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ARTICLE

Immobilized molybdenum acetylacetonate complex on expanded starch for epoxidation of stillingia oil

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An active heterogeneous, namely molybdenum acetylacetonate complex immobilized on expanded corn starch (ECS-MoO₂(acac)₂), was prepared and its catalytic activity for epoxidation of stillingia oil with *tert*-butyl hydroperoxide (TBHP) was investigated. The heterogeneous catalysts were characterized using inductively coupled plasma optical emission spectrometry, Fourier transform infrared spectra, thermogravimetry and differential thermal analyses, scanning electron microscopy, N₂ adsorption-desorption and X-ray photoelectron spectroscopy. By using this catalyst, an environmentally benign process for epoxide production in a heterogeneous manner was developed. The catalyst could be recovered easily and reused without significant degradation in activity for at least 5 times.

1 Introduction

Stillingia oil is the seed oil of Chinese tallow tree. It has great potential as an important raw material for the production of oleochemicals because it has ca. 90% of unsaturated compounds and it is a non-edible oil. This oil could lead to a lower consumption of edible oils for chemical purposes. In addition, tallow tree can grow on most types of soil. The seed output is more than 100,000 metric tons every year in China.¹

The epoxidation of vegetable oils is commercially important since the epoxides produced from these renewable raw materials present numerous applications, including the fabrication of polyurethane foams (via oxirane ring opening to generate polyols),² synthetic detergents,³ coatings⁴ and lubricants.⁵ The production of biodegradable lubricants from epoxidized vegetable oils is of particular interest considering the undesirable impact on the environment associated with the use of mineral oil-based lubricants.

On an industrial scale, the epoxidation of plant oils is currently carried out with a percarboxylic acid, such as peracetic or performic acid. Soluble mineral acids, commonly sulfuric acid, are used as catalysts for this reaction. Therefore, environmental concerns related to the disposal of the salts formed during the final neutralization of the mineral acid and other technical problems associated with their use, such as corrosion and separation operations, constitute a strong driving force for searching alternatives to this technology.

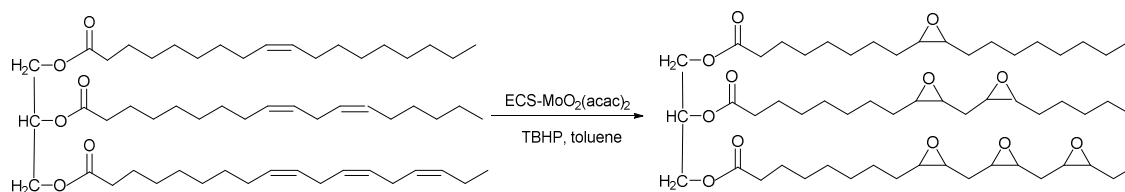
The use of transition metal complexes as homogeneous or heterogeneous catalysts could eliminate many of these problems and also provides a reaction that is very selective.^{6,7} Heterogeneous catalysts have some advantages over

homogeneous catalysts, such as facile separation and recovery of solid catalyst from the reaction mixture for recycling without tedious work.⁸ Among the transition metal complexes chiefly used as catalysts, molybdenum complexes are currently of considerable interest to promote oxidation reactions. Several studies in the literature have reported the epoxidation of alkenes using homogeneous⁶ or heterogeneous Mo(VI) catalysts with *tert*-butyl hydroperoxide (TBHP) as oxygen source.⁹ Recently Farias¹⁰ reported the use of molybdenum compounds heterogenized on montmorillonite K-10 for catalytic epoxidation of soybean and castor oils with TBHP. Epoxidation reactions presenting high yields and selectivity have been observed, as well as no leaching of metal, with an increase in the catalytic activity of recycling experiments.

