

Ti complexes assembled HMS as effective catalysts for epoxidation of alkene

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Abstract

The exchange reactions between Ti compounds and hexagonal mesoporous silicas (HMS) have been investigated in detail by means of UV-Vis diffuse reflection spectra, FT-IR, N₂ volumetric adsorption, chemical and elemental analyses. It was found that the exchange of titanium tetraisopropoxide (Ti(OⁱPr)₄), and especially titanium tetrachloride (TiCl₄) with the surface hydroxyls of the HMS easily occurred, this exchange interaction caused the distortion of the supports Si-O₄ tetrahedron and resulted in the appearance of 960 cm⁻¹ band in their IR spectra. The UV-Vis diffuse reflection spectra showed that the Ti-assembled HMS materials did not exist the bulk titania and had the very similar Ti-sites to the Ti-substituted HMS, indicating the high dispersed Ti species upon the surface of HMS. The surface area and pore volume of HMS after the Ti complexes grafting have been significantly reduced, further confirming the introduction of Ti complexes into the channels of HMS by chemically grafting. A chiral Ti tartrate complex (Ti(OⁱPr)₄ + DET) could be successfully grafted onto HMS through three assembled pathways. In catalyzing epoxidation of styrene and cyclohexene with tetrabutyl hydroperoxide (TBHP), the above described catalysts showed a higher catalytic activity and selectivity for the epoxides than those unloading Ti tartrate complexes (Ti(OⁱPr)₄ + DET) and the Ti-substituted HMS catalysts, among them, the HMS-Ti catalyst prepared with Ti(OⁱPr)₄ at 393 K possessed the best catalytic activity, but the lowest epoxidative selectivity, which is mainly due to the Lewis acid sites of HMS-Ti for further catalyzing the rearrangement of the epoxides. The adjusting of D-(+)-diethyl (DET) to the Ti-sites anchored on the supports led to the decrease in the catalytic activity and the increase in the epoxidative selectivity. The obvious advantages of these assembled catalysts are that they can be recycled for many times without significant loss of activity. The assembled HMS catalysts with the chiral Ti tartrate complex were enantioselective for asymmetric epoxidation of styrene with TBHP, about 20~32% enantiomeric excess (e.e.) of the epoxides could be obtained over these chiral Ti mesoporous catalysts. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The synthesis of hexagonal mesoporous silicas MCM-41 [1], HMS [2] and MSU [3] by the cooperative assembly of silica and surfactants has attracted a great deal of research interest recently. These mesoporous materials have larger pore sizes (1.5–10 nm), internal surface areas (~1000 m²/g) [1,2], and a large number of surface OH groups [4,5]. They, therefore, are potential to be used as catalysts for large molecule conversions and as hosts for assembly of a wide variety of transition metal complexes. Based on these characteristics, many researchers have recently reported

transition metal Ti-substituted mesoporous silicas [6–8], and the transition metal complexes such as titanocene [9], titanium tetraisopropoxide (Ti(OⁱPr)₄) [10], Mn Schiff-base complexes [11], Mn₂(CO)₁₀ [12], Co complexes [13], and other transition metal complexes-grafted mesoporous silicas [14]. These metal-substituted or -grafted mesoporous materials were claimed to be effective catalysts for the selective oxidation of aromatics and alcohols [6,7], and the photocatalytic decomposition of NO into N₂ and O₂ [8], as well as the epoxidation of alkene with tetrabutyl hydroperoxide (TBHP) [9,10,13–17]. However, there are few reports on the assemblies of chiral Ti tartrate complex over mesoporous materials.

Here, we firstly report the assemblies of Ti(OⁱPr)₄ and TiCl₄ as well as their chiral Ti tartrate complexes over HMS mesoporous materials by the exchange reaction of Ti

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compounds or D-tartaric acid (TA) with the surface OH groups of HMS support, and the characterizations of these assembled mesoporous materials by X-ray diffraction (XRD), UV-Vis diffuse reflection spectra, FT-IR, elemental and chemical analysis methods as well as the catalytic oxidative properties of these assembled HMS catalysts in the epoxidation of styrene and cyclohexene with TBHP as an oxidant.

