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Cobalt(II) acetylacetonate complex immobilized on aminosilane-modified SBA-15 as an efficient catalyst for epoxidation of *trans*-stilbene with molecular oxygen

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From environmental and economic points of view, it is highly desirable to develop a clean and efficient catalytic process to produce epoxides. An attractive approach is to use a solid, recyclable catalyst and molecular oxygen as the oxidant without any sacrificial reductant or other additives. Nonetheless, the catalysts reported up to now still cannot balance catalytic activity with epoxide selectivity. It is of great importance to explore novel catalysts with both high activity and selectivity for the epoxidation of olefins. In this work, cobalt(II) acetylacetonate ($Co(acac)_2$) was covalently bonded to the silica surface of SBA-15 molecular sieve by multi-step grafting using 3-aminopropytrimethoxysilane (APTS) as coupling agent. Characterizations with nitrogen physisorption, X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis suggested that the metal complex was successfully immobilized on the aminosilane-modified SBA-15 surface and the channel structure remained intact. The synthesized $Co(acac)_2$APTS@SBA-15 catalyst was used in the epoxidation of *trans*-stilbene (TS) with molecular oxygen. Compared to the sample prepared by the impregnation method as well as $Co(acac)_2$ solutions under the same reaction conditions, the $Co(acac)_2$ immobilized catalyst exhibited remarkably higher TS conversion and *trans*-stilbene oxide (TSO) selectivity. An increase in TS conversion with Co content was observed when the Co loading was lower than 0.70% and the 0.70$Co(acac)_2$APTS@SBA-15 sample exhibited the best catalytic performance. Up to 50.1% of TS conversion could be achieved within 6 h, affording TSO selectivity as high as 96.7%. The superior catalytic performance of this particular catalyst is attributed to the high activity of the immobilized $Co(acac)_2$ species on SBA-15.

Keywords: SBA-15; cobalt acetylacetonate; *trans*-stilbene; epoxidation; molecular oxygen

Introduction

Epoxides are commercially important intermediates in the synthesis of various fine chemicals and pharmaceuticals. Currently, epoxides are mainly produced either by using organic peracid as the oxidant or by a chlorohydrins process, and a large amount of chemical waste is formed in both cases.[1] From environmental and economic points of view, it is highly desirable to develop a clean and efficient catalytic process to produce epoxides.[2] An attractive approach is to use a solid, recyclable catalyst and molecular oxygen as the oxidant without any sacrificial reductant or other additives.[3,4]

Due to their superior catalytic performances in epoxidation, cobalt-based catalysts have attracted significant attention in the past few years.[5–12] A composite catalyst of Co–ZSM-5 coordinated with organic ligands was reported to achieve 96.9% conversion and 94.0% selectivity for the epoxidation of styrene with air.[6] Cobalt oxide (CoO_x) prepared by a direct calcination of cobalt nitrate was also reported to be considerably active for the epoxidation of styrene with air in *N*,*N*-dimethylformamide (DMF) under mild conditions.[7] Cui *et al.* introduced a certain amount of cobalt ions into SBA-15 framework using a pH-adjusting method or an adsorption method, and the afforded Co–SBA-15 was highly active in epoxidation.[8,9] In our previous work, Co^{2+} introduced into NaX, MCM-41 and TUD-1 using an ion exchange method or a direct hydrothermal synthesis method showed high activity in epoxidation.[10–12] Nonetheless, the catalysts reported up to now still cannot balance catalytic activity with epoxide selectivity. It is of great importance to explore novel catalysts with both high activity and selectivity for the epoxidation of olefins.

In the study reported here, cobalt(II) acetylacetonate ($Co(acac)_2$) was covalently bonded to the silica surface of SBA-15e_k; molecular sieve by multi-step grafting using 3-aminopropytrimethoxysilane (APTS) as the coupling agent. The resulting material was used for the epoxidation of *trans*-stilbene (TS) with molecular oxygen.

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Experimental

Catalyst synthesis

SBA-15 silica was synthesized according to a well-established procedure reported by Zhao *et al.* using tetraethylorthosilicate (TEOS) as the silica source and surfactant P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800; Aldrich) as the structure-directing agent under acidic conditions.[13] Typically, a solution of P123:HCl:TEOS:H_2O = 2:60:4.25:12 (mass ratio) was prepared by dissolving 4.0 g of P123 in 80 g of 2 M HCl and 20 g of water under stirring before adding 8.8 g of TEOS dropwise. The gel solution was stirred at 40°C for 24 h followed by aging at 100°C for 48 h. After cooling to room temperature, the resulting solid was recovered by filtration, washed with deionized water and dried under ambient conditions overnight. The resulting SBA-15 powder was calcined at 540°C for 6 h in air to remove the template.

