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Highly Active/Selective Heterogeneous Catalyst Co/Ts-1 for Epoxidation of Styrene by Molecular Oxygen: Effects of Catalyst Preparation Conditions and Reaction Conditions on the Reaction

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Abstract In the study, highly active/selective heterogeneous catalyst Co/TS-1 has been prepared successfully. The catalyst was characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), diffuse reflectance UV–visible(DR UV–vis) and transmission electron microscopy (TEM). Liquid-phase catalytic epoxidation of styrene to styrene epoxide by molecular oxygen was carried out at atmospheric pressure in the presence of Co/TS-1 catalyst. Sacrificial co-reductant or other promoted reagent such as t-butyl hydroperoxide (TBHP) was not added in the reaction system. A 94.5 mol% conversion of styrene with an epoxide selectivity of 74.3 mol% was attained after 3.5 h reaction. It is noteworthy that there is a synergy between the Co and the Ti in the catalyst in the liquid phase epoxidation of styrene.

Keywords Styrene epoxidation · Molecular oxygen · Co/TS-1 · Effect factors

1 Introduction

Epoxide compounds are commercially important intermediates [1–4] in the synthesis of the chemicals and pharmaceuticals as they can be easily transformed into a large variety of compounds by means of regioselective ring opening reactions [5]. Epoxide compounds are usually synthesized by epoxidation of alkenes. Therefore, the epoxidation of alkenes is a highly significant chemical reaction.

Conventionally, the epoxidation of alkenes was usually carried out with organic peracid as an oxidant or by a chlorohydrin process [3, 6]. A lot of waste was formed in either case [7–9]. Now, organic peroxides and especially hydrogen peroxide are used as oxidants for the epoxidation of alkenes under the condition of heterogeneous catalyst. For example, N.S. Patil and coworkers researched the epoxidation of styrene by anhydrous t-butyl hydroperoxide over Au/TiO_2 catalyst [10, 11]. D. H. Yin and co-workers found that gold nanoparticles deposited on mesoporous alumina could efficiently catalyze the epoxidation of styrene by anhydrous t-butyl hydroperoxide (TBHP) [12]. Meanwhile, hydrogen peroxide was also widely used as an oxidant for epoxidation of alkenes. Titanium silicalite (TS-1) was reported to catalyze the epoxidation of styrene by anhydrous urea–hydrogen peroxide adduct with good conversion and selectivity [13, 14]. The epoxidation of styrene by aqueous hydrogen peroxide was carried out over TS-1 with high selectivity to styrene oxide (>92%) under the alkali promoted condition [15].

Compared with organic peroxides and hydrogen peroxide, molecular oxygen is a more environmental and economic oxidant for the epoxidation of alkenes. However, developing an efficient catalyst, especially heterogeneous catalyst for the epoxidation of alkenes with O_2 in the absence of sacrificial co-reductant is rather difficult. Many epoxidation reactions were carried out by O_2 under the heterogeneous or homogeneous catalysis condition, but a sacrificial co-reductant was needed. Direct vapor phase propylene epoxidation over deposition-precipitation gold-titania catalysts in the presence of H_2/O_2 was researched by E. E. Stangland [16] and T. A. Nijhuis [17]. In the propylene epoxidation, H_2 was used as a sacrificial co-reductant. P. Aguirre and co-researchers' work showed the catalytic activity of a series of carbonyl ruthenium

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complexes in the epoxidation of olefins co-catalyzed by isobutyl-aldehyde which was a sacrificial co-reductant [18]. At the assistance of sacrificial co-reductant, active oxide species which played an important role in the oxidation were formed.

To our knowledge, only a few studies have achieved epoxidation of styrene by O_2 in the absence of a sacrificial co-reductant. Copper hydroxyphosphate ($Cu_2(OH)PO_4$) was reported to catalyze the epoxidation of styrene without sacrificial co-reductant [19]. Q.H. Tang and co-workers found that cobalt (II)-containing molecular sieves and iron-based heterogeneous catalysts could catalyze the epoxidation of styrene by O_2 in the absence of sacrificial co-reductant [3, 20]. Recently, some cobalt-containing catalysts were applied to catalyze the epoxidation of styrene by air and exhibited good performance [7, 8, 21, 22]. V.R.Choudhary and co-workers reported the epoxidation of styrene by anhydrous H_2O_2 over TS-1 and γ-Al_2O_3 catalysts [23]. Ag/TS-1 was reported to catalyze the epoxidation of propylene with molecular oxygen by R.P. Wang et al. [24]. However, to date, no report has approached the catalytic activity of Co/TS-1 in the epoxidation of alkenes by O_2 without sacrificial co-reductant. Here, we report for the first time that the heterogeneous catalyst Co/TS-1 catalyze the epoxidation of styrene by O_2 in the absence of sacrificial co-reductant under atmospheric pressure condition.

