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Chiral Mn(III) salen complexes immobilized directly on pyrolytic waste tire char for asymmetric epoxidation of unfunctionalized olefins

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ABSTRACT

Two kinds of chiral Mn(III) salen complexes were synthesized and directly immobilized on pyrolytic waste tire char (PWTC) without modification of any organosilicon, which was an economic support, having rich oxy functionalized groups inherently. The as-prepared heterogeneous catalysts were characterized by X-ray photoelectron spectra (XPS), N_2 sorption, Fourier transform infrared spectra (FT-IR) and thermogravimetric analysis (TG), and possessed of good catalytic performance in asymmetric epoxidation of unfunctionalized olefins. They obtained higher enantiomeric excess (ee) values than that of homogeneous catalysts for asymmetric epoxidation of 1-phenylcyclehexene and could be recycled three times.

Chiral epoxides are useful organic building blocks in the synthesis of pharmaceuticals and agrochemicals. Chiral Mn(III) salen complexes are one of the most efficient successful catalysts in the asymmetric epoxidation of unfunctionalized olefins [1–3]. In recent decades, the heterogenization of Mn(III) salen complexes has attracted substantial attention as a result of the advantage of easy separation and simple recycling [4–8] of heterogeneous catalysts. The supports are adopted for the immobilization of Mn(III) salen complexes, including mesoporous silica [9–13], polymers [14–17] and activated carbon [18–20]. Generally, organosilicons are necessary for the heterogeneous Mn(III) salen catalysts immobilized on inorganic supports. Very few examples [21,22] existed for the achiral transition metal salen complexes that are anchored directly on activated carbon. To date, the heterogeneous Mn(III) salen catalyst supported on carbonous materials, has not been applied in asymmetric epoxidation of unfunctionalized olefins.

With the rapid development of automobile industry, an enormous number of waste tires cause a series of environmental problems. How to deal with these waste tires is common challenge for human beings. Compared with other technologies of disposing waste tires such as incineration and landfill, pyrolysis of waste tires proves to be a high-value-added and environmentally friendly technology in numerous technologies of disposing waste tires. During the pyrolyzing process, pyrolytic waste tire char (PWTC) as one of the main products is obtained. It possesses similar structure of carbon black, owning general properties of carbonous materials such as high thermal stability, great corrosion resistance in acid/base and low cost in economy. Specially, compared with commercial activated carbon, which needs oxidation disposal to increase its oxygen content, the surface of PWTC has rich oxy functional groups inherently without any oxidation process, which makes PWTC anchor the catalysts conveniently. Hence, the PWTC has great potential application in catalysis. In this work, this novel support was employed and two kinds of chiral Mn(III) salen complexes were immobilized on PWTC directly without any silane coupling agent as an anchor for asymmetric epoxidation of unfunctionalized olefins.

The PWTC needed to be extracted by toluene before using [23]. The synthesis of heterogeneous catalysts was shown in Scheme 1. The chiral Mn(III) salen complexes (**1** and **2**) [24] and PWTC were refluxed in anhydrous toluene for 24 h under stirring. After the evaporation of solvent, the obtained catalysts were extracted by dichloromethane for 12 h. The synthesized heterogeneous Mn(III) salen catalysts were marked as PWTC-**1** and PWTC-**2** and evaluated by the epoxidation of unfunctionalized olefins. The content of Mn was detected by ICP-AES and the results were 0.167 mmol/g for PWTC-**1** and 0.206 mmol/g for PWTC-**2**.