SBA-15 surface modification was performed according to a procedure similar to that reported by Oliveira and co-workers.[14] The calcined SBA-15 (1.0 g) was dehydrated at 150°C under vacuum overnight, and then added to a solution of APTS (3 mmol) in anhydrous toluene. The mixture was refluxed for 6 h with continuous stirring under dry nitrogen atmosphere. The resultant solid was filtered, washed with anhydrous toluene and dried overnight under vacuum at 80°C. The obtained material was denoted as APTS@SBA-15. This APTS@SBA-15 (1.0 g) was refluxed with a solution of $Co(acac)_2$ in anhydrous toluene (1.0–10.0 mmol l^{-1}) for 10 h. The solid material was then filtered, washed with anhydrous toluene and dried at 100°C overnight. The material was named as $Co(acac)_2$APTS@SBA-15. For comparison, Co–SBA-15 was prepared by a conventional wet impregnation method. The calcined SBA-15 was immersed in an aqueous solution of $Co(NO_3)_2$ stirred for 4 h, and allowed to rest for 20 h. The impregnated sample was obtained by heating at 70°C to evaporate excess water, followed by drying at 100°C overnight and calcining at 500°C for 3 h.

Catalyst characterization

Powder X-ray diffraction (XRD) patterns were measured using a Bruker Advance 8 X-ray diffractometer equipped with a rotating anode using Cu Kα radiation (40 kV and 40 mA). Diffraction data were recorded from 0.5° to 8° (resolution of 0.02°). Nitrogen physisorption isotherms were measured at −196°C with a static volumetric instrument (Autosorb-6B, Quanta Chrome). Prior to each measurement, the SBA-15 powder was degassed at 150°C to a residual pressure below 10^{-4} Torr. The specific surface area was estimated using the BET method. The pore size distribution were calculated from the desorption branch using the BJH method. Transmission electron microscopy (TEM) observations were performed with a JEOL JEM-2100F operated at 200 kV. Samples were suspended in ethanol and dried on carbon-coated copper grids. Fourier transform infrared (FT-IR) spectra were recorded in the range 400–4000 cm^{-1} with a Nicolet Nexus FT-IR spectrometer using KBr pellets as matrix. Thermogravimetric analyses (TG-DTA) were performed using a Netzsch STA449C system at a heating rate of 10°C min^{-1} under nitrogen. The cobalt content was analyzed with a Dualview Optima 5300DV inductively coupled plasma optical emission spectroscopy (ICP-OES) system after the sample was dissolved in a HF (40 wt%) solution.

Catalytic reaction

The epoxidation of TS was carried out using a bath-type reactor operated under atmospheric conditions. TS (1 mmol, 96 wt%, Aldrich), 0.1 g of $Co(acac)_2$APTS@SBA-15 catalyst and 10 ml of DMF were introduced into a round-bottom flask, followed by bubbling pure molecular oxygen at a flow rate of 10 ml min^{-1} under vigorous stirring (800 rpm). The reaction was initiated by immersing the flask into an oil bath at the desired reaction temperature and maintained for the designated reaction time. Each liquid product was analyzed using an Agilent GC (6890) equipped with a flame ionization detector and a DB-5 capillary column (30 m × 0.32 mm × 0.25 mm).

Results and discussion

Catalyst characterizations

Table 1 summarizes the content of cobalt determined using ICP analysis. Evidently, with a certain amount of APTS@SBA-15 and a fixed volume of solution for preparation, the cobalt loading of a sample can be regulated by changing the concentration of $Co(acac)_2$ solutions. At a low concentration of $Co(acac)_2$, e.g. the concentration of $Co(acac)_2$ is 1.0 mmol l^{-1} or less, more than 70% of the $Co(acac)_2$ can be incorporated into SBA-15. Further increasing the concentration of $Co(acac)_2$ solution leads to an increase in the cobalt content in the final sample, but the proportion of $Co(acac)_2$ capable of being incorporated into SBA-15 decreases markedly. For example, when a $Co(acac)_2$ solution of 10.0 mmol l^{-1} is used for the preparation, the final cobalt content in the sample is 1.46 wt%, but only 49% of the $Co(acac)_2$ in solution can be immobilized on the surface of SBA-15.