2. Experimental

2.1. Synthesis of mesoporous HMS

HMS was synthesized via a neutral S^{010} templating pathway using dodecylamine (DDA) as the surfactant, ethanol (EtOH) as a co-solvent, tetraethyl orthosilicate (TEOS) as Si source. In a typical preparation, the TEOS was added dropwise to the solution of DDA in water and ethanol under vigorous stirring. The molar composition of the reaction mixtures was 1.0Si:0.2DDA:9.0EtOH:72H₂O. The reaction mixture was aged at room temperature (293 K) under vigorous stirring for 24 h. The solid obtained was filtered off, washed thoroughly with ethanol, dried at 393 K for 4.0 h and calcined at 873 K for 6 h (denoted as HMS). Finally, HMS was degassed at 413 K for 4 h under vacuum prior to use. For comparison purposes, Ti-HMS was prepared by use of the similar method to HMS.

2.2. Assembly of Ti complexes over mesoporous supports

Three pathways for assembling Ti tartrate over HMS supports were as follows:

The first pathway: the prepared conditions for **Scheme 1**: (1) 0.5 g of the support degassed at 413 K for 4 h under vacuum, 1.25 mmol Ti(O^{*i*}Pr)₄ (denoted as Ti) or TiCl₄

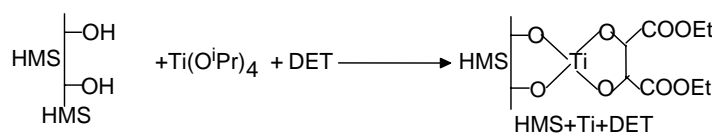
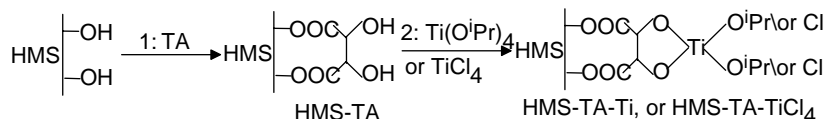
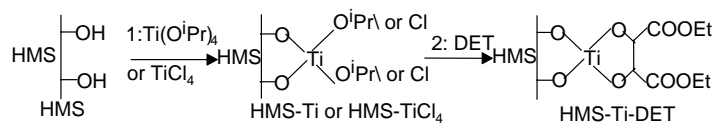
and 10 ml of toluene were added to the three-necked flask equipped with a condenser and thermometer under N₂, and stirred for 48 h at 393 K. The solid modified was repeatedly washed with anhydrous toluene, and then activated at 413 K under vacuum overnight prior to use; (2) 0.25 g of HMS-Ti, 0.75 mmol of D-(+)-diethyl tartrate (DET) and 10 ml of CH₂Cl₂ were added to the three-necked flask, the mixtures were stirred for 12 h at 288 K under N₂. The solid modified was repeatedly washed with CH₂Cl₂ and then dried under vacuum at 323 K for 4 h prior to use.

The second pathway: the prepared conditions for **Scheme 2**: (1) 0.5 g of HMS, 1.0 g of D + tartaric acid, 0.2 g of *p*-toluenesulfonic acid, and 20 ml of toluene were mixed and refluxed at 393 K for 21 h. The treated solid (denoted as HMS-TA) was repeatedly washed with water, and degassed at 393 K for 4 h under vacuum. The TA-loading measured by PE-2400 CHN elemental analysis instrument was ca. 2.55 mmol TA g⁻¹ HMS; (2) 0.25 g of HMS-TA, 1.25 mmol of Ti compounds and 10 ml of CH₂Cl₂ were mixed and stirred at 288 K for 12 h under N₂. The modified solid was repeatedly washed with CH₂Cl₂, and then dried at 323 K for 4 h under vacuum.

The third pathway: the prepared conditions for **Scheme 3**: 0.5 g of HMS, 1.25 mmol of Ti(O^{*i*}Pr)₄, 1.5 mmol of DET, and 10 ml of CH₂Cl₂ were mixed and stirred at 288 K for 12 h under N₂. The solid modified was repeatedly washed with CH₂Cl₂, and then dried under vacuum at 323 K for 4 h.

