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Assemblies of Ti active sites over HMS supports containing surface's OH or NH_2 groups

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Three types of HMS supports, which were as-synthesized, HMS(u), HMS(c) calcined from HMS(u), and HMS(m) prepared by the modification of HMS(c) with 3-amino propyltriethoxysilane, were first used to assemble the Ti catalytic sites through the exchange reactions between them and Ti compounds such as Ti tetraisoproxide ($Ti(O^iPr)_4$), Ti tetrachloride ($TiCl_4$)) and their Ti tartrate complexes. The Ti-assembled HMS catalysts were investigated in detail by means of FT-IR, UV–vis reflection spectra, chemical and elemental analyses. It is found that in $Ti(O^iPr)_4$ and especially $TiCl_4$, the exchange that takes place with the surface hydroxyls of the HMS(c) is easier than with the surface NH_2 groups of HMS(u) and HMS(m). Ti tartrate complex can be successfully assembled on the HMS(c) through three assembled pathways. The UV–vis reflection spectra indicates that the Ti species are highly dispersed upon the surface of HMS. In catalyzing epoxidation of styrene with TBHP, the above-described catalysts show a higher catalytic activity and selectivity for the epoxides than unloading Ti tartrate complex, and the Ti-substituted HMS catalysts. Their outstanding advantage is that they can be reused many times with little loss of activity.

KEY WORDS: mesoporous silicas; HMS; assembly; binding; Ti complexes; XRD\FT-IR, catalytic epoxidation; styrene.

1. Introduction

The recent 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. These mesoporous materials have larger pore sizes ($1.5 \sim 10.0$ nm) and internal surface areas ($\sim 1000\,m^2/g$) [1,2] as well as a large number of surface OH groups [4,5]. They, therefore, are potential catalysts for large molecule conversions and hosts for the assembly of a wide variety of transition metal complexes. On the basis of this concept, many researchers have recently reported that the surface hydroxyls on mesoporous silica bonding transition metal complexes such as titanocene [6], Ti tetraisopropoxide ($Ti(O^iPr)_4$) [7], Mn Schiff-base complexes [8], $Mn_2(CO)_{10}$ [9], Co complexes [10], and other transition metal complexes [11]. These materials were claimed to be effective catalysts for the epoxidation of alkene with tetrabutyl hydroperoxide (TBHP) [6,7,10–14]. However, there were few reports on the assemblies of Ti tartrate complex over mesoporous materials.

Here, we first reported the assemblies of $Ti(O^iPr)_4$ and $TiCl_4$ as well as their Ti tartrate complex over HMS mesoporous materials by the exchange reaction of Ti compounds or tartaric acid with the surface OH or NH_2 groups of HMS support, and the characterizations of these assembled mesoporous materials by XRD, FT-IR, UV–vis reflection spectra, elemental, and chemical analysis methods, as well as the catalytic oxidative properties of these assembled HMS catalysts in the epoxidation of styrene with TBHP as an oxidant.

2. Experimental

2.1. Synthesis of mesoporous HMS

HMS was synthesized via a neutral S^oI^o templating pathway using tetradecylamine (TDA) as the surfactant, ethanol (EtOH) as a co-solvent and tetraethyl orthosilicate (TEOS) as an Si source. In a typical preparation, the TEOS was added dropwise to the solution of TDA in water and ethanol under vigorous stirring. The molar composition of the reaction mixtures was 1.0Si : 0.2TDA : 9.0EtOH : $72H_2O$. The reaction mixtures were aged at room temperature (293 K) under vigorous stirring for 24 h. The solid obtained was filtered off, washed thoroughly with ethanol and dried at 393 K for 4.0 h. The dried sample was divided into two parts, one part calcined at 873 K for 6 h was denoted as HMS(c), another untreated part was denoted as HMS(u). Both the samples were degassed at 413 K for 4 h under vacuum prior to use.

2.2. HMS(c) modified by 3-amino propyltriethoxysilane (APTES)

0.5 g of HMS(c), 0.268 g of APTES and 10 mL of toluene were added to the three-necked flask equipped with a condenser and thermometer and the mixtures were refluxed at 393 K for 12 h under stirring. The modified solid (denoted as HMS(m)) was filtered off, repeatedly washed with toluene and dried at 393 K for

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4 h. The measured NH_2 loading on HMS(m) was ca. 1.64 mmol NH_2g^{-1} by means of PE-2400 CHN elemental analysis instrument.