The physical properties of SBA-15 and $Co(acac)_2$APTS@SBA-15 samples are summarized in Table 2. A decrease in total pore volume (from 0.93 to 0.51 cm^3 g^{-1}) and BET surface area (from 632 to 421 m^2 g^{-1}) can be observed after the SBA-15 support is modified with APTS. The monotonic decrease in average pore size from 5.1 to 4.8 nm with Co content changing from 0 to 1.46 wt% might reflect a homogeneous coverage of the SBA-15 inner pores, which is consistent with the deceased pore volumes.[14]

The XRD pattern in Fig. 1(a) shows that SBA-15 exhibits three well-resolved reflections at 2θ of 0.5–3°, including one strong (100) peak and two weak (110) and (200) peaks. These results suggest that the synthesized SBA-15 possesses a highly ordered hexagonal mesoporous silica framework. The surface modification and grafting $Co(acac)_2$ species onto SBA-15 slightly decrease the intensity of these diffraction peaks. The decrease in intensity becomes notable when the Co content is 1.46 wt%, although the hexagonal regularity of the SBA-15 support remains intact. The decrease in peak intensity suggests the irregular organization at long-range order of the mesoporous structure, arising from the

Table 1. Cobalt content in samples

Sample	Concentration of $Co(acac)_2$ (mmol l^{-1})	Proportion of cobalt immobilized (%)	Cobalt content (wt%)[a]
0.21$Co(acac)_2$APTS@SBA-15	1.0	70	0.21
0.39$Co(acac)_2$APTS@SBA-15	2.0	65	0.36
0.70$Co(acac)_2$APTS@SBA-15	4.0	58	0.70
1.46$Co(acac)_2$APTS@SBA-15	10.0	49	1.46

[a] Cobalt content determined by ICP analysis.

Table 2. Physical properties of synthesized $Co(acac)_2APTS@SBA-15$ samples

Sample	BET ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
SBA-15	632	0.93	6.3
APTS@SBA-15	421	0.51	5.1
$0.21Co(acac)_2APTS@SBA-15$	409	0.50	5.0
$0.36Co(acac)_2APTS@SBA-15$	403	0.49	4.9
$0.70Co(acac)_2APTS@SBA-15$	397	0.48	4.9
0.70Co/SBA-15[a]	583	0.88	6.2
$1.46Co(acac)_2APTS@SBA-15$	390	0.47	4.8

[a] Prepared by the impregnation method.

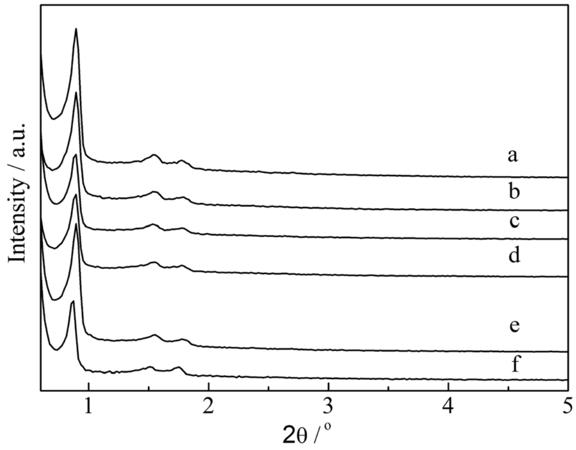


Figure 1. XRD patterns of SBA-15 and $Co(acac)_2APTS@SBA-15$ samples: (a) SBA-15; (b) APTS@SBA-15; (c) $0.21Co(acac)_2APTS@SBA-15$; (d) $0.36Co(acac)_2APTS@SBA-15$; (e) $0.70Co(acac)_2APTS@SBA-15$; (f) $1.46Co(acac)_2APTS@SBA-15$.