Starch is a non-toxic, naturally abundant, biodegradable and high-functional biopolymer which can easily be modified by relatively simple chemical/physical modifications.¹¹⁻¹³ However, the application of starch as a material in areas such as composites,¹⁴ adsorbents^{15,16} and catalyst supports¹⁷ is restricted by its naturally low surface areas (<1 m² g⁻¹), pore volumes (<0.1 cm³ g⁻¹) and low site accessibility. Therefore, expanded starches, which have high surface area and pore volumes have emerged to be promising materials and their uses in catalysis are a key enabling area for the development of new and improved processes for chemical reactions.¹⁸

In the present study, we anchored molybdenum acetylacetonate onto expanded corn starch (ECS) functionalized with 3-aminopropyltriethoxysilane (APTES), through Schiff condensation between the carbonyl groups of the acetylacetonate ligands and the APTES amine. The ability of

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Scheme 1 The epoxidation of stilingia oil using TBHP as oxidant.

this heterogeneous catalytic system to catalyze the epoxidation of stilingia oil, using toluene as solvent and TBHP as oxidizing agent has been investigated (Scheme 1). Reusability is one of the most important properties of a supported heterogeneous catalyst because transition-metal complexes are often expensive and difficult to prepare. Therefore, recycling experiment of the catalyst was also performed in this work.

2 Experimental

2.1 Materials

Degummed stilingia oil was purchased from Dawu County, Hubei Province, PR China. The fatty acid composition (based on gas chromatography) is as follows: palmitic acid, 6.1%; stearic acid, 2.2%; oleic acid, 14.9%; linoleic acid, 31.4%; linolenic acid, 44.3% and traces of other fatty acids.

Toluene was acquired from Nanjing Chemical Factory (Nanjing, China). Sodium bisulphite and anhydrous sodium sulphate were purchased in analytical grade from Sigma-Aldrich. The solution of anhydrous TBHP in toluene was obtained by careful azeotropic distillation of 70% aqueous solution (Merck) in toluene and the concentration of the resulting solution was determined by ^1H NMR spectroscopy. Quantofix® Peroxide 100 test strips (Sigma) were used for the semi-quantitative determination of peroxide. All chemicals were used without further purification. High amylose corn starch and molybdenum acetylacetonate ($\text{MoO}_2(\text{acac})_2$) were purchased from Merck and used as received. It has been found that higher amylose starches generally give materials with higher surface area after treatment than lower amylose starches and retrograde more rapidly.¹⁹

2.2 Catalyst preparation

Expanded corn starch (ECS) was prepared according to previously reported method.¹³ In general, high amylose corn starch was initially gelatinized by heating in water at 100 °C for

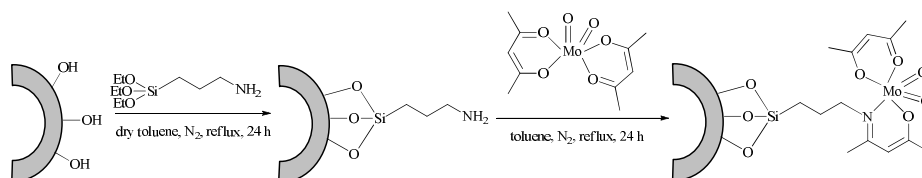
45 min and the gelatinous mixture was kept at 5 °C for 24 h. Precipitation and washing this gel with ethanol retains a rigid porous gel network with surface areas of $> 100 \text{ m}^2 \text{ g}^{-1}$.