2.3. Characterization of catalysts

The catalysts thus obtained were studied through X-ray powder diffraction, UV-Vis spectrophotometry and FT-IR spectroscopy. Their Ti-loading was measured by chemical analysis. The XRD measurements were carried out with a Siemens D-500 diffractometer with Cr K α radiation ($\lambda = 2.292 \text{ \AA}$) and a scan speed of 2° (2θ) min⁻¹. The surface



area and pore volume of the samples were measured by Micromeritics ASAP2400 low temperature N₂ adsorption apparatus on the basis of the china standard GB/T5816-1995. The UV-Vis spectroscopic measurements were carried out on a TU1221 UV-Vis scanning spectrophotometer equipped with an integrating sphere (Beijing, China). A reflection mode with a resolution of 2 nm and BaSO₄ reference were used for the measurements. The infrared measurements were carried out with a Nicolet 510P spectrometer, using KBr pellets.

2.4. Catalytic testing

Styrene or cyclohexene (3.6 mmol), TBHP (1.2 mmol), catalyst (0.1 g) and CH₂Cl₂ (2 ml) were added to a three-necked flask equipped with a condenser and thermometer, the mixtures were stirred at 323 K (or 303 K for cyclohexene) for 7 h. The reaction products were analyzed by GC on a SE-30 capillary column with a FID. The enantioselectivity of the epoxides for the epoxidation of styrene was analyzed on acylized D-(+)-diethyl tartrate capillary column (*R,S*-styrene oxide enantio-mixtures could be successfully detached into 52% versus 48% over this chiral capillary column, using Oven temperature programmed from 343 to 403 K with a heating rate β of 2.5 K min⁻¹ and with N₂ as carrier gas).

3. Results and discussions

3.1. XRD characterization

The low-angle powder XRD patterns of the calcined HMS and Ti-HMS only featured a strong first-order (*d*₁₀₀) diffraction peak accompanied by broader, unresolved higher order reflections, indicating that both materials possess a mesostructure with the lack of long-range order [2]. As the transition metal Ti was incorporated into the mesostructures, the *d*₁₀₀ peak of the Ti-HMS became shifted to lower diffraction angles and slightly broad, indicating progressive expansion of the latticed-spacings upon heteroatom Ti incorporating. An increase on the unit cell size parameter has been also noted [18] to occur upon Ti incorporation into ZSM-5 frameworks (Fig. 1).

3.2. UV-Vis diffuse reflectance spectroscopy

The Ti species grafted on the surface of HMS were further verified and compared with the relative Ti-substituted HMS by UV-Vis diffuse reflectance spectroscopy, their corresponding spectra are shown in Fig. 2. The spectra for the Ti-grafted HMS samples (HMS-Ti and HMS-Ti-DET) showed the much broader character of absorption bands at 220–300 nm, and the lack of a 325 nm band characteristic for segregated titania, but the same spectra character as the Ti-HMS. According to the characterized results of

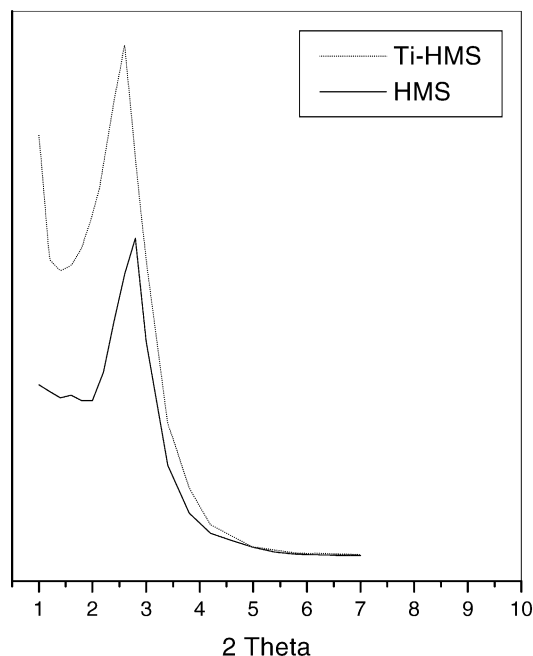


Fig. 1. XRD patterns of calcined HMS and Ti-HMS.

the Ti-substituted MCM-41 and HMS early reported in literatures [19,6] through the Ti-K-edge XANES, UV-Vis diffuse reflectance spectroscopy and XPS, the coordination states of Ti-sites in Ti-MCM-41 and Ti-HMS materials may well be a mixture of 4-, 5-, and 6-fold coordinations, with tetrahedral coordination being in the majority, the higher coordination Ti-sites are most likely generated through hydration of the tetrahedrally coordinated sites. We believe