2.3. Assembly of Ti complexes over mesoporous supports

Three pathways for assembling Ti tartrate complexes over mesoporous 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 of $Ti(O^iPr)_4$ (denoted as Ti) or $TiCl_4$ and 10 mL of toluene were added to the three-necked flask equipped with a condenser and a thermometer under N_2 and stirred for 48 h at different temperature. The modified solid was repeatedly washed with anhydrous toluene, and then activated at 413 K under vacuum overnight prior to use. (2) 0.25 g of HMS(c)–Ti or HMS(m)–Ti, 0.75 mmol of diethyl tartrate (DET) and 10 mL of CH_2Cl_2 were added to the three-necked flask and the mixtures were stirred for 12 h at 288 K under N_2. The modified solid was repeatedly washed with CH_2Cl_2 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(c), 1.0 g of tartaric acid(TA), 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(c)–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(c). (2) 0.25 g of HMS(c)–TA, 1.25 mmol of Ti compounds and 10 mL of CH_2Cl_2 were mixed and stirred at 288 K for 12 h under N_2. The modified solid was repeatedly washed with CH_2Cl_2 and then dried at 323 K for 4 h under vacuum.

The third pathway:

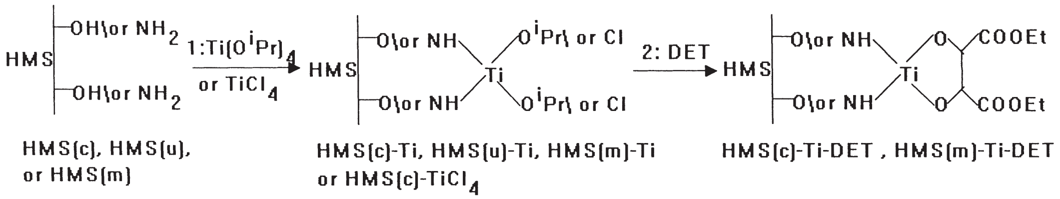
The prepared conditions for scheme 3: 0.5 g of HMS(c), 1.25 mmol of $Ti(O^iPr)_4$, 1.5 mmol of DET, and 10 mL of CH_2Cl_2 were mixed and stirred at 288 K for 12 h under N_2. The modified solid was repeatedly washed with CH_2Cl_2 and then dried under vacuum at 323 K for 4 h.

2.4. Characterization of catalysts

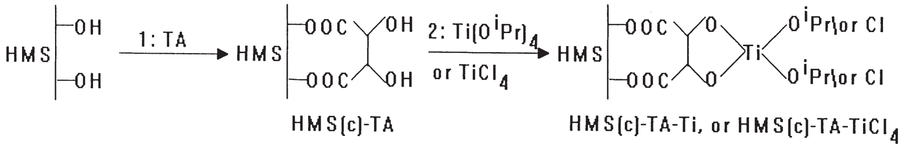
The catalysts thus obtained were studied through X-ray powder diffraction, UV–vis scanning spectrophotometer and FT-IR spectroscopy. Their Ti loading was measured with chemical analysis. The XRD measurements were carried out with a Siemens D-500 diffractometer with Cr Kα radiation ($\lambda = 2.292$ Å) and a scan speed of 2° (2θ)/ min. The UV–vis spectroscopic measurements were carried out on a UV–vis scanning spectrophotometer equipped with an integrating sphere. A reflection mode with a resolution of 2 nm and $BaSO_4$ reference were used for the measurements. The infrared measurements were carried out with a Nicolet 510P spectrometer, using KBr pellets.

2.5. Catalytic testing

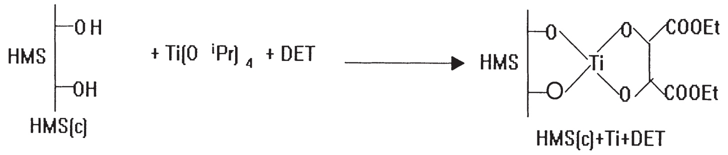
3.6 mmol of styrene, 1.2 mmol of TBHP, 0.1 g of catalyst and 2 mL of CH_2Cl_2 were added to a three-necked flask equipped with a condenser and a thermometer and the mixtures were stirred at 323 K for 7 h.



Scheme 1.



Scheme 2.



Scheme 3.

The reaction products were analyzed by GC on a SE-30 capillary column with a FID.

3. Results and discussions

3.1. XRD characterization

Figure 1 illustrates XRD patterns of the calcined HMS(c) and the untreated HMS(u). The HMS(c) and HMS(u) only exhibited 100 reflection peak accompanied by broader unresolved higher-order reflections, indicating that HMS possesses a mesostructure with the lack of a long-range order [2]. A comparison of HMS(c) with HMS(u) might show, when the templating agent is removed from HMS by calcination, that its 100 reflection peak is shifted to higher diffraction angles, indicating progressive contraction of the lattice *d*-spacing.