2 Experimental

2.1 Materials

The main reagents used in the synthesis of Co/TS-1 were tetra-butyl- orthotitanate (TBOT, ≥98.0%), tetraethyl orthosilicate (TEOS, based on SiO_2, ≥28.4%), tetrapropyl ammonium bromide (TPABr, ≥98.0%), silver oxide (Ag_2O, ≥99.7%), tetrapropylammonium hydroxide (20 wt. %, prepared by ourselves), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2$ ≥99.0%) and phosphoric acid(H_3PO_4, ≥85.0%). The main regents used in the catalytic reaction were styrene (C_8H_8, ≥98.0%), *N*, *N*-dimethylformamide (DMF, ≥99.5%), and molecular oxygen.

2.2 Synthesis of Catalyst

In a typical preparation, TPABr (8.0047 g) and silver oxide (4.0 g) were added into a 50 mL round-bottom flask filled with 24.66 g distilled water. The slurry was stirred by a magnetic stirrer under atmospheric temperature for 7 h. After that, the tetrapropylammonium hydroxide (TPAOH, 20% aqueous solution) was gained by filtration. Then the 20% TPOH aqueous solution was added to a 100 mL round-bottom flask filled with 11.2 mL TEOS under vigorous stirring for 2 h. Then 0.56 mL TBOT dissolved in 3.63 mL dry isopropanol was added slowly to the above clear solution of TPA-silicate under vigorous stirring. Stirring was continued for another 30 min and then a solution of 0.36 mL H_3PO_4 (85%) in 2.2 mL water was added very slowly under vigorous stirring, which was continued for another hour. The crystallization of the sample was carried out in a stainless-steel autoclave at 433 K for 7 h. The solid product was collected by centrifugation without washing, and dried at 373 K over night.

Typically, appropriate amount of as-synthesized (uncalcined) TS-1 containing template was immersed in an ethanolic solution containing certain amount of $Co(NO_3)_2$ for 4 h at ambient temperature while stirring. Then the as-synthesized Co/TS-1 was separated by filtration without washing and dried in air at 373 K overnight. The sample was finally calcined at 723 K in air for 6 h to remove the remaining organic template.

2.3 Characterizations

The content of cobalt in each sample was determined by atomic absorption spectroscopic analysis on a varian-AA240 spectrometer. Powder X-ray diffraction (XRD) for samples was measured with a XRD-6000 diffractometer made in Japan. Cu–K_α radiation was used as the X-ray source. Transmission electron microscopy (TEM) for samples was detected with a Hitachi-600 microscope. Samples for TEM measurements were suspended in ethanol and ultrasonically dispersed. Fourier transform infrared (FT-IR) spectra was recorded with a Nicolet NEXUS 670 FT-IR instrument with a DTGS detector. DR UV–vis spectra of samples were recorded on a varian cany100 spectrometer. For the diffuse reflectance mode (solid), the powdered sample was loaded into a quartz cell, and the spectra were collected in the range of 200–800 nm referenced to BaSO4.

2.4 Catalytic Epoxidation Reactions

The epoxidation of styrene with O_2 was carried out with a round-bottomed glass flask reactor at 373 K. In a typical run, a 100 mL round bottomed flask equipped with an efficient water condenser was kept in a constant temperature oil bath with the temperature maintained at 373 ± 2 K. In the study, six catalysts with different Co loading were prepared. As shown in Table 1, they are denoted as Co/TS-1(xx wt.%), in which xx stands for the mass content of Co in the catalyst. Then 6 mmol styrene solved in 20 mL DMF

Table 1 The epoxidation of styrene by O_2 on Co/TS-1 with different Co loadings

Entry	Co loading(%)	Styrene conversion	Slectivity(%)			
			Epoxide	Benzaldehyde	benzoic acid	TOF(h^{-1})
1	No catalyst	9.3	51.2	47.3	1.5	–
2	TS-1	21.2	51.5	35.9	12.6	–
3	0.21	38.5	49.2	33.2	17.6	45.6
4	0.97	88.2	68.9	25.6	5.5	31.7
5	1.14	94.2	68.5	22.0	9.5	28.6
6	2.32	94.5	74.3	20.5	5.2	15.3
7	3.13	46.5	53.1	33.2	13.7	4.0
8	5.68	33.2	47.8	29.9	22.3	1.4
9	Co/S-1[a](1.39 wt%)	45.2	49.4	26.2	24.4	8.1
10[b]	Co/TS-1(2.32 wt%)	0	0	0	0	0

Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; reaction temperature, 373 K; flow rate of O_2, 80 mL/min; duration, 3.5 h

[a] In the preparation of the catalyst Co/S-1(1.39 wt%), the TBOT dissolved in dry isopropanol was not added. The other preparation steps were the same with other Co/TS-1 catalyst

[b] In the run, hydroquinone (50 mg) was added to the reaction system

and 200 mg of catalyst were added to the flask. The reaction started under stirring by bubbling O_2 at atmospheric pressure into the reaction mixture at the rate of 80 mL min^{-1}. *n*-Decane was used as an internal standard. The liquid organic products were quantified using a gas chromatograph (HP 5890 Series II) equipped with a flame ionization detector and an SE-54 column (30 m × 0.32 mm × 0.33 μm), a programmed oven (temperature from 323 K to 473 K at the ramping rate of 8 C/min), and N_2 as the carrier gas. The liquid organic products were identified by a GC-mass spectroscopy (TRACE DSQ) analysis. The conversion was calculated on the basis of molar percent of styrene. The initial molar percent of styrene was divided by initial area percent (styrene peak area from GC) to get the response factor. The conversion, selectivity, and turn over frequency (TOF) were calculated as follows:

$$\text{Styrene conversion (mol\%)} = \frac{\text{(initial mol\%)} - \text{(final mol\%)}}{\text{(initial mol\%)}} \times 100\% \tag{1}$$

$$\text{Styrene oxide selectivity} = \frac{\text{GC peak area of styrene oxide}}{\text{GC peak area of all products}} \times 100\% \tag{2}$$

$$\text{Benzaldehyde selectivity} = \frac{\text{GC peak area of benzaldehyde}}{\text{GC peak area of all products}} \times 100\% \tag{3}$$

$$\text{Benzoic acid selectivity} = \frac{\text{GC peak area of benzoic acid}}{\text{GC peak area of all products}} \times 100\% \tag{4}$$

$$\text{TOF} = \frac{\text{No. of moles of styrene oxide formed}}{\text{No. of moles of cobalt in the catalyst} \times \text{reaction time}} \tag{5}$$

3 Results and discussion

3.1 Characterizations of Co/TS-1

Figure 1 shows the X-ray diffraction (XRD) pattern of TS-1 and Co/TS-1 loaded with different of amount cobalt (0.21 wt.%, 2.32 wt.%, 5.68 wt.%). XRD investigation for the Co/TS-1 revealed that only diffraction peaks ascribed to TS-1 [25] were observed. The CoO_x crystalline peaks are not present. This result indicated that the CoO_x particles were not aggregated but highly dispersed on the surface of TS-1 [20].

The TEM micrographs of TS-1 and Co/TS-1 (2.15 wt.%) are showed in Fig. 2. It can be seen that the particle size of catalyst is reasonable uniform, with an average value of about 180 nm. The diffraction graph of Co (Fig. 3) was observed. This confirmed that the CoO_x particles had been loaded on the support (TS-1.) As can be

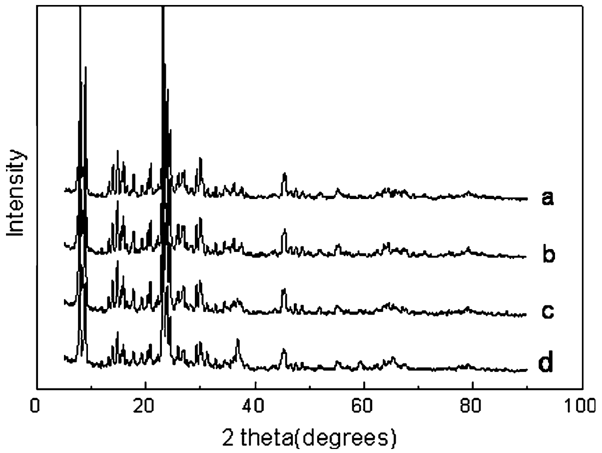


Fig. 1 XRD pattern of (a) TS-1, (b) Co/TS-1 (0.21 wt.%), (c) Co/TS-1 (2.32 wt.%) and (d) Co/TS-1 (5.68 wt %)

seen from Fig. 2, no any CoO_x particles were observed in the catalyst. This result is consistent with the XRD result which proved that CoO_x particles were highly dispersed on the surface of TS-1.