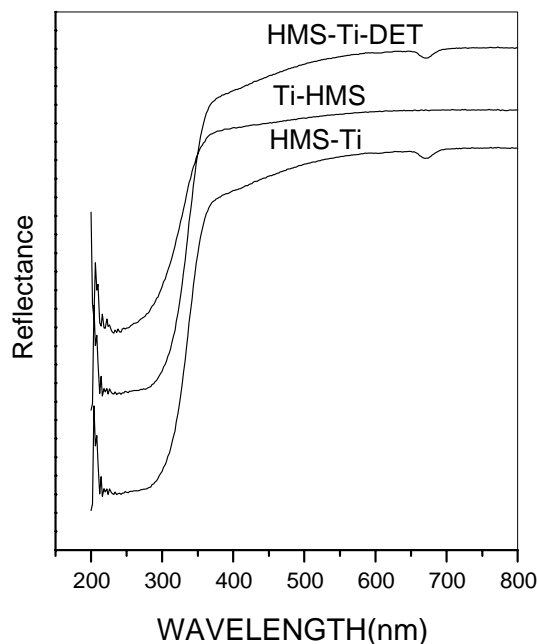


Fig. 2. UV-Vis diffuse reflectance spectroscopy of Ti-containing HMS materials.

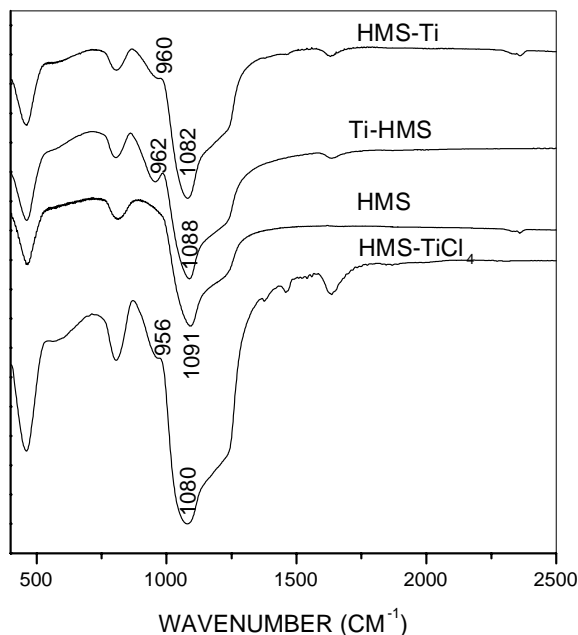


Fig. 3. FT-IR spectra of Ti-substituted and Ti-grafted HMS materials.

that the hydrolysis of $\text{Ti}(\text{O}^i\text{Pr})_4$ or its tartrate was little in the process of them to be grafted onto HMS, and the Ti-grafted HMS materials had very similar coordination states to the Ti-substituted HMS.

3.3. FT-IR characterizations

In order to investigate the binding interaction between Ti compounds and the surface functional groups of HMS supports, the Ti compounds and its tartrate complexes-grafted HMS samples were characterized by FT-IR spectra, and their IR spectra were shown in Figs. 3 and 4. A very weak adsorption band near 960 cm^{-1} was observed in their spectra. Much interestingly, a relatively strong 960 cm^{-1} band could also be observed in the spectroscopy of the Ti-substituted HMS and the tartaric acid or DET-grafted HMS (see Figs. 3, 4b and f). Although there are still some disputes [20,21] to the assignment of the 960 cm^{-1} band, but more evidences, in which a similar band was previously observed in TS zeolites [22,23], in titanium siloxane polymers [24], or in TiO_2 -grafted on silica [25], have supported that the 960 cm^{-1} should be due to a modification of SiO_4 units indirectly related to the presence of the guest molecules, indicating a strong binding of the surface functional groups of HMS with Ti compounds.