The expanded corn starch is known to possess extensive hydroxyl groups on the framework surface of the porous material. These hydroxyl groups can react with APTES to yield amine functionalized expanded corn starch (ECS- NH_2). $\text{MoO}_2(\text{acac})_2$ was anchored onto the surface of amine functionalized expanded corn starch (ECS- $\text{MoO}_2(\text{acac})_2$) through Schiff-base condensation with free amine groups, covalently attached to the expanded corn starch surface with the carbonyl groups of the acetylacetonate ligand coordinated to molybdenum (VI). Namely, expanded corn starch (4.23 g) was added to a round bottom flask containing dry toluene (35 mL) and stirred under nitrogen. APTES (4.82 g, 22 mmol) was then added and the slurry was refluxed for 24 hours. After this time the vessel was cooled to room temperature and ethanol (135 mL) were added. The resulting ECS- NH_2 was recovered by filtration and washed with excess ethanol. The ECS- NH_2 (2 g) was then reacted with $\text{MoO}_2(\text{acac})_2$ (0.30 g, 0.92 mmol) in toluene for 24 h under nitrogen and refluxing conditions. The colored material was then filtered and thoroughly washed with acetone to remove impurities and non-anchored material to yield the final catalyst product ECS- $\text{MoO}_2(\text{acac})_2$. The preparation steps of the immobilization of $\text{MoO}_2(\text{acac})_2$ on expanded corn starch is presented in Scheme 2.

2.3 Catalyst characterization

The molybdenum content of the resulting solid ECS- $\text{MoO}_2(\text{acac})_2$ was quantitatively determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin Elmer Instruments Optima 2000 DV spectrometer and the loading was found to be 0.37 mmol g^{-1} . The specific surface area (SBET) of the samples was measured on a Autosorb-iQ instrument by N_2 adsorption-desorption isotherms at 77 K using the Brunauer-Emmett-Teller (BET) method. The IR spectra were recorded on a Nicolet 380 FT-IR instrument. A Quanta 200 field emission scanning electron

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Scheme 2 Schematic representation of molybdenum acetylacetonate immobilization onto APTES-functionalized expanded corn starch.

microscope (SEM) was used for the determination of the morphology of the catalyst. Thermogravimetry (TG) and differential thermal analyses (DTA) were carried out with a TGA instruments thermal analyzer TG 209F1 under N_2 atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The X-ray photoelectron spectrometer (XPS) spectra of the catalyst were carried out on a Kratos Axis Ultra DLD spectrometer. ^1H NMR spectra were recorded at a Bruker Avance 300 spectrometer.

2.4 Epoxidation of stilingia oil

Stilingia oil (1 g; 1.2 mmol; equivalent to 7.2 mmol of double bonds based on ^1H NMR) was placed in a 50 mL round bottomed flask connected to a reflux condenser. ECS- $\text{MoO}_2(\text{acac})_2$ (0.29 g; equivalent to 1.5 mol% of double bonds present in stilingia oil) and anhydrous TBHP (10.8 mmol; equivalent to 1.5 of double bonds present in oil) in toluene were added. The mixture was kept under vigorous stir and refluxed for 2 h. At the end of the required reaction time, the catalyst was removed from the reaction mixture by filtration. The filtrate flask was placed into an ice bath, sodium bisulphite solution (15%, w/v) was added slowly and the consumption of peroxide monitored using Quantofix Peroxide 100 test strips. The organic phase was separated, dried over anhydrous sodium sulphate, filtered and the solvent was removed using a rotary evaporator. A small quantity of the sample was analyzed by ^1H NMR techniques. ^1H NMR spectra of original and epoxidized stilingia oil are provided in Supplementary Information (S1 and S2). Conversions of double bonds, epoxide yields and selectivity were calculated based on ^1H NMR according to the following expression:⁶

$$NF = \frac{B}{4} \quad (0)$$

$$ND_i = \frac{A - NF}{2NF} \quad (0)$$

$$\text{Conversion}(\%) = \left[\frac{ND_r - ND_p}{ND_r} \right] \times 100 \quad (0)$$

$$\text{Epoxidation}(\%) = \left[\frac{I/2}{NF \times ND_r} \right] \times 100 \quad (0)$$

$$\text{Selectivity}(\%) = \left[\frac{\text{Epoxidation}(\%)}{\text{Conversion}(\%)} \right] \times 100 \quad (0)$$