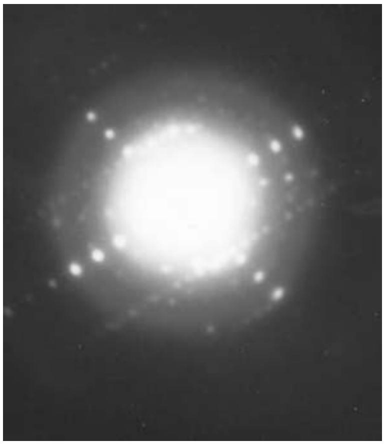


Fig. 3 Diffraction graph of Co in the catalyst

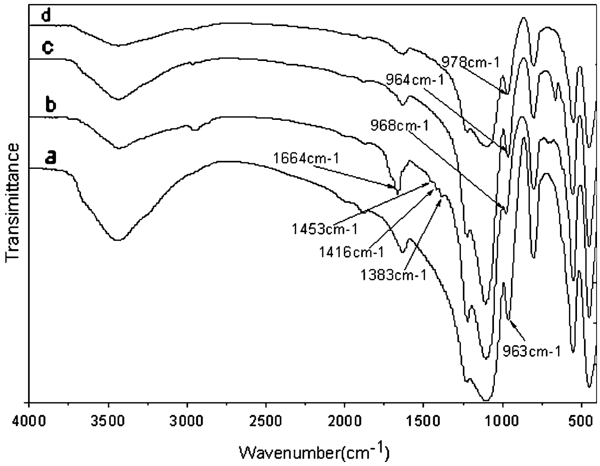


Fig. 4 FT-IR spectra of catalysts: (a) TS-1, (b) Co/TS-1 (1.14 wt.%)*, (c) Co/TS-1 (5.68 wt.%), (d) Co/TS-1 (2.15 wt.%). *The catalyst was used once

Figure 4 shows the FT-IR spectra of TS-1, Co/TS-1 loaded with different amount cobalt (2.15 wt.%, 5.68 wt.%) and the Co/TS-1 (1.14 wt.%)* catalyst dried after the first use. The FT-IR spectrum for all samples present a band near 960 cm^{-1} which indicates the incorporation of Ti in the framework of TS-1 [14, 26]. The intensity of the band near 960 cm^{-1} presented in FT-IR spectra of TS-1, Co/TS-1 (2.15 wt.%) and Co/TS-1(5.68 wt.%) is obviously stronger than that of Co/TS-1(1.14 wt.%)*. The reason is probably that there is function between Ti atom and C=O of DMF. In the catalytic reaction, the electron cloud between the Ti atom and the O atom in the zeolite framework could be transferred to the neighborhood of the C=O of DMF the Co/TS-1(1.14 wt.%)* catalyst was used once but the other were not). Therefore, the intensity of the band near 960 cm^{-1} presenting in FT-IR spectra of Co/TS-1(1.14 wt.%)* is weaker compared with that of TS-1, Co/TS-1(2.15 wt.%) and Co/TS-1(5.68 wt.%). In addition, the FT-IR spectra for Co/TS-1(1.14 wt.%)* presents the band near 1664 cm^{-1} which is attributed to the C = O stretching of DMF and the bands near 1453, 1416 and 1383 cm^{-1} which are attributed to the stretching of N–C of C–N–C of DMF [12]. Therefore,

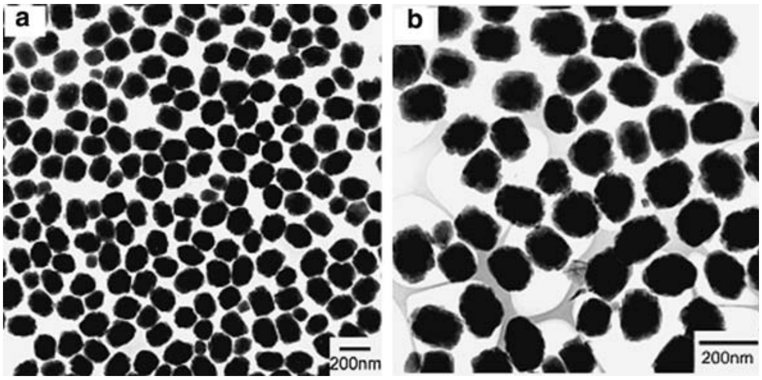


Fig. 2 TEM images of the samples: (**a**) TS-1 and (**b**) Co/TS-1 (2.15 wt.%)

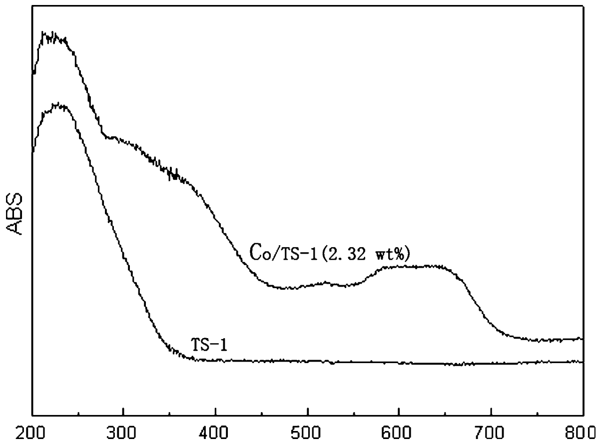


Fig. 5 UV–vis spectra of TS-1 and Co/TS-1(2.15 wt.%)

it is probable that DMF was coordinated to the Ti in the framework of TS-1 in the process of epoxidation of styrene by molecular oxygen.