The Ti tartrate-grafted HMS samples all exhibited a weak carbonyl band of tartrate in their spectra (see Fig. 4), and the shifts of their carbonyl bands were few in comparison with these of relative free-DET and HMS-TA. The FT-IR spectroscopy of homogeneous Ti tartrate complex in toluene exhibited a strong carbonyl band at 1736 cm^{-1} and a relative weak carbonyl band at 1674 cm^{-1} , that the later is assigned to the coordination carbonyl band of DET with $\text{Ti}(\text{O}^i\text{Pr})_4$

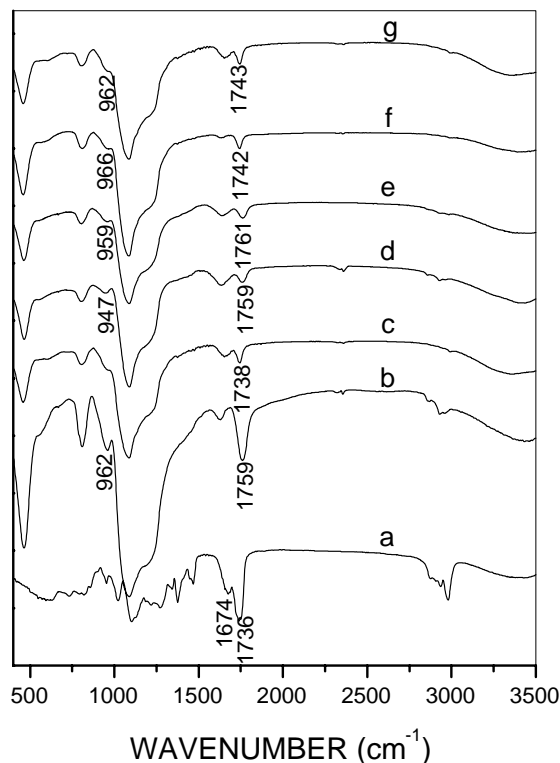


Fig. 4. FT-IR spectra of various assembled HMS samples with Ti tartrate complexes: (a) $\text{Ti}(\text{O}^i\text{Pr})_4 + \text{DET}$; (b) HMS-TA; (c) HMS-Ti-DET; (d) HMS-TA- TiCl_4 ; (e) HMS-TA-Ti; (f) HMS-DET; (g) HMS + Ti + DET.

[26,27] (see Fig. 4a). But the Ti tartrate-grafted HMS samples prepared by us did not exhibit this coordination carbonyl band in their IR spectra, it is maybe mainly due to the loading of Ti tartrate is low and this band is too weak and not detected by FT-IR, or DET is grafted the Ti-sites through the exchange of its hydroxyls rather than its carbonyls with $\text{Ti}(\text{O}^i\text{Pr})_4$. It was noteworthy that a carbonyl band of DET was observed on the IR spectroscopy of the DET-treated HMS at room temperature (see Fig. 4f), perhaps indicating that DET molecules also occupy the OH-sites of HMS by H-bonding interactions. But we still incline to that DET molecules are perhaps mainly grafted onto the Ti-sites because the Ti-sites have much stronger coordination or bond capacities than the OH-sites.

3.3.1. N_2 volumetric adsorptions

The N_2 volumetric adsorption method was employed to measure the surface area (S_g ($\text{m}^2\text{ g}^{-1}$)) and pore volume (PV ($\text{cm}^3\text{ g}^{-1}$)) of HMS materials before and after Ti complexes grafting, the measured results are listed in Tables 1 and 2, and compared with those for the Ti-HMS. It may be clearly discovered that the surface area and pore volume of HMS, after the Ti and especially its tartrate grafting, have very obviously decreased, further indicating that the Ti complexes have been anchored in the channels of HMS through chemically grafting.

Table 1
Effects of exchanged temperature on catalytic properties of Ti compounds assembled catalysts for epoxidation of styrene

Samples	Ti-loading (mmol g ⁻¹)	S _g ^a (m ² /g)	PV ^a (cm ³ /g)	X _{ST} ^b (mol%)	X _{TBHP} ^b (mol%)	Product distribution ^c (%)		
						PhCHO	PhCH ₂ CHO	PhCHOCH ₂
HMS		793	0.95	–	1.6	–	–	–
HMS-Ti	0.93	644	0.70	30.1	91.9	14.7	64.6	20.7
HMS-TiCl ₄	0.80			10.2	32.2	8.4	70.0	21.6
Ti-HMS ^d	0.33	730	0.90	21.3	65.5	10.9	62.7	26.4
HMS-Ti ^e	0.93	644	0.70	2.9	–	75.1	24.9	–
HMS-Ti ^f	0.93	644	0.70	–	1.8	–	–	–
HMS-Ti ^g	0.93	644	0.70	–	–	4.8	65.4	29.8

^a Prior to measurement, the samples were degassed at 378 K for 5 h under the vacuum, the N₂ volumetric adsorption measurement was carried out at low temperature (77 K) the surface area (S_g) and pore volume were calculated by BET and BJH methods, respectively, on the basis of the N₂ adsorption isotherms.