PWTC and prepared catalyst PWTC-**2** were characterized by X-ray photoelectron spectra (XPS). The XPS spectrum of PWTC in O1s region is presented in Fig. 1, and the XPS results are listed in Table 1. As shown in Fig. 1, the XPS spectrum of PWTC in O1s region could be deconvoluted into four components, and according to the literature [25], the peaks of O1s region at 531.2 eV (1) and 534.0 eV (4) were due to the groups of ketone and carboxylic acid, and other

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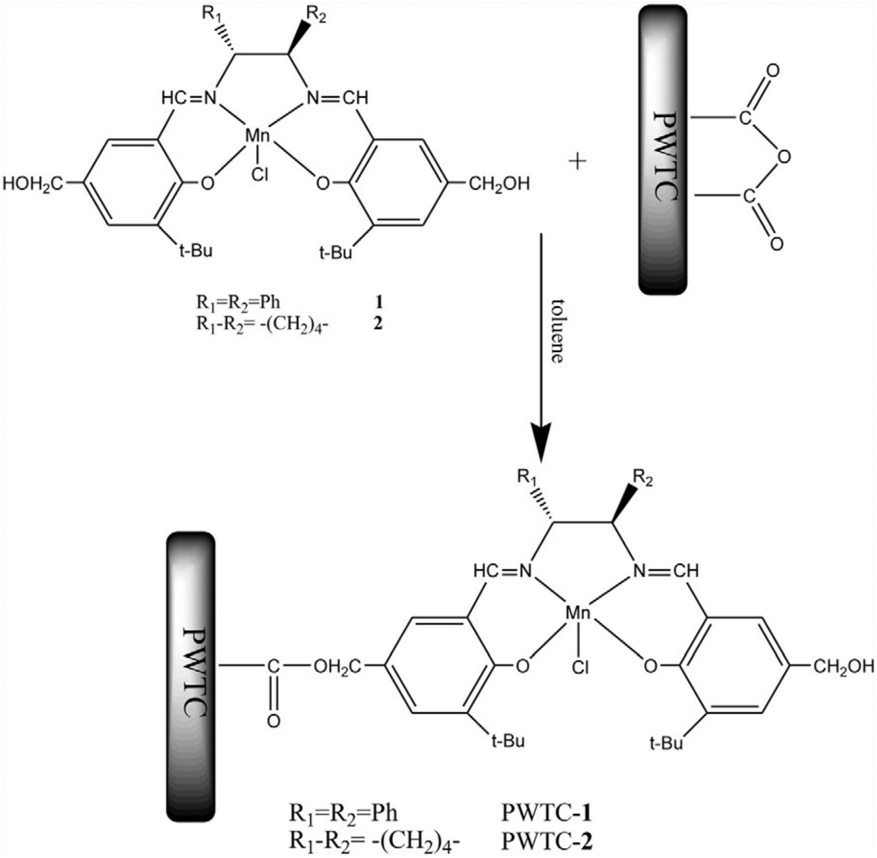

Scheme 1. The synthesis of heterogeneous chiral Mn(III) salen catalysts.

two peaks at 532.3 eV (2) and 533.3 eV (3) were attributed to the oxygen atoms of anhydride, lactone or hydroxyl group. As a result of high temperature during pyrolyzing process, the surface of PWTC was apt to the synthesis of anhydride. The group of anhydride was an active esterification agent, which could react with the hydroxyl of Mn(III) salen complexes, and that was the proposed way of immobilizing homogeneous catalysts [21]. From Fig. 1 and Table 1, the PWTC was a born material with rich oxy function groups, especially for the group of anhydride, so it was very convenient for the immobilization of the synthesized chiral Mn(III) salen complexes (**1** and **2**).

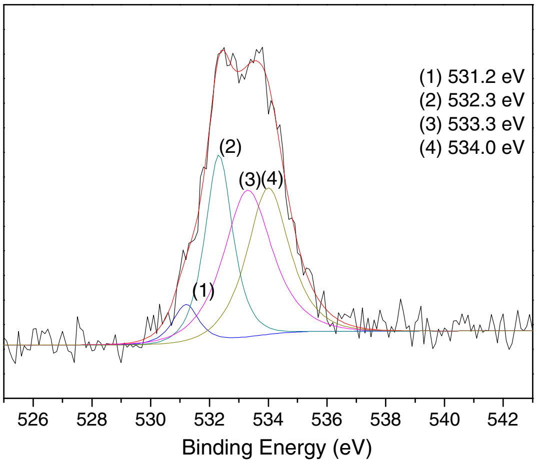

Fig. 1. The XPS spectrum of PWTC in O1s region.