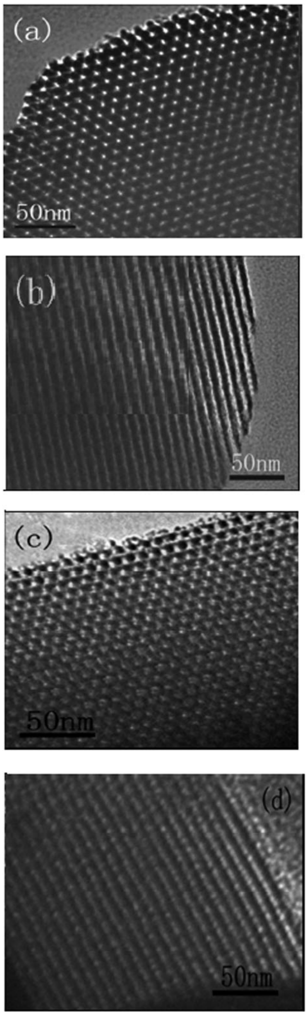


Figure 2. TEM images: (a) $0.70Co(acac)_2APTS@SBA-15$ (viewed along the pore direction); (b) $0.70Co(acac)_2APTS@SBA-15$ (parallel fringes, side on view); (c) $1.46Co(acac)_2APTS@SBA-15$ (viewed along the pore direction); (d) $1.46Co(acac)_2APTS@SBA-15$ (parallel fringes, side on view).

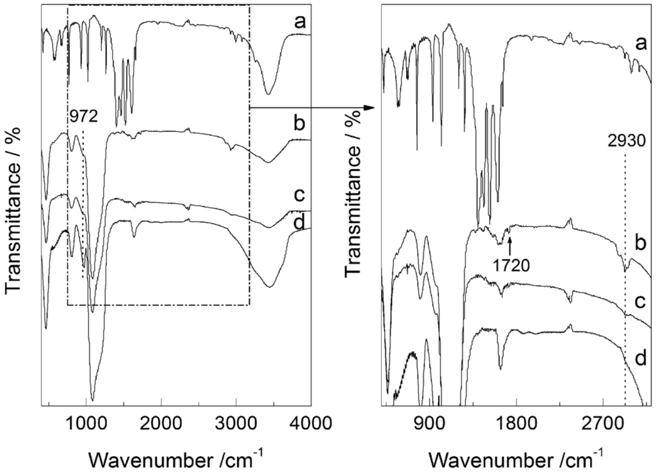


Figure 3. FT-IR spectra: (a) $Co(acac)_2$; (b) $0.70Co(acac)_2APTS@SBA-15$; (c) APTS@SBA-15; (d) SBA-15.

incorporation of APTS and $Co(acac)_2$ species into the channels of SBA-15. TEM observations rule out the possibility of pore collapse during the modification and grafting procedures. Figure 2 clearly shows that the hexagonal arrays of mesoporous channels of SBA-15 are well preserved for $Co(acac)_2APTS@SBA-15$ samples synthesized in this work.

Figure 3 shows the FT-IR spectra of $Co(acac)_2$, $0.7Co(acac)_2APTS@SBA-15$, APTS@SBA-15 and SBA-15. The spectrum of $Co(acac)_2$ exhibits well-defined bands at about 1604 and 1520 cm^{-1}, which can be ascribed to C O and C C vibrations, respectively.[15] The band at about 1398 cm^{-1} is due to CH_3 vibration.[16] The spectra of SBA-15 and modified support are dominated by strong bands characteristic of the support framework. The bands in the range 3300–3800 cm^{-1} are due to surface hydroxyl groups, while the bands in the range 750–1300 cm^{-1} are due to lattice vibrations. The bands at about 801 and 1085 cm^{-1} are assigned to Si O Si vibrations and the band at about 972 cm^{-1} is attributable to Si OH vibrations.[17] No significant changes are observed in the SBA-15 structure vibrations after the modification, indicating that its framework remains unchanged. The spectrum of APTS@SBA-15 shows an additional band at about 2930 cm^{-1} due to the aliphatic (CH_2) stretching of the propyl chain of APTS, suggesting that the SBA-15 surface is functionalized with the linking agent. The marked decrease in the intensity of the band at 972 cm^{-1} compared to that of the unmodified SBA-15 is probably due to the functionalization of the surface silanol groups. After $Co(acac)_2$ species are introduced into SBA-15 by grafting, as shown in Fig. 3(b), the characteristic band at about 1720 cm^{-1}, which is ascribed to the imine group (C N) vibration, can be observed.[18] At the same time, a band at about 1578 cm^{-1} which is assignable to the vibration of acetylacetonate ring can be also seen in the spectrum of 0.7Co(acac)$_2$APTS@SBA-15.[19]