^b X_{ST} and X_{TBHP} indicated the conversions of Styrene and TBHP, respectively by GC analysis.

^c Reaction was carried out at 323 K; product distributions included benzaldehyde (PhCHO), phenylacetaldehyde (PhCH₂CHO) and styrene oxide (PhCHOCH₂).

^d Ti-HMS was prepared on the basis of reference [19].

^e Use of 31% aq. H₂O₂ instead of TBHP as an oxidant.

^f Decomposition of 0.5 M TBHP in toluene (5 ml) was carried out at 323 K for 7 h over 0.2 g of HMS-Ti, its decomposed ratio was measured by chemical analysis.

^g 3.6 mmol of styrene oxide, 0.1 g of catalyst and 2 ml of CH₂Cl₂ as solvent at 323 K for 7 h.

3.4. Catalytic testing

3.4.1. Epoxidation of styrene

The catalytic properties of the Ti compounds-grafted HMS materials were tested and compared with that of the Ti-substituted HMS (Ti-HMS) in the epoxidation of styrene with TBHP. The results listed in Table 1 indicated that styrene was selectively oxidized to styrene oxide (PhCHOCH₂), phenylacetaldehyde (PhCH₂CHO) and a small of benzaldehyde (PhCHO) over these catalysts. The converted efficiency of TBHP was more than 90% and its decomposed ratio was lower than 1.8% over the Ti-grafted HMS. The Ti-substituted and -grafted HMS catalysts exhibited a very similar catalytic behavior, the activity differences of them are due probably to the difference in Ti content. This is also consistent with the above characterized results.

It is known that water, that would come from hydrogen peroxide, can significantly affect the activity of microporous

and mesoporous catalysts [28], this situation also exists in the Ti-grafted HMS, for example, if using a convenient hydroperoxide (31% aq. H₂O₂) instead of TBHP as an oxidant, a very poor conversion of styrene was obtained on the HMS-Ti (see Table 1). There are perhaps two explanations for this result, the first is that a large number of water in H₂O₂ had an obstacle to the catalysis of the Ti-sites, as reported in the homogeneous Ti tartrate catalyzing the asymmetric epoxidation [29]; The second is that hydrogen peroxide is easily decomposed over the mesoporous materials, leading to the decline of the use efficiency [28].

3.4.1.1. Effects of Ti compounds. Among the Ti compounds-grafted HMS catalysts, the Ti(OⁱPr)₄-grafted HMS (HMS-Ti) have a higher activity and selectivity for the epoxides than the TiCl₄-grafted HMS (HMS-TiCl₄). We propose that the Lewis acid sites of the Ti species anchored on the supports may catalyze the polymerization of styrene

Table 2
Adjusting effects of DET ligand on catalytic properties of various assembled catalysts in epoxidation of styrene with TBHP

Samples	Ti-loading (mmol g ⁻¹)	S _g ^a (m ² /g)	PV ^a (cm ³ /g)	X _{ST} (mol%)	X _{TBHP} (mol%)	Product distribution (%)			e.e. (%)
						PhCHO	PhCH ₂ CHO	PhCHOCH ₂	
HMS-Ti	0.93	644	0.70	30.1	91.9	14.7	64.6	20.7	1.2
HMS + DET ^a	–	780	0.68	0.0	1.5	–	–	–	–
HMS-Ti-DET	0.93	501	0.56	15.7	47.8	5.8	49.8	44.4	30.5
HMS + Ti + DET	1.33	427	0.50	22.0	67.1	3.7	56.7	43.6	32.4
HMS-TA-Ti	0.94	374	0.46	15.4	47.3	–	70.2	29.8	21.3
HMS-TA-TiCl ₄	1.49	312	0.39	7.8	26.8	5.8	50.6	43.6	–
Ti(O ⁱ Pr) ₄ ^b	–	–	–	100	1.8	–	–	–	–
Ti(O ⁱ Pr) ₄ + DET ^c	–	–	–	7.0	–	28.2	55.3	16.5	27.8

^a 0.1 g of HMS plus 0.12 mmol of DET was used as catalyst.