DR UV–vis spectra of TS-1 and Co/TS-1(2.32 wt%) are presented in Fig. 5 As can be seen from Fig. 5, intense absorption bands at 210 nm are obtained in the spectra for TS-1 and Co/TS-1(2.32 wt%)samples. The appearance of the band indicates the incorporation of Ti in the framework of TS-1 [14]. For Co/TS-1(2.32 wt.%), two broad peaks locate in the ranges of 280–450 nm and 560–700 nm, respectively, which can be attributed to ultraviolet adsorbances of CoO_x oxide. This can prove that the very small crystallites of CoO_x highly dispersed on the surface of TS-1exist in the catalysts, although they are undetectable by XRD and TEM.

3.2 Epoxidation Styrene with Co/TS-1 Catalyst

Co/TS-1 was proved to be an active and reasonably selective catalyst for the epoxidation of styrene with molecular oxygen in the absence of sacrificial co-reductant. Many factors including preparation conditions (the Co loading, calcination temperature and support) and reaction conditions (temperature and flow rate of O_2) affect the catalytic epoxidation activity and selectivity.

3.2.1 *Effects of Preparation Conditions of Catalyst*

3.2.1.1 Effect of the Co Loading Table 1 lists the effect of the Co loading on styrene epoxidation. The styrene conversion and the epoxide selectivity were only 9.3 mol% and 51.2 mol% respectively in the absence of catalyst. It can be seen that the Co loading has an important effect on the catalytic properties. With an increase in the Co loading, both the styrene conversion and the selectivity to styrene oxide increased drastically, and then leveled off. With an increase in the Co loading from 0.21 to 2.32 wt.%, the styrene conversion shows a drastic increase from 38.5 to 94.5 mol%, accompanied with an increase of the epoxide selectivity from 49.2 to 74.3 mol%. When the Co loading increases continually, both the styrene conversion and the epoxide selectivity decreased markedly. It can also be found that TOF value decreased with increasing amount of cobalt loaded in TS-1. These results indicate that the cobalt loaded on TS-1 is the active site to the styrene epoxidation. When the Co loading is too low, TOF value is still high due to the high catalytic efficiency of Co active site although the styrene conversion is low. In order to study the effect of Ti in the catalyst in the reaction, we prepared the catalyst Co/S-1(1.39 wt.%). In the preparation process of the catalyst Co/S-1(1.39 wt.%), the TBOT dissolved in dry isopropanol was not added but the other preparation steps were the same with other typical catalyst. It is noteworthy that the activity and selectivity of the catalyst (Co/S-1(1.39 wt.%)) were lower than those of the Co/TS-1(1.14 wt.%). This indicates that Ti plays an important role in the styrene epoxidation. In addition, when using TS-1 as the catalyst, only 21.2 mol% styrene conversion with the 51.5 mol% epoxide selectivity was attained. Therefore, there is a synergy between the Co and the Ti in the catalyst in the liquid phase epoxidation of styrene by O_2.

3.2.1.2 Effect of Calcination Temperature The effect of calcination temperature of Co/TS-1(1.14 wt.%) catalyst on the styrene epoxidation is illustrated in Fig. 6. It can be seen that, when the calcination temperature rose from 723 to 823 K, both the styrene conversion and the epoxide selectivity decreased drastically. When the calcination temperature increased to 923 K, the styrene conversion decreases markedly, but the epoxide selectivity decreases in a lower degree. Accordingly, the sample calcined at 723 K exhibits the highest activity with 91.2 mol% of styrene conversion and 64.3mol% of epoxide selectivity.