Figure 4 shows the TG-DTA traces of SBA-15, APTS@SBA-15 and Co(acac)$_2$APTS@SBA-15. It is evident that an endothermal peak at about 80°C can be observed in the TG-DTA traces of all samples, which is attributed to the evaporation of the adsorbed water in these samples. The weight loss behavior of water shows that, after the pores of SBA-15 are modified by APTS or occupied by Co(acac)$_2$, its water adsorption capacity is significantly decreased, indicating that the SBA-15 sample becomes more hydrophobic. A sharp exothermal peak at about 320°C can be observed for the APTS@SBA-15 sample, which is attributed to the decomposition of surface organic NH$_2$ groups.[20] It can be noted that this exothermal peak for the Co(acac)$_2$APTS@SBA-15 sample becomes weak and broad and shifts to higher temperature at about 425°C. These observations suggest that an axial coordination between the organic amine molecules and the Co(acac)$_2$ complexes occurs in the pores of SBA-15, which is consistent with the result reported by Fu and co-workers.[20] It is known that the decomposition of Co (acac)$_2$ usually occurs near 276°C. This shift to a high temperature (425°C) as compared with uncombined Co(acac)$_2$ suggests that there is a strong coordination between the organic amine molecules and the Co(acac)$_2$ complexes. We also note that the weight loss of this decomposition of 0.7Co(acac)$_2$APTS@SBA-15 (11.6%) is obviously higher than that of APTS@SBA-15 (9.1%). These are essentially consistent with the results of nitrogen physisorption, FT-IR spectroscopy and the measured Co content.

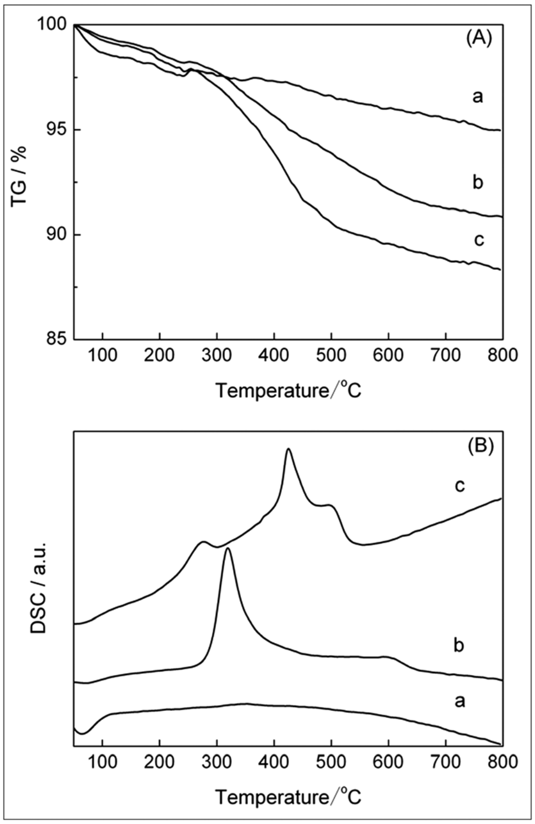
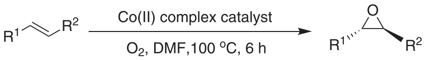


Figure 4. TG-DTA traces: (a) SBA-15; APTS@SBA-15; (c) 0.70Co (acac)$_2$APTS@SBA-15.