Fig. 2 presents the XPS spectra of the heterogeneous catalysts PWTC-**2** in N1s and Mn 2p regions. As shown in Fig. 2(A) and (B), the peaks at 339.2 eV in N1s region and at 642.1 eV in Mn 2p region were both characteristic of Mn(III) salen complexes, which was in agreement with the previous report [26]. It indicated that the structure of Mn(III) salen complex **2** was kept well after immobilization. Additionally, the content of O_{total} of the heterogeneous catalysts PWTC-**2** increased (seen in Table 2), implying that the Mn(III) salen complex was anchored.

PWTC and the catalysts PWTC-**1** were characterized by N_2 sorption. Fig. 3 shows the isotherms of PWTC and PWTC-**1** and the structure parameters of samples are listed in Table 2. The isotherm of PWTC in the range of low relative pressure ($P/P_0<0.3$) is type I isotherm, indicating that the supports PWTC possessed microporous structure. However, because of the rareness of microporous structure, the N_2 quantity absorbed of PWTC was not high and the BET area of PWTC was only 85 m^2/g. In the range of high relative pressure ($P/P_0>0.95$), as a result of the cumulation of the pellets of PWTC, the adsorption quantity of N_2 increased sharply, which implied that the stacking of PWTC grains formed macroporous structure. The similar isotherm was obtained for the heterogeneous catalyst PWTC-**1**, which accounted for no obvious change in the structure of support. As shown in Table 2, compared with PWTC, the BET area and pore

Table 1
XPS results of PWTC and PWTC-**2** for O1s regions (atom %).

Sample	O1s binding energy (eV)				Ototal (%)
	531.2	532.3	533.3	534.0	
PWTC	0.4	2.1	2.8	2.5	7.8
PWTC-**2**	1.5	4.5	3.9	2.0	11.9

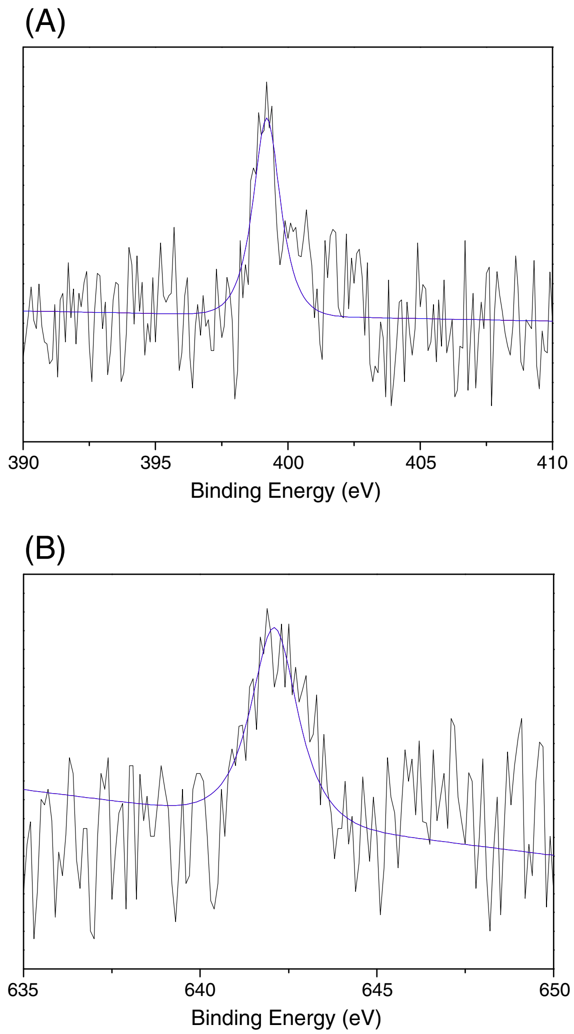

Fig. 2. The XPS spectra of PWTC-2 in (A) N1s region and (B) Mn2p region.