Where B is the signal area of the 4 hydrogens on the methylene groups of the glycerol moiety. NF is the normalisation factor (i.e., relative peak area of one hydrogen). B was used as the reference because it remained unchanged before and after the epoxidation. A is the total peak area of the olefinic hydrogens ($-\text{CH}=\text{CH}-$) and the methine hydrogen of the glycerol moiety, which all appear at the same shift region (5.3-5.4 ppm). ND_r is the number of double bonds present in the original stilingia oil, obtained by substitution into Eq. (2) of the appropriate peak areas in spectrum of original stilingia oil. ND_p is the number of double bonds after epoxidation, obtained by substitution into Eq. (2) of the appropriate peak areas in spectrum of the epoxidized oil. I is the peak area associated with hydrogens of the epoxide groups ($-\text{CHOCH}-$) in spectrum of the epoxidized oil and occurs at chemical shifts of 2.9-3.1 ppm.²⁰

Recycling test of the catalyst was carried out as follows: the catalyst collected from last run by filtration was washed with toluene, dried at $110\text{ }^\circ\text{C}$ under reduced pressure for 6 h and subjected to the next catalytic run under optimized reaction conditions. Reactions using only the ECS as catalyst were also done. All of the above reactions were performed at least three times independently and presented good reproducibility (error < 5%).

3 Results and Discussion

3.1 Catalyst characterization

The texture of the samples was assessed by N_2 adsorption-desorption analysis. The surface area of corn starch calculated by BET method was $18\text{ m}^2/\text{g}$, whereas in ECS it was $135\text{ m}^2/\text{g}$. The surface area of ECS- NH_2 was found to be $52\text{ m}^2/\text{g}$. In the case of ECS- $\text{MoO}_2(\text{acac})_2$ catalyst, the surface area was determined to be $38\text{ m}^2/\text{g}$. Obviously, The decrease in the

surface area of the ECS-MoO₂(acac)₂ catalyst as compared to the ECS material was due to the presence of organic functionalities anchored on the surface of the ECS material.

The morphology of the catalyst was studied using the SEM as shown in Fig. 1. The expanded corn starch particles (Fig. 1a)

displayed a dispersed and smooth texture. The surface of ECS-MoO₂(acac)₂ (Fig. 1b) was found to be fine homogeneous powder with a clear appearance of catalyst loading.

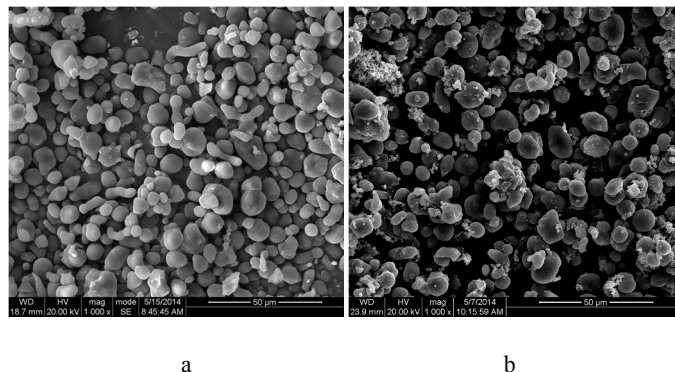


Fig. 1 Scanning electronic microscopy analysis (SEM) of (a) ECS; and (b) ECS-MoO₂(acac)₂.

The FT-IR spectra of ECS, ECS-NH₂, MoO₂(acac)₂, and ECS-MoO₂(acac)₂ samples were presented in Fig. 2. No significant changes were observed in the ECS structure sensitive vibrations after its modification, indicating that the framework of ECS remained unchanged. There was an overall narrowing of the peak width in the 3700-3000 cm⁻¹ range. It could be due to the decrease of the interlayer water content of the ECS, which was a consequence of the APTES grafting onto the ECS-OH surface groups. The NH₂ stretching band was not observed in Fig. 2b. It could be masked by the broad OH stretching band. A new weak band at 1560 cm⁻¹ of ECS-NH₂ was due to the N-H bending vibrations of primary amines.²¹ After Schiff condensation, the spectrum of ECS-MoO₂(acac)₂ showed the appearances of new bands centered at 1605 and 1562 cm⁻¹ which were due to the combinational vibration of the newly formed C=N bonds.²² The appearance of the C=N bond also confirmed the successful grafting of MoO₂(acac)₂ onto the APTES functionalized starch by covalent bond (Scheme 2).

