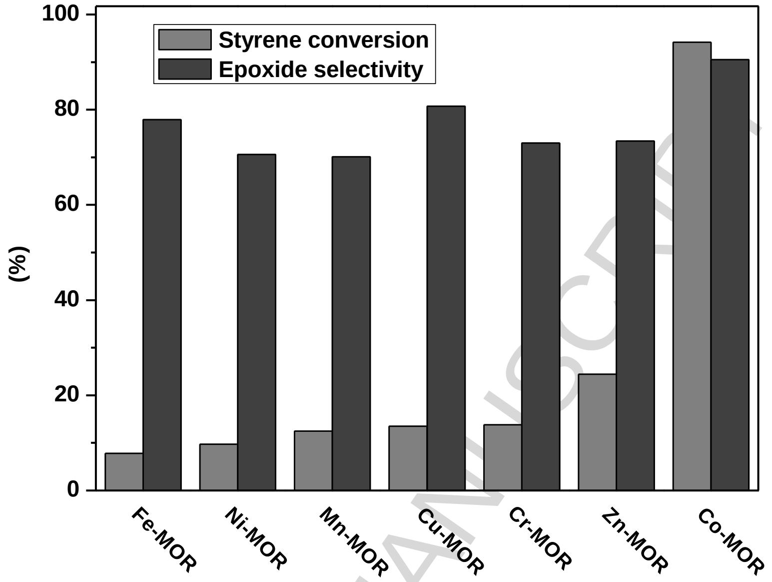
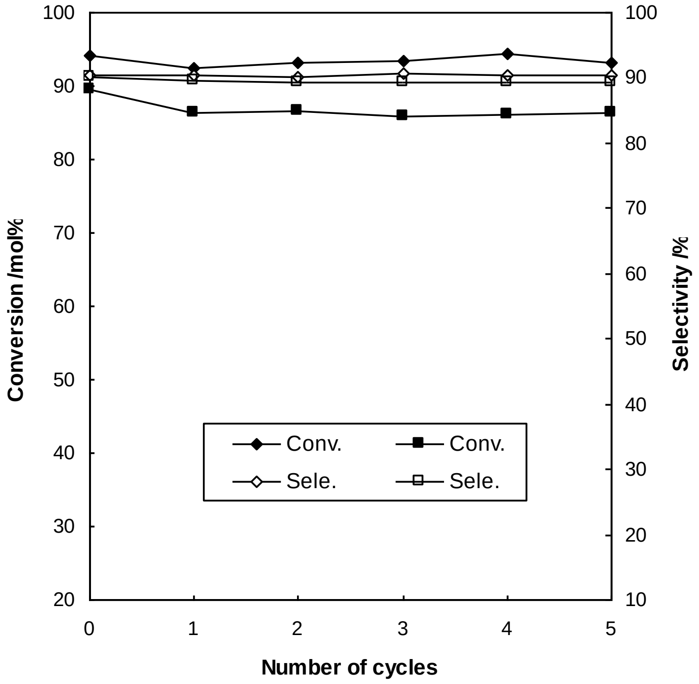
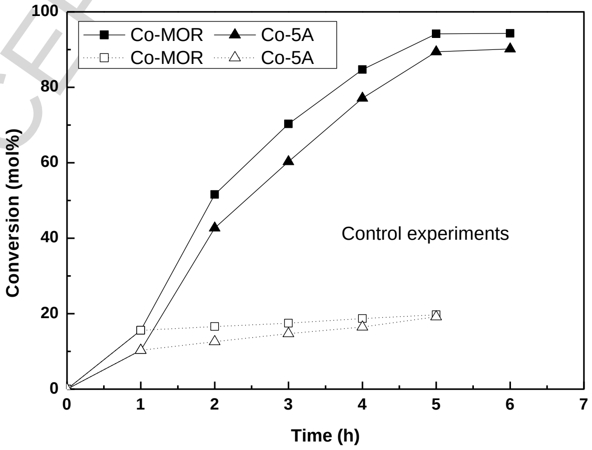

Styrene conversion
Epoxide selectivity
(%)
0
20
40
60
80
100
Fe-MOR
Ni-MOR
Mn-MOR
Cu-MOR
Cr-MOR
Zn-MOR
Co-MOR

Figure 3


100
90
80
70
60
50
40
30
20
Conversion /mol%
100
90
80
70
60
50
40
30
20
10
Selectivity /%
0
1
2
3
4
5
Number of cycles
Conv.
Conv.
Sele.
Sele.

(a)


Co-MOR
Co-5A
Co-MOR
Co-5A
100
80
60
40
20
0
Conversion (mol%)
Control experiments
0
1
2
3
4
5
6
7
Time (h)

(b)

Figure 4

Research Highlights

- Co^{2+}-exchanged MOR and 5A are firstly used in the aerobic epoxidation of alkenes.
- 89.4–94.2 mol% conversion of styrene with epoxide selectivity of > 90% is obtained.
- A route to catalyze epoxidation of alkenes over simply-prepared cheap catalysts.