3.2.1.3 Effect of Support In order to study the effect of supports, different supports loaded with Co were prepared. Their catalytic activities for the epoxidation of styrene under the same condition were investigated and are shown in Table 2. It can be seen that, when using NaY molecular sieve as the support, a 50.3 mol% styrene conversion with the 55.9 mol% epoxide selectivity was attained. The result is similar to that of Q. Tang et al. [20]. When using MCM-41 molecular sieve as the support, the result is similar to that of NaY molecular sieve. More benzoic acid was

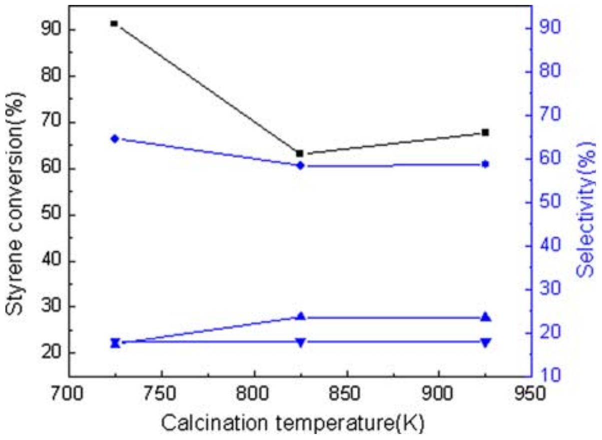


Fig. 6 Effect of calcination temperature on the epoxidation of styrene by O_2 over Co/TS-1 (2.15 wt.%): (■) styrene conversion, (●) epoxide selectivity, (▲) benzaldehyde selectivity, (▼) benzoic acid selectivity. Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; reaction temperature, 373 K; flow rate of O_2, 60 mL/min; duration, 3.5 h

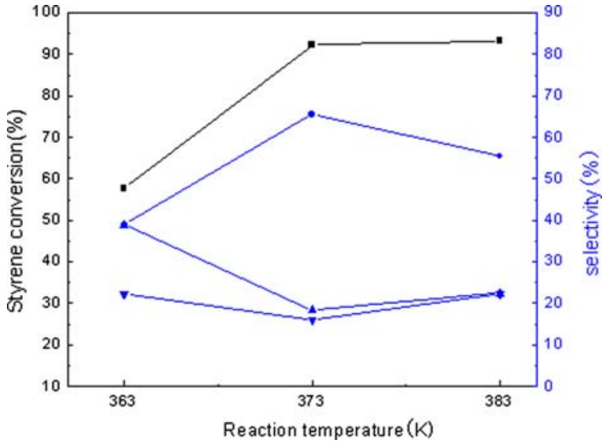


Fig. 7 Effect of reaction temperature on the epoxidation of styrene by O_2 over Co/TS-1(1.03 wt.%): (■) styrene conversion, (●) epoxide selectivity, (▲) benzaldehyde selectivity, (▼) benzoic acid selectivity. Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; flow rate of O_2, 60 mL/min; duration, 3.5 h

formed when using Co/γ-Al_2O_3 as the catalyst. This may be related to the acid site of γ-Al_2O_3. The above results show that the Co/TS-1(2.32 wt.%) exhibits good performance in the liquid phase epoxidation of styrene by molecular oxygen in the absence of sacrificial co-reductant.

3.2.2 *Effects of Reaction Conditions*

3.2.2.1 Effect of Reaction Temperature The impact of reaction temperature on the epoxidation of styrene over Co/TS-1(1.03 wt.%) is depicted in Fig. 7. With increasing the temperature from 363 to 383 K, the styrene conversion and the epoxide selectivity change trend appeared an arch shape. The benzaldehyde selectivity and the benzoic acid selectivity first decreased, and then increased a little with increasing the reaction temperature from 363 to 383 K.

3.2.2.2 Effect of Flow Rate of O_2 As can be seen from Fig. 8, the styrene conversion and the epoxide selectivity increased with increasing the flow rate of oxygen from 40 to 80 mL/min. The benzaldehyde selectivity and benzoic acid selectivity kept in a constant value in all with an increase of the flow rate of O_2.

3.3 Recycling Studies

In order to study the stability of the catalyst, repeated runs of the recovered Co/TS-1 (2.15 wt.%) for the epoxidation of styrene have been carried out. The results are shown in Fig. 9. Neither styrene conversion nor epoxide selectivity was changed significantly in the repeated runs. The results indicate that the Co/TS-1 catalyst is stable for the epoxidation of styrene.

3.4 Reaction Mechanism

Effect of reaction time on the epoxidation of styrene with molecular oxygen over Co/TS-1(2.32 wt.%) was studied. The result is shown in Fig. 10. It can be seen that the styrene conversion increased linearly and the epoxide selectivity increased slowly with prolonging reaction time (from 0.5 to 3.5 h). However, the benzaldehyde selectivity

Table 2 Effect of support on the styrene epoxidation by O_2

Catalyst	Styrene conversion	Slectivity(%)			
		Epoxide	Benzaldehyde	Benzoic acid	TOF(h^{-1})
Co/NaY(2.03 wt.%)	50.3	55.9	36.5	7.6	7.0
Co/MCM-41(1.76 wt.%)	50.9	53.0	40.1	6.9	7.6
Co/γ-Al2O3(2.12 wt.%)	33.1	44.7	37.2	18.1	3.5
Co/TS-1(2.32 wt.%)	94.5	74.3	20.5	5.2	15.3

Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; reaction temperature, 373 K; flow rate of O_2, 80 mL/min; duration, 3.5 h

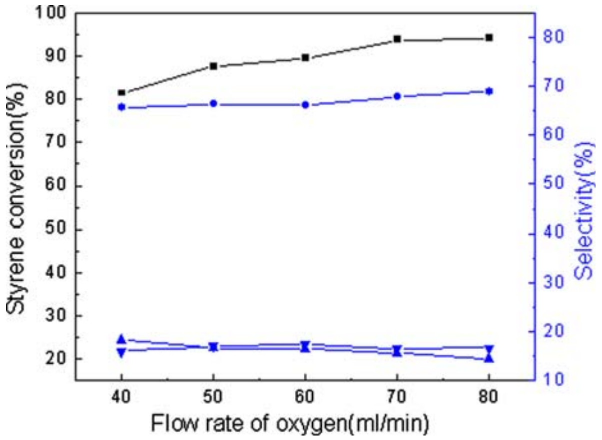


Fig. 8 Effect of O_2 flow rate on the epoxidation of styrene by O_2 over Co/TS-1(1.03 wt.%): (■) styrene conversion, (●) epoxide selectivity, (▲) benzaldehyde selectivity, (▼) benzoic acid selectivity. Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; reaction temperature, 373 K; duration, 3.5 h

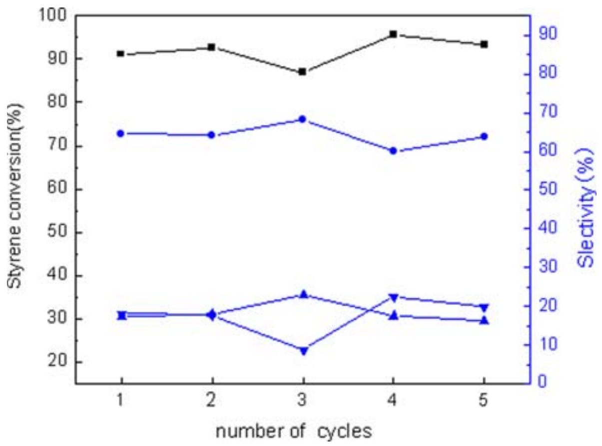


Fig. 9 Recycling study of the catalyst:(■) styrene conversion, (●) epoxide selectivity, (▲) benzaldehyde selectivity, (▼) benzoic acid selectivity. Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, Co/TS-1(2.15 wt.%), 200 mg; reaction temperature, 373 K; flow rate of O_2, 80 mL/min; duration, 3.5 h

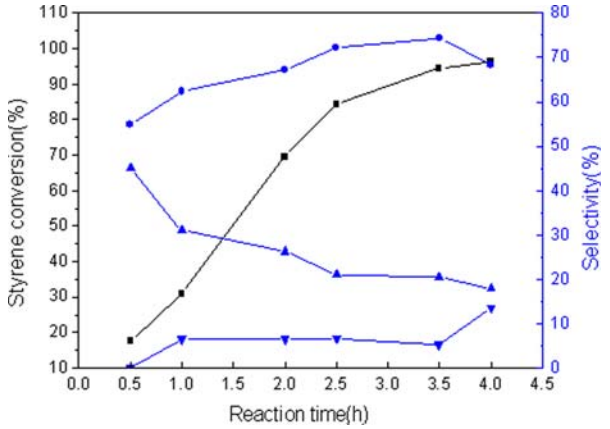
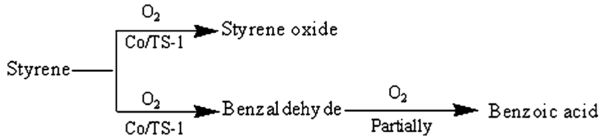


Fig. 10 Effect of reaction time on the epoxidation of styrene by O_2 over Co/TS-1(2.32 wt.%): (■) styrene conversion, (●) epoxide selectivity, (▲) benzaldehyde selectivity, (▼) benzoic acid selectivity. Reaction conditions: styrene, 6 mmol; DMF, 20 mL; catalyst, 200 mg; reaction temperature, 373 K; flow rate of O_2, 80 mL/min