3.2. UV–vis diffuse reflectance spectroscopy

The $Ti(O^iPr)_4$ and $Ti(O^iPr)_4 + DET$ chemically bound HMS(c) as well as Ti-substituted HMS were further verified by UV–vis diffuse reflectance spectroscopy. The spectra for HMS(c)–Ti, HMS(c)–Ti–DET and Ti–HMS (figure 2) showed a much broader character of absorption bands at 220 ~ 300 nm, and lacked the 325 nm band characteristic for segregated titania. This broad absorption band may be indicative of the presence of Ti species in the mixed tetrahedral, distorted tetrahedral and octahedral coordination environments [15]. This suggests that most of Ti species in our HMS(c)–Ti and HMS(c)–Ti–DET are highly dispersed onto the surfaces of HMS(c) and most of Ti atoms in Ti-HMS occupy site-isolated positions in the silica framework.

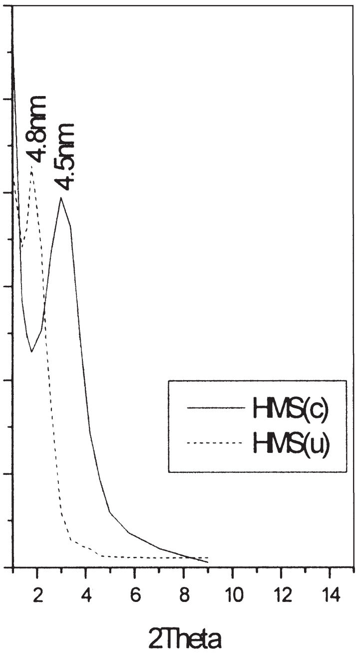


Figure 1. XRD patterns of calcined HMS(c) and uncalcined HMS(u).

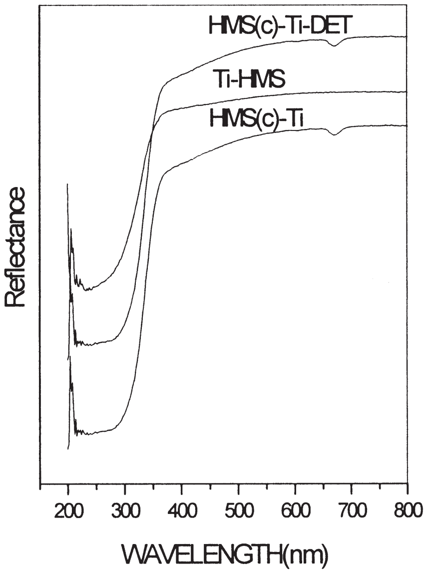


Figure 2. UV–vis diffuse reflectance spectroscopy and of Ti-containing HMS materials.

3.3. FT-IR characterizations and Ti-loading measurements

3.3.1. Binding interaction of Ti compounds with HMS supports

In order to investigate the binding interaction between Ti compounds and the surface functional groups of HMS supports, FT-IR was used to characterize the various HMS samples binding Ti compounds. The IR spectra shown in figures 3 and 4 indicated that a new weaker IR band near 960 cm^{-1} was observed in the HMS supports treated with $Ti(O^iPr)_4$ and especially $TiCl_4$. Furthermore, the intensity of this band corresponded well with its measured Ti loading (see table 1). Very interestingly, a similar 960 cm^{-1} band could also be observed in the HMS modified by other guest molecules such as APTES (see figure 4(a)) and TA (see figure 5(b)). Although there are still some disputes [16,17] to the assignment of this band, more evidences that a similar band was previously observed in TS zeolites [18,19], in Ti siloxane polymers [20] or in TiO_2 grafted on silica [21] support the fact that the 960 cm^{-1} should be due to a modification of SiO_4 units indirectly related to the presence of the guest molecules and indicate a strong binding of the surface functional groups of HMS with Ti compounds.

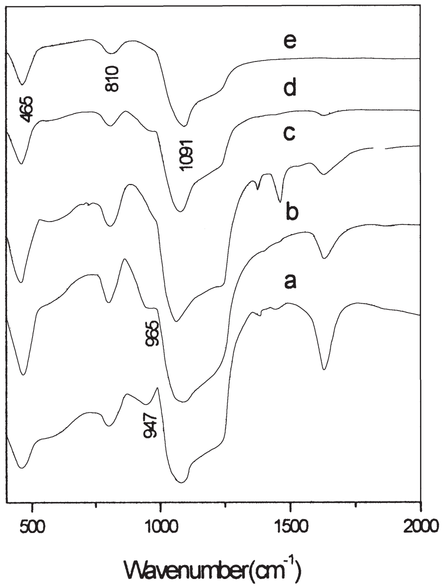


Figure 3. FT-IR spectra of HMS(c) binding Ti compounds at different temperature. (a) HMS(c)−$TiCl_4$ prepared at 303 K, (b) HMS(c)−Ti prepared at 303 K, (c) HMS(c)-$TiCl_4$ prepared at 393 K, (d) HMS(c)−Ti prepared at 393 K, (e) HMS(c).