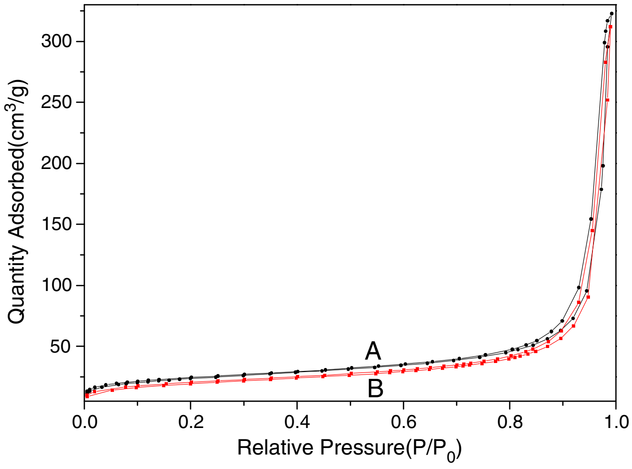

Fig. 3. The N_2 sorption isotherms of PWTC and PWTC-**1**.

volume of PWTC-**1** decreased, due to the blockage of Mn(III) salen complex **1** at the entrance of micropore of PWTC.

The FT-IR spectra of Mn(III) salen complex **2**, the support PWTC and heterogeneous catalyst PWTC-**2** are shown in Fig. 4. For Mn(III) salen complex **2** and the support PWTC (Fig. 4), the absorption bands around 2900 cm^{-1} were due to the C–H stretching vibrations of alkyl groups. The band at 1547 cm^{-1} in Fig. 4 was the characteristic IR absorption band of Mn(III) complexes, attributed to the stretching vibration of azomethine groups (H–C═N). The C–H deformation vibrations of Mn(III) complex **2** were located at 1426 cm^{-1} and 1390 cm^{-1}. In the spectra of parent support PWTC (Fig. 4), the peaks in the range of 1540–1480 cm^{-1} were assigned to the C═C stretching vibrations of polynuclear aromatics structure on the surface of PWTC. The C–H deformation vibrations of the functionalized groups on the surface of PWTC were observed between 1450 and 1400 cm^{-1}. In the FT-IR spectrum of PWTC-**2** (Fig. 4), the heterogeneous catalyst PWTC-2 possessed of all absorption bands of Mn(III) salen complex **2** and PWTC except that slight shifts were presented in Fig. 4. It confirmed that the Mn(III) salen complex was anchored on PWTC successfully.

The thermogravimetry (TG) curves of the samples PWTC and PWTC-**1** are presented in Fig. 5. The weight loss of parent support PWTC was 22.8% when the temperature got to 1100 °C under the atmosphere of nitrogen, while the percentage of weight loss of heterogeneous catalyst PWTC-**1** reached 27.5%. The additional weight loss of PWTC-1 was attributed to the decomposition of Mn(III) salen complex **1**. It also confirmed that the homogeneous catalyst **1** was immobilized on the support PWTC.

The prepared heterogeneous catalysts were evaluated in asymmetric epoxidation of unfunctionalized olefins. The oxidant was the solution of NaClO and the substrates were styrene, α-methylstyrene, indene and 1-phenylcyclohexene. The conversions and enantiomeric excess (ee) values were determined by gas chromatography (GC). The results of epoxidation of unfunctionalized olefins catalyzed by homogeneous and heterogeneous catalysts are shown in Table 3. The

Table 2
The structure parameters of PWTC and heterogeneous Mn(III) salen catalysts PWTC-**1** and PWTC-**2**.