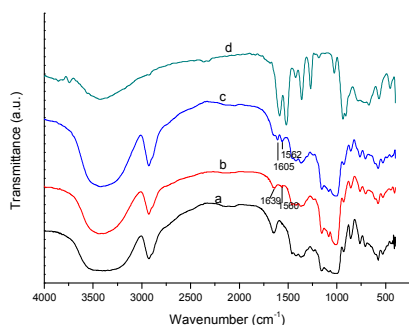


Fig. 2 FTIR spectra for (a) ECS; (b) ECS-NH₂; (c) ECS-MoO₂(acac)₂; and (d) MoO₂(acac)₂.

The thermal stability of ECS-MoO₂(acac)₂ catalyst was determined by thermal analysis. The TGA curves of ECS, ECS-NH₂, ECS-MoO₂(acac)₂ and free MoO₂(acac)₂ are shown in Fig. 3. The first stage of a slight mass loss in the TGA curves of all ECS based materials at ranging from 50 up to 150 °C could be ascribed to the removal of physically adsorbed water and solvent trapped in the ECS materials. A further sharp mass loss occurred around 300 °C was due to the loss of the grafted organic functionality and starch.²³ In addition, the immobilized complex ECS-MoO₂(acac)₂ shows a higher decomposition temperature similar to other two ECS based materials than that of the free complex MoO₂(acac)₂, suggesting that the molybdenum complex was anchored on the ECS support by covalent bond.

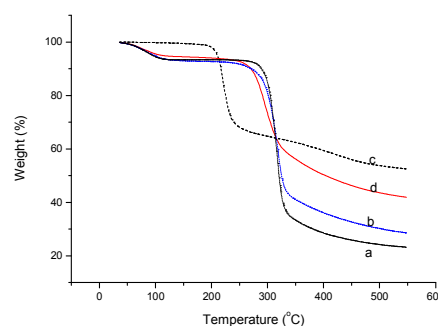


Fig. 3 TGA curves for (a) ECS; (b) ECS-NH₂; (c) MoO₂(acac)₂; and (d) ECS-MoO₂(acac)₂.

X-ray photoelectron spectroscopy (XPS) spectra of ECS-MoO₂(acac)₂ demonstrates the presence of molybdenum atoms in the ECS-MoO₂(acac)₂ materials. The XPS spectrum of ECS-MoO₂(acac)₂ showed a characteristic Mo 3d_{5/2} peak with a binding energy (BE) of 232.5 eV in the Mo3d region (Figure 4). The Mo

3d3/2 and 3d5/2 peaks were sharp, indicating that Mo existed in the form of Mo⁶⁺ on the catalyst surface.²⁴

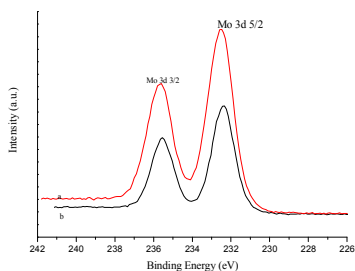


Fig. 4 High-resolution XPS spectra at the Mo 3d region for (a) ECS-MoO₂(acac)₂; and (b) ECS-MoO₂(acac)₂_Used.