Epoxidation of TS catalyzed by Co(acac)$_2$APTS@SBA-15

The epoxidation of TS with molecular oxygen over Co (acac)$_2$APTS@SBA-15 catalyst was carried out at 100°C for 6 h (as shown in Scheme 1), and the results are summarized in Table 3. *trans*-Stilbene oxide (TSO) is the main product, along with benzaldehyde (1.8–3.3%) and benzoic acid (0.1–0.5%) as by-products. In the absence of any catalyst, no TS conversion is found. Pure silica SBA-15 or modified SBA-15 without Co gives a TS conversion of less than 1.0%. Adding Co markedly increases the TS conversion, and the TS conversion increases with the Co content, suggesting the Co species immobilized on the surface SBA-15 as the active sites for the epoxidation of TS with O$_2$. The 0.7Co(acac)$_2$APTS@SBA-15 sample exhibits the best catalytic performance with a TS conversion of 50.1% and a TSO selectivity of 96.7%. A further increase in the Co content, however, lowers the TS conversion. Only 45.3% of TS conversion can be achieved over the 1.46Co(acac)$_2$APTS@SBA-15 sample. Our previous work has shown that oxygen species with a radical nature produced via the activation of molecular oxygen play an important role in the epoxidation reaction.[11] It is possible that the Co content in samples can control the concentration of oxygen free radicals produced. A suitable Co content may maintain the concentration of radical intermediates which is beneficial for the high conversion of TS. Compared to a 0.70Co/SBA-15 catalyst prepared by the impregnation method and 1.0Co-TUD-1[12] prepared by a direct hydrothermal synthesis method under the same reaction conditions, 0.70Co(acac)$_2$APTS@SBA-15 exhibits markedly higher TS conversion (50.1% versus 28.6% and 40.1%) and TSO selectivity (96.7% versus 94.4% and 94.1%). Although a Co(acac)$_2$ solution can also catalyze the oxidation of TS with molecular oxygen to afford TSO as the main product, only 25.4% of TS conversion can be obtained. The work of Canali and Sherrington shows that acetylacetonate complexes can easily deactivate in homogeneous liquid solution due to the formation of μ-oxo dimers and other polymeric species.[21] This may be a possible explanation for the



Scheme 1. Immobilized Co(II) complex-catalyzed *trans*-stilbene epoxidation.

Table 3. Epoxidation of *trans*-stilbene over Co(acac)$_2$APTS@SBA-15 samples[a]

Sample	Conversion (%)	Epoxide selectivity (%)	Yield (%)
SBA-15	<1.0	—	—
APTS@SBA-15	<1.0	—	—
0.21Co(acac)$_2$APTS@SBA-15	30.6	98.1	30.0
0.36Co(acac)$_2$APTS@SBA-15	40.4	97.6	39.4
0.70Co(acac)$_2$APTS@SBA-15	50.1	96.7	48.4
1.46Co(acac)$_2$APTS@SBA-15	45.3	96.2	43.6
Co(acac)$_2$	25.4	91.9	23.4
0.70Co-SBA-15[b]	28.6	94.4	27.0
1.0Co-THD-1[c]	40.1	94.1	37.7

[a] Catalyst, 0.1 g; TS, 1 mmol; DMF, 10 ml; time, 6 h; temperature, 100°C; O$_2$ flow rate,10 ml min^{-1}.

[b] Prepared by the impregnation method.

[c] Reported in the literature.[12]

low activity of the $Co(acac)_2$ solution. Therefore, the $Co(acac)_2$ species immobilized in the pores of SBA-15 are suggested as the highly active components for the epoxidation of TS with molecular oxygen.

Various reaction parameters such as amount of solvent, temperature and oxygen pressure were investigated for the purpose of improving the catalytic performance of the $0.7Co(acac)_2APTS@SBA-15$ catalyst.

Figure 5 shows the effect of the amount of solvent on the epoxidation. TS conversion increases with the amount of solvent up to 15 ml. Nevertheless, an adverse effect is observed on further increasing the amount of solvent. Based on our previous studies and other researchers' work,[5,9,11] the epoxidation with O_2 using Co-based catalyst proceeds via a radical intermediate. A suitable amount of solvent may maintain the concentration of radical intermediate which is beneficial for the high conversion of TS. TSO selectivity also increases with the amount of solvent, but the change is not very evident. With the amount of solvent increasing from 5 to 30 ml, the TSO selectivity increases from 96.0 to 98.3%.

Figure 6 shows the effect of reaction temperature on the epoxidation. At temperatures lower than 70°C, almost no TS conversion can be found. As the temperature increases from 70 to 120°C, the TS conversion and TSO selectivity increase from 1.6 to 89.5% and from 95.8 to 99.3%, respectively. These results suggest that a high reaction temperature is advantageous to the epoxidation.

Figure 7 shows the effect of O_2 pressure on the epoxidation. With an increase in O_2 pressure, which was regulated by dilution of O_2 with Ar at different O_2/Ar ratios, the TS conversion increases significantly, especially when the O_2 pressure is lower than 0.02 MPa. This confirms that the active oxygen species responsible for the epoxidation reaction are generated from the activation of O_2. However, a slight decrease in the selectivity towards TSO occurs with increasing O_2 pressure. This might suggest that an increase in oxygen pressure results in the preferential formation of parallel by-products benzaldehyde and benzoic acid.