Sample	S_{BET} (m^{2}g^{-1})	Pore volume (cm^{3}g^{-1})
PWTC	85	0.28
PWTC-**1**	68	0.14
PWTC-**2**	57	0.22

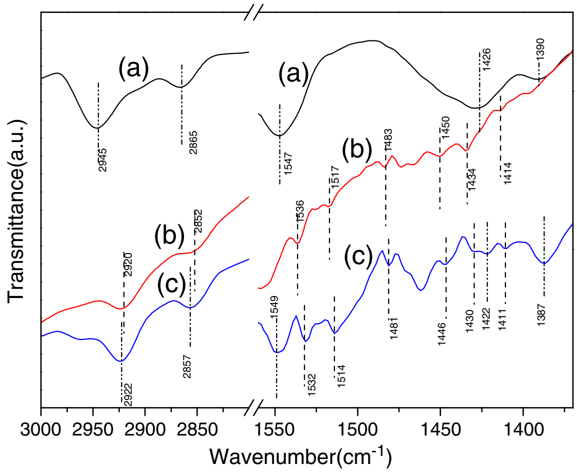

Fig. 4. The FT-IR spectra of (a) Mn(III) salen complex **2**, (b) the support PWTC and (c) the heterogeneous catalyst PWTC-**2**.

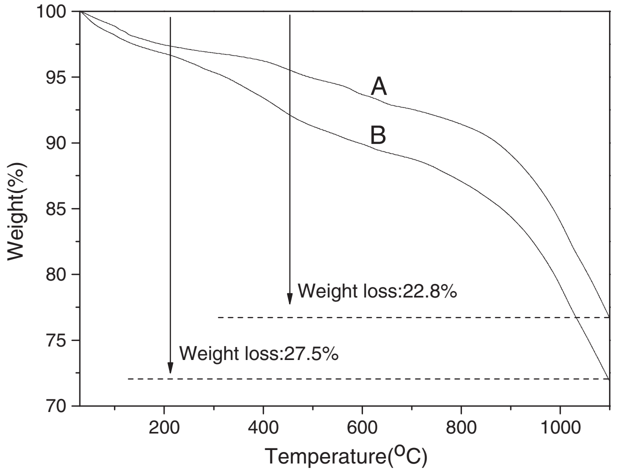

Fig. 5. The curves of TG analysis of PWTC and PWTC-**1**.

Table 4
The recycle results of asymmetric epoxidation of styrene catalyzed by heterogeneous catalysts PWTC-**1**.

	Catalyst	Substrate	Time (h)	Conv. (%)	ee (%)
1st	PWTC-**1**	Styrene	48	>99	49.0 (1*R*)
2nd				>99	51.2 (1*R*)
3rd				72.1	44.8 (1*R*)

[a] Reactions were carried out in CH_2Cl_2 (3 mL) with substrate (1 mmol), toluene (internal standard, 1 mmol), PPNO (0.38 mmol), catalysts (1.5 mol%) and NaClO (3 mmol) at 273 K.
[b] The conversion was determined by gas chromatography using toluene as internal standard and calculated by ([substrate]$_0$-[substrate])/[substrate]$_0$ × 100%.
[c] The ee value was determined by gas chromatography with chiral β-cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m × 0.25 mm × 0.25 μm) and was calculated by |([R] − [S])|/([R] + [S]) × 100%.

heterogeneous catalysts PWTC-**1** and PWTC-**2** obtained high conversions, and the conversions of substrates were all >90% after 48 h. In the epoxidation of styrene and indene, PWTC-**1** obtained almost the same ee values as the homogeneous catalyst **1** (entries 1, 2, 7 and 8), while PWTC-**2** showed slightly lower enantioselectivities compared with the homogeneous catalyst **2** (entries 3, 4, 9 and 10). Particularly, in the epoxidation of 1-phenylcyclohexene, the heterogeneous catalysts PWTC-**1** and PWTC-**2** catalyzed this reaction with 61.9% and 66.1% ee values, respectively (entries 12 and 14), which were higher than the results obtained by the homogeneous catalysts (50.4% and 60.9%). The increase of ee values might be attributed to the positive confinement effect of the surface of PWTC [27]. In other words, the size of 1-phenylcyclohexene was comparable with the space which was built by Mn(III) salen complex and the surface of PWTC [28].