^b 0.1 mmol of Ti(OⁱPr)₄ as catalyst. Styrene was completely polymerized.

^c 0.1 mmol of Ti(OⁱPr)₄ plus 0.12 mmol of DET as catalyst.

and the rearrangement of the epoxides, this may be confirmed from $\text{Ti}(\text{O}^i\text{Pr})_4$ only catalyzing the polymerization of styrene and the HMS-Ti efficiently catalyzing the rearranged reaction (Table 1: about 70% styrene oxide can be rearranged to PhCH_2CHO and a small amount of PhCHO over the HMS-Ti). The polymerization by-reaction can poison the Ti-sites of the catalysts and cause the decrease in the catalytic activity and the rearrangement by-reaction will reduce the selectivity of the epoxides. TiCl_4 has a stronger Lewis acidic sites than $\text{Ti}(\text{O}^i\text{Pr})_4$, and then the HMS- TiCl_4 catalysts have the worse catalytic properties than the HMS-Ti catalysts.

3.4.1.2. Effects of DET ligand. When the HMS-Ti further bonds DET ligand, its activity abruptly decreased from 30.1 to 15.1% and its selectivity significantly increased from 20.7 to 44.4% (HMS-Ti-DET sample, see Table 2), which may be due to the strong adjusting of DET to the Ti-sites on HMS. The assembled pathways for HMS grafting Ti tartrate complexes also affected their catalytic properties, HMS + Ti + DET catalyst prepared by the third pathway showed the best activity (ca. 22.0% conversion), being in agreement with its high Ti-loading. The HMS-TA-Ti catalyst prepared by the second pathway showed the similar activity to the HMS-Ti-DET, but a lower selectivity (only 29.8% styrene oxide), which is mainly because it has a similar Ti coordination environment to the HMS-Ti. These catalysts exhibited higher activities and selectivities for the epoxide than unloading Ti tartrate complex in the epoxidation of styrene (only 7.0% conversion and 16.5% selectivity can be obtained over $\text{Ti}(\text{O}^i\text{Pr})_4$ + DET complex). Much importantly, these mesoporous catalysts grafting chiral Ti tartrate complex showed a definite enantio-selectivity for

the epoxides (the enantiomeric excesses (e.e. (%)) of the epoxides range from 20 to 32% over these chiral catalysts), and the non-chiral Ti-grafted HMS is little in chiral induction for catalyzing asymmetric epoxidation of styrene with TBHP.

On the basis of above described results, a reasonable mechanism for this catalytic reaction is proposed as follows: at first, the active Ti-OO^tBu intermediate ([A]) is formed by replacement of TBHP to one ligand of the Ti-sites anchored on HMS supports, and then oxidizes styrene to form the epoxides (see Eqs. (1) and (2)). Besides, the Lewis acidic sites of the Ti-sites can promote the opening of the epoxides to form a carbon positive ion intermediate ([B]), and then the [B] is further rearranged to form PhCH_2CHO (see Eq. (3)); another, the [B] combines with water or TBHP to form the unsteady intermediates ([C] and [D]), following, the [C] and [D] are further cracked into PhCHO , HCHO and CH_3OH (see Eqs. (4) and (5) in Scheme 4).