Recycling tests of the $Co(acac)_2APTS@SBA-15$ catalyst were carried out at 100°C. As shown in Fig. 8, the TS conversion and TSO selectivity are essentially constant in the repeat runs, implying the high stability and recyclability of the immobilized $Co(acac)_2$ on SBA-15 as an efficient catalyst for TS epoxidation. The loss of only 3.0 wt% of cobalt after six runs, determined using ICP analysis, supports the observed catalytic stability.

More oxidations using molecular oxygen were carried out for a variety of olefins, with the results summarized in Table 4. The $0.7Co(acac)_2APTS@SBA-15$ sample was chosen as a representative catalyst for all reactions due to its high activity. A variety of olefins

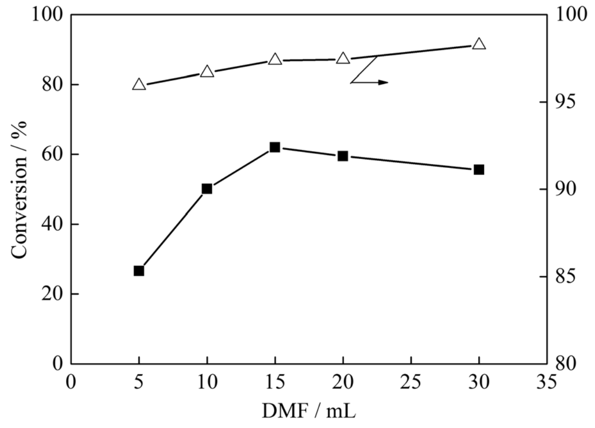


Figure 5. Effect of amount of solvent on epoxidation of TS. Catalyst = 0.1 g; TS = 1 mmol; t = 6 h; T = 100°C; O_2 flow rate = 10 ml min^{-1}.

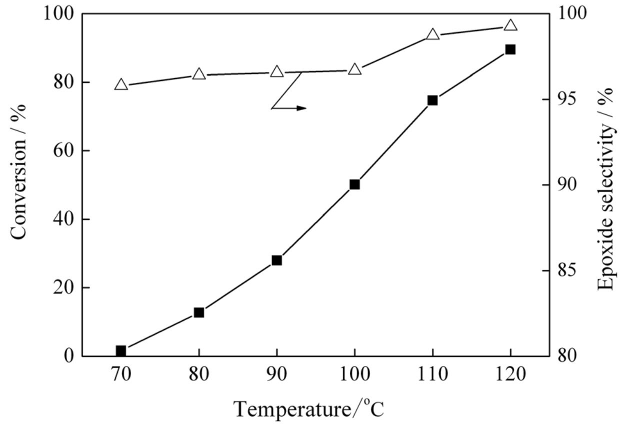


Figure 6. Effect of reaction temperature on catalytic performances for the epoxidation of TS. Catalyst = 0.1 g; TS = 1 mmol; DMF = 10 ml; t = 6 h; O_2 flow rate = 10 ml min^{-1}.

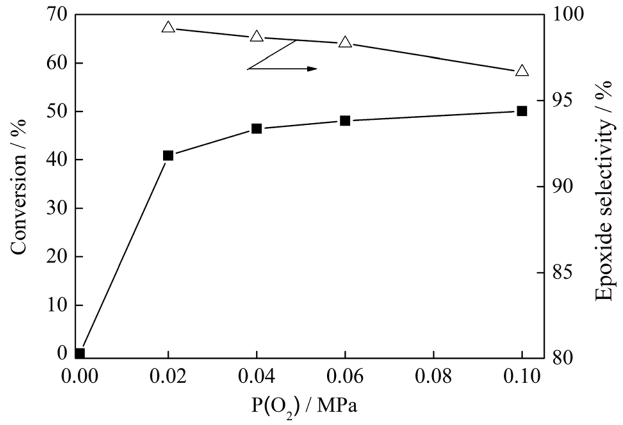


Figure 7. Effect of O_2 pressure on catalytic performances for the epoxidation of TS. Catalyst = 0.1 g; TS = 1 mmol; DMF = 10 ml; t = 6 h; T = 100°C; total flow rate = 10 ml min^{-1}.