3.2 Influence of reaction parameters on the conversion of stillingia oil

“Neat” expanded corn starch was found to be weakly active in the epoxidation of stillingia oil at our reaction conditions. A significant enhancement in double bonds conversion and epoxide yield of stillingia oil were observed when expanded starch-supported metal acetylacetonate was used as the

catalysts (Table 1). Different metal acetylacetonates supported on expanded starch (i.e., ECS-Ni(acac)₂, ECS-Cr(acac)₃, ECS-VO(acac)₂ and ECS-MoO₂(acac)₂) were also evaluated as the catalysts for the epoxidation of stillingia oil. Among all the catalysts investigated, ECS-MoO₂(acac)₂ were found to be the most effective catalyst for the epoxidation reaction (Table 1, entry 6). The catalytic activity of the ECS-MoO₂(acac)₂ was compared with MoO₂(acac)₂ for the epoxidation of stillingia oil under the same reaction conditions (Table 1, entry 2). It showed that the catalytic activities of these two catalysts were very close, suggesting that grafting of MoO₂(acac)₂ to the ECS support did not sacrifice its catalytic activity while adding the advantages of heterogeneous catalyst. Stillingia oil was also epoxidized with percarboxylic acid generated *in situ* with hydrogen peroxide as oxygen donor and glacial acetic acid as active oxygen carrier in the presence of H₂SO₄ (Table 1, entry 7). As can be seen from Table 1, the results obtained by using ECS-MoO₂(acac)₂/TBHP were superior in the epoxide yield and selectivity to those of the H₂SO₄/H₂O₂ system. Other reaction parameters of using ECS-MoO₂(acac)₂ as the catalyst were further investigated.

Table 1 Epoxidation of stillingia oil with different metal acetylacetonates anchored onto ECS,^a determined by ¹H NMR spectroscopy.

Entry	Catalyst system	Conversion (%)	Epoxidation (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1	ECS/TBHP	8.5	5.6	65.8	-	-
2	MoO ₂ (acac) ₂ /TBHP	83.6	68.3	81.7	45.5	22.8
3	ECS-Ni(acac) ₂ /TBHP	19.3	15.7	81.3	10.5	5.2
4	ECS-Cr(acac) ₃ /TBHP	28.4	22.4	78.7	14.9	7.5
5	ECS-VO(acac) ₂ /TBHP	32.2	25.8	80.2	17.2	8.6
6	ECS-MoO ₂ (acac) ₂ /TBHP	78.5	67.1	85.5	44.7	22.4
7	H ₂ SO ₄ /H ₂ O ₂ ^d	80.9	40.7	50.3	28.5	28.5

^a Reaction conditions: molar ratio TBHP : oil double bounds : catalyst 150 : 100 : 1.5, reactions carried out at 110 °C with toluene, 2 h.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst]×time (h⁻¹).

^d Reaction conditions: molar ratio acetic acid : H₂O₂: oil double bounds : catalyst 70 : 245 : 70 : 1, reaction carried out at 65 °C, 60 min.

As illustrated in Table 2, the conversion of double bonds increased with increasing amount of the catalyst from 1 mol% to 1.5 mol% (Table 2, entries 1 and 2). A further increase in the amount of catalyst did not improve the double bonds conversion significantly. It is known that the epoxidation reaction is highly influenced by the amount of peroxide used. The conversion could be elevated by introducing slightly excess

amount of TBHP to shift the equilibrium of the reaction to the right-hand side. The conversion to epoxide product attained a maximum value of 67.1% at the TBHP/double bond molar ratio of 1.5:1. When the molar ratio exceeded 1.5:1, there was a slight decrease in the conversion of double bonds and epoxide yield (Table 2, entry 5).

Table 2 Effect of different catalyst loading and molar ratio TBHP to double bond on the epoxidation of stillingia oil with ECS-MoO₂(acac)₂,^a determined by ¹H NMR spectroscopy.

Entry	Catalyst	TBHP/double	Conversion	Epoxidation	Selectivity	TON ^b	TOF ^c
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	loading (mol%)	bond (molar ratio)	(%)	(%)	(%)		(h ⁻¹)
1	1	1.5	38.6	33.0	85.4	33	16.5
2	1.5	1.5	78.5	67.1	85.5	44.7	22.4
3	2	1.5	78.7	67.3	85.5	33.7	16.8
4	1.5	1	50.4	42.4	84.1	28.3	14.1
5	1.5	2	78.0	64.9	83.2	43.3	21.6

^a Reaction conditions: reactions carried out at 110 °C with toluene, 2 h.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst]×time (h⁻¹).