The recycle results of asymmetric epoxidation of styrene catalyzed by heterogeneous catalyst PWTC-**1** are listed in Table 4. As shown in Table 4, the catalysts possessed the ability of recycling, and the catalyst PWTC-**1** could be reused three times. The filtrate was analyzed by ICP-AES, and a little Mn leaching (3%) was detected. However, in the fourth recycling the conversion decreased to 17.2%, which may be due to the loss of PWTC-**1** during the process of filtrating and the coverage of active species by the salt produced in the reaction. So the catalyst could not be reused further.

In summary, two kinds of Mn(III) salen complexes **1** and **2** were immobilized on PWTC without any organosilane. The structure of supports was kept well and the property of Mn(III) complex did not change during the preparation of heterogeneous catalyst (PWTC-**1** and PWTC-**2**). The synthesized heterogeneous catalysts obtained high conversions and enantioselectivities in the asymmetric epoxidation of unfunctionalized olefins, and notably, they obtained higher enantioselectivity than the homogeneous catalysts in the epoxidation of 1-phenylcyclohexene. The heterogeneous catalysts could be reused three times.

More details about the experiment and characterizations of heterogeneous catalysts can be seen in supporting information (SI).

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Table 3
The results of asymmetric epoxidation of unfunctionalized olefins catalyzed by homogeneous and heterogeneous catalysts.[a]

Entry	Catalyst	Substrate	Time (h)	Conv. (%)[b]	ee (%)[c]	Sele. (%)[d]	TOF[e]$\times 10^{-4}$ (s^{-1})
1	1	Styrene	2	>99	48.8 (*R*)	96.9	34.7
2	PWTC-**1**		48	>99	49.0 (*R*)	97.2	1.45
3	2		2	>99	33.7 (*R*)	96.9	34.7
4	PWTC-**2**		48	>99	29.1 (*R*)	96.3	1.45
5	2	α-Methylstyrene	2	>99	42.3 (1*R*)	94.4	34.7
6	PWTC-**2**		48	>99	39.3 (1*R*)	91.1	1.45
7	1	Indene	2	>99	66.9 (1*R*,2*S*)	88.9	34.7
8	PWTC-**1**		48	>99	68.4 (1*R*,2*S*)	50.3	1.45
9	2		2	>99	71.1 (1*R*,2*S*)	66.9	34.7
10	PWTC-**2**		48	>99	65.6 (1*R*,2*S*)	85.8	1.45
11	1	1-Phenylcyclohexene	2	>99	50.4 (1*S*,2*S*)	95.2	34.7
12	PWTC-**1**		48	>99	61.9 (1*S*,2*S*)	>99	1.45
13	2		2	>99	60.9 (1*S*,2*S*)	93.2	34.7
14	PWTC-**2**		48	>99	66.1 (1*S*,2*S*)	>99	1.45

[a] Reactions were carried out in CH_2Cl_2 (3 mL) with substrate (1 mmol), toluene (internal standard, 1 mmol), PPNO (0.38 mmol), catalysts (1.5 mol%) and NaClO (3 mmol) at 273 K.
[b] The conversion was determined by GC using toluene as internal standard and calculated by ([substrate]$_0$-[substrate])/[substrate]$_0$ × 100%.
[c] The ee value was determined by GC with chiral β-cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m × 0.25 mm × 0.25 μm) and was calculated by |([R] − [S])|/([R] + [S]) × 100%.
[d] The selectivity of epoxide was determined by GC and calculated by [epoxide]/[product] × 100%.
[e] TOF was calculated by [product]/([catalyst] × time).

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.09.001.

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