Scheme 1 Reaction scheme for the epoxidation of styrene

decreased markedly with prolonging reaction time (from 0.5 to 4 h). After 1 h reaction, the benzoic acid selectivity maintained at around 5% until the reaction time reached 3.5 h. Being the main products at the begin of the reaction, the styrene oxide and benzaldehyde were formed simultaneously in the reaction. However, benzoic acid was mainly formed by oxidation of benzaldehyde. When the reaction time reached 4 h, the epoxide selectivity decreased and benzoic acid selectivity increased slightly in comparison with 3.5 h of reaction time. Therefore, the optimum reaction time is 3.5 h. The observed variations of the product selectivities suggest an occurrence of two parallel reactions in the styrene epoxidation, as shown in scheme 1. To study the mechanistic behaviour and also to identify the active species formed in the epoxidation of styrene, a small amount of free radical scavenger hydroquinone (50 mg) was added to the reaction system, and catalytic activity with Co/TS-1(2.32 wt.%) was studied. Under the same reaction conditions specified in Table 1, the conversion of styrene to styrene oxide is found to be almost zero. So, this can prove that the reaction may follow the free-radical type mechanism [7]. The relevant research in depth on the reaction mechanism is still under way, and the result will be published elsewhere.

4 Conclusion

Styrene epoxidation was carried out over eco-friendly and efficient heterogeneous Co/TS-1 by molecular oxygen in the absence of sacrificial co-reductant. A 94.5 mol% conversion of styrene with 74.3 mol% styrene oxide selectivity was achieved using Co/TS-1(2.32 wt.%). Many factors including catalyst preparation conditions (the Co loading, calcination temperature and support) and reaction conditions (temperature and flow rate of O2) have an evident influence on the catalytic epoxidation activity and selectivity. The optimum conditions are as follows: the Co loading, about 2 wt.%; calcination temperature, 723 K; the optimum support, TS-1; reaction temperature, 373 K; the flow rate of O_2, 80 mL/min. The reaction follows the radical type mechanism.

References

1. Choudhary VR, Jha R, Chaudhari NK, Jana P (2007) Catal Commun 8:1556
2. Chatterjee D, Basak S, Muzart J (2007) J Mol Catal A: Chem 271:270
3. Liang J, Zhang Q-H, Wu H-L, Meng G-Y, Tang Q-H, Wang Y (2004) Catal Commun 5:665
4. Opre Z, Mallat T, Baiker A (2007) J Catal 245:482
5. Rahiman AK, Rajesh K, Bharathi KS, Sreedaran S, Narayanan V (2006) Appl Catal A Gen 314:216
6. Tsuda Y, Matsui S, Takahashi K (1999) J Mol Catal A: Chem 148:183
7. Sebastian J, Jinka KM, Jasra RV (2006) J Catal 244:208
8. Zhan H-J, Xia Q-H, Lu X-H, Zhang Q, Yuan H-X, Su K-X, Ma X-T (2007) Catal Commun 8:1472
9. Jin GJ, Lu GZ, Guo YL, Guo Y, Wang JS (2005) J Mol Catal A: Chem 232:165
10. Patil NS, Uphade BS, Jana P, Sonawane RS, Bhargava SK, Choudhary VR (2004) Catal Lett 94(1–2):89
11. Patil NS, Uphade BS, McCulloh DG, Bhargava SK, Choudhary VR (2004) Catal Commun 5:681
12. Yin DH, Qin LS, Liu JF, Li CY, Jin Y (2005) J Mol Catal A: Chem 240:40
13. Laha SC, Kumar R (2001) J Catal 204:64
14. Laha SC, Kumar R (2002) J Catal 208:339
15. Rode CV, Nehete UN, Dongare MK (2003) Catal Commun 4:365
16. Stangland EE, Taylor B, Andres RP, Delgass WN (2005) J Phys Chem B 109:2321
17. Nijhuis TA, Gardner TQ, Weckhuysen BM (2005) J Catal 236:153
18. Aguirre P, Zolezzi S, Parada J, Bunel E, Moya SA, Sariego R (2006) Appl Organomet Chem 20:260
19. Meng XJ, Sun ZH, Wang RW, Lin S, Sun JM, Yang M, Lin KF, Jiang DZ, Xiao FS (2001) Catal. Lett 76(1–2):105
20. Tang QH, Zhang QH, Wu HL, Wang Y (2005) J Catal 230:384
21. Kantama ML, Rao BPC, Reddy RS, Sekhar NS, Sreedhar B, Choudary BM (2007) J Mol Catal A: Chem 272:1
22. Xu G, Xia Q-H, Lu X-H, Zhang Q, Zhan H-J (2006) J Mol Catal A: Chem 266:180
23. Choudhary VR, Patil NS, Bhargava SK (2003) Catal. Lett 89(1–2):55
24. Wang RP, Guo XW, Wang XS, Hao JQ, Li G, Xiu JH (2004) Appl Catal A Gen 261:7
25. Cumaranatunge L, Delgass WN (2005) J Catal 232:38
26. Liu XW, Wang XS, Guo XW, Li G (2004) Catal Today 93–95:505