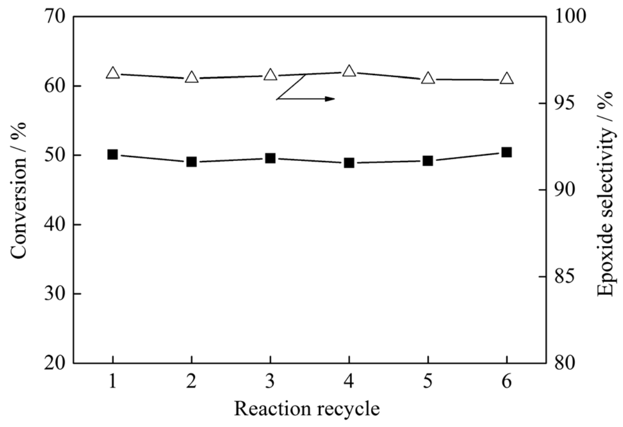


Figure 8. Recycling of $0.70Co(acac)_2APTS@SBA-15$ for the epoxidation of TS with O_2. Catalyst = 0.1 g; TS = 1 mmol; DMF = 10 ml; t = 6 h; T = 100°C; O_2 flow rate = 10 ml min^{-1}.

Table 4. Epoxidation of various olefins with O_2 over Co(acac)$_2$APTS@SBA-15[a] RR'C C R" + O_2 → RR'COC R"

Entry	Substrate	Time (h)	Conversion (%)	Epoxide selectivity (%)	Yield (%)
1	PhCH CH_2	12	75.4	58.2[b]	43.9
2	H_3CPhCH CH_2	12	93.1	60.9[c]	56.7
3	ClPhCH CH_2	24	64.9	40.6[d]	26.3
4	$Ph(CH_3)C$ CH_2	12	97.7	62.4[e]	61.0
5	PhCH $CHCH_3$	24	91.3	92.9	84.8
6	Ph_2C CH_2	24	87.6	72.1[f]	63.2
7	PhCH CHPh	24	85.3	98.5	84.0
8	$(CH_2)_6CH$ CH	24	61.8	94.6	58.5

[a] Catalyst, 0.1 g; olefin, 1 mmol; DMF, 10 ml; temperature, 100°C; O_2 flow rate, 10 ml min^{-1}.

[b] Benzaldehyde and benzoic acid were formed as side products.

[c] 4-Methylbenzaldehyde and 4-methylbenzoic acid were formed as side products.

[d] 4-Chlorobenzaldehyde and 4-chlorobenzoic acid were formed as side products.

[e] Acetophenone was formed as side product.

[f] Benzophenone was formed as side product.

are converted to the corresponding epoxide with high yields within 12–24 h of reaction at 100°C. The substrates containing an electron-donating group (such as CH_3 or phenyl) adjacent to the double bond (entry 2) or in the aromatic ring of olefins (entry 4) are more easily oxidized than those containing an electron-withdrawing group (entry 3). Although non-terminal olefins (such as *trans*-β-methylstyrene and TS) can show a high epoxide selectivity, their conversion is lower than that of similar terminal olefins under the same reaction conditions. We note that cycloolefins, i.e. cyclooctene, can also be efficiently oxidized to the corresponding epoxides, thereby obtaining a high yield (entry 8).

Conclusions

The anchoring of Co(acac)$_2$ on SBA-15 was successfully achieved by a post-synthetic method using APTS as a linking agent. Various characterization techniques such as nitrogen physisorption, XRD, TEM, FT-IR spectroscopy and TG-DTA suggested that the metal complex was covalently attached to the inner surface of SBA-15 and its channel structure remained unchanged. The synthesized Co(acac)$_2$APTS@SBA-15 samples were catalytically active in the liquid-phase epoxidation of TS using molecular oxygen. Up to 50.1% of TS conversion can be achieved over 0.70Co(acac)$_2$APTS@SBA-15 within 6 h, with a TSO selectivity as high as 96.7%. The superior catalytic performance of this particular catalyst is attributed to the high activity of the immobilized Co(acac)$_2$ species on SBA-15. The Co content can control the concentration of oxygen free radicals produced, and a suitable Co content may maintain the concentration of radical intermediate which is beneficial for the high yield of TSO.

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