Table 3 Effect of reaction temperature and time on the epoxidation of stillingia oil with ECS-MoO₂(acac)₂,^a determined by ¹H NMR spectroscopy.

Entry	Temperature (°C)	Reaction time	Conversion (%)	Epoxidation (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1	60	2	48.0	33.7	70.2	22.5	11.2
2	80	2	58.0	44.6	76.9	29.7	14.9
3	110	2	78.5	67.1	85.5	44.7	22.4
4	110	1.5	57.2	44.1	77.1	29.4	14.7
5	110	2.5	83.5	67.5	80.8	45.0	22.5

^a Reaction conditions: molar ratio TBHP : oil double bonds : catalyst 150 : 100 : 1.5, reactions carried out in toluene.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst]×time (h⁻¹).

The effects of reaction time and temperature were also investigated and the results were shown in Table 3. The maximum conversion of double bonds occurred after 2 h of reaction at the temperature of 110 °C. The double bonds conversion and epoxide yield increased sharply when the reaction temperature increased from 80 °C to 110 °C (Table 3, entries 2 and 3). This result might be due to the loss of water trapped in the expanded corn starch at 110 °C, which could improve the access of the substrates to the active sites.¹⁰

3.3 Reusability of the catalyst

Reusability is important for a heterogeneous catalyst. The reusability of the catalyst was examined by carrying out subsequent reaction cycles under the optimized reaction conditions as described previously. The used catalyst was separated from the reaction mixture by filtration, and washed thoroughly with toluene to remove compounds attaching the surface of catalyst. The catalysts were reused in recycling tests after vacuum-drying overnight at 110 °C. The epoxide yields of the reused catalysts were 67.1%, 66.3%, 65.7%, 64.5% and 62.8%, respectively, when the catalyst was used for 1, 2, 3, 4, 5 cycles under the optimized reaction conditions. The XPS result showed a similar Mo 3d band profile with that of a fresh prepared catalyst after it was used for five catalytic cycles (denoted as ECS-MoO₂(acac)₂_Used, Fig. 4b), which confirms the highly stability of the molybdenyl complex during the catalytic process. These results suggested that the catalyst developed in this study can be recycled without significant loss in catalytic activity for at least 5 times. The slight decrease of the conversion may be due to the leaching of the active species

(less than 0.5% determined by ICP analysis of the catalyst after the 5th run).

4. Conclusion

Molybdenum acetylacetonate covalently anchored onto amine functionalized expanded corn starch was prepared and characterized. The catalytic activity of the catalyst for the epoxidation of stillingia oil was evaluated using TBHP as the oxidant. The heterogeneous catalyst was found to be highly active and selective. Under optimal conditions, the double bonds conversion and epoxide yield of stillingia oil of 78.5% and 67.1%, respectively, were obtained at the refluxing temperature of toluene after 2 h. The heterogeneous catalyst was proved to be easily recovered and could be recycled for at least five consecutive runs without significant loss of catalytic activity. Thus, the properties of inexpensive, non-toxic, highly active, highly stable, easily recoverable and reusable render them potentially valuable catalysts for industrial applications.

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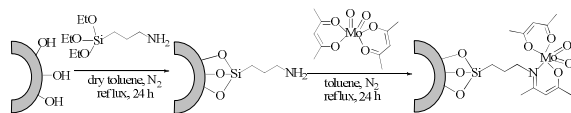
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Graphical Abstract



Epoxidation of stillingia oil was catalysed by ECS-MoO₂(acac)₂, presenting high selectivity towards the epoxide as well as excellent catalytic recyclability.