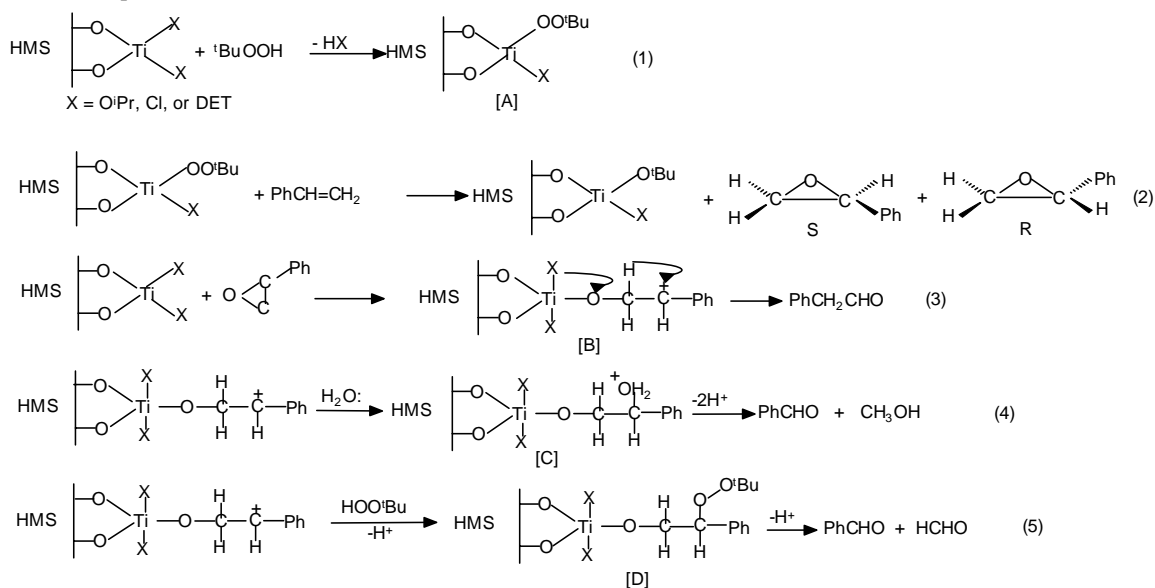
3.4.2. Epoxidation of cyclohexene

Table 3 lists the epoxidation results of cyclohexene with TBHP over the HMS-Ti catalyst. The results indicate that the Ti-grafted HMS catalyst is also very effective for this reaction, cyclohexene can be high-selectively oxidized to its epoxide with more than 30% conversion and 99% selectivity over the HMS-Ti. The adjusting of DET to the HMS-Ti can lead to decreases in its catalytic activity (22.3% conversion can be obtained over HMS + Ti + DET sample).

3.4.3. Re-use testing

Table 4 lists the re-used results of the recovered HMS-Ti catalyst for the epoxidation of styrene and cyclohexene. The results indicate that the catalyst has very stable catalytic

Please comparisons:



Scheme 4.

Table 3

Results obtained from epoxidation of cyclohexene over HMS-Ti and HMS-Ti + DET catalysts^a

Samples	Ti-loading (mmol g ⁻¹)	X _{CYH} ^b (mol%)	X _{TBHP} (mol%)	S _{EPO} ^b (%)
HMS-Ti	0.93	30.0	92.1	100
HMS + Ti + DET	1.33	22.3	67.8	100

^a Reaction temperature and time were 303 K and 9 h, respectively.^b X_{CYH} and S_{EPO} indicated the conversion of cyclohexene and the selectivity for the epoxide, respectively.

Table 4

Recycle performance of HMS-Ti catalyst

No.	X _{ST} (mol%)	X _{TBHP} (mol%)	Product distribution (%)			X _{CYH} (mol%)	X _{TBHP} (mol%)	S _{EPO} (%)
			PhCHO	PhCHOCH ₂	PhCH ₂ CHO			
1	30.3	93.1	13.2	68.7	18.1	30.0	91.2	100
2	29.7	91.5	4.6	69.2	26.2	29.7	91.5	100
3	30.1	91.9	4.4	63.0	32.6	28.1	90.2	100

properties and can be repeatedly used many times with little loss of activity.

4. Conclusions

The binding of them with the surface hydroxyls on the supports can successfully assemble Ti compounds and its complexes on HMS supports. The Ti compound-grafted HMS have very similar spectra characteristics to the Ti-substituted HMS in their UV-Vis reflection and IR spectra, perhaps indicating the similarity in their Ti coordination environments.

In catalyzing epoxidation of styrene and cyclohexene with TBHP, the assembled catalysts have higher activities and selectivities for epoxide than unloading Ti(O^{*i*}Pr)₄+DET complex and Ti-substituted HMS catalysts. The HMS-Ti possesses the best catalytic activity, and can be reused many times with little loss of activity. The adjusting of DET to the Ti active sites anchored on the supports leads to the decreases in the catalytic activity and the increases in the epoxidative selectivity. A kind of chiral Ti tartrate complex (Ti(O^{*i*}Pr)₄+DET) can be successfully bound to HMS support by three assembled pathways, furthermore, these chiral mesoporous catalysts show a definite enantioselectivity for styrene oxides in asymmetric epoxidation of styrene with TBHP.

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