3.3.2. *Effects of exchange temperature on exchange reactions of Ti compounds with HMS*

Table 2 listed the measured results of the Ti loading and the intensity of 960 cm^{-1} band on the various HMS supports modified by Ti compounds at different temperatures. It might be clearly shown that the exchange behaviors of Ti compounds with the surface OH groups of HMS(c) were completely different from that of Ti compounds with the surface NH_2 groups of HMS(m) and HMS(u). The exchange reactions of $Ti(O^iPr)_4$ and especially $TiCl_4$ with the HMS(c) occurred easily, and a high Ti loading and a strong 960 cm^{-1} band even at low temperature (303 K) could be obtained. As the exchange temperature was increased, the Ti loading and the intensity of 960 cm^{-1} band on HMS(c)−Ti was inversely decreased. We propose that the temperature may affect the exchange model of Ti compounds with HMS(c), namely, it would be very likely that one Ti compound mainly occupies one surface OH site under the low temperature but several surface OH sites under high temperature. This proposal can be confirmed from the continuous decrease in the content of isopropanol ligand measured on HMS(c)−Ti as the temperature increases. On the contrary, the exchange reactions of $Ti(O^iPr)_4$ with both HMS supports containing the surface NH_2 groups become difficult at the low temperature (303 K), and hence need high exchange temperature for obtaining a high Ti loading. This may mean that the exchange temperature does not modify the exchange model of $Ti(O^iPr)_4$ with the supports containing surface NH_2 groups. A further comparison of HMS(u)−Ti with HMS(m)−Ti might show that the former had more Ti loading than the latter under the same exchange conditions; this may be because the former (with 3.3 mmol $NH_{2.}g^{-1}$) can supply more exchange sites than the latter (1.64 mmol NH_2g^{-1}) for binding $Ti(O^iPr)_4$.

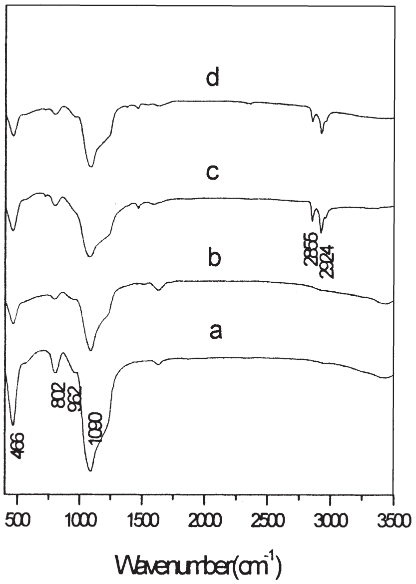


Figure 4. FT-IR spectra of $Ti(O^iPr)_4$ assembled HMS(u) and HMS(m) at 373 K. (a) HMS(m), (b) HMS(m)−Ti, (c) HMS(u), (d) HMS(u)−Ti.

3.3.3. *FT-IR of Ti complexes assembled mesoporous samples*

FT-IR spectra of the various HMS samples binding the Ti tartrate complex were shown in figure 5. The spectrum of HMS(c)−TA (figure 5(b)) exhibited a very strong ester carbonyl band at 1759 cm^{-1} and a weak 960 cm^{-1} band; the appearance of 960 cm^{-1} band further confirms the previous assignment to this band, and the appearance of 1759 cm^{-1} band indicates the strong esterification of the surface hydroxyls of HMS(c) with tartaric acid. When the HMS(c)−TA was further treated with $Ti(O^iPr)_4$ or $TiCl_4$, their carbonyl band were slightly reduced and had a small shift (figure 5(c) and (d)). When the HMS(c)−Ti and the HMS(m)−Ti samples (prepared at 393 K) were further treated with DET or the HMS(c) was simultaneously treated with Ti compounds and DET, their IR spectra also exhibited a weaker ester carbonyl band near 1738 ~ 1743 cm^{-1} (see figure 5(e), (f), and (g)). This band took slight place shifts in comparison with the carbonyl of free DET (at 1740 cm^{-1}), but this carbonyl shift was by far smaller than that of DET + $Ti(OiPr)_4$ in toluene(figure 5(a), the latter shifted to 1751 cm^{-1}), which indicates that DET has been bound on the supports by the exchange of its hydroxyls rather than its carbonyls with Ti compounds anchored on the supports.

Table 1
Effects of exchanged temperature on the exchanged reaction between Ti compounds and HMS

Temp. (K)	HMS(c)−Ti			HMS(c)−$TiCl_4$		HMS(u)−Ti	HMS(m)−Ti
	Loading ($mmol\,g^{-1}$)		$960\,cm^{-1}$ intensity[a]	Ti Loading ($mmol\,g^{-1}$)	$960\,cm^{-1}$ intensity[a]	Ti Loading ($mmol\,g^{-1}$)	Ti Loading ($mmol\,g^{-1}$)
	Ti	i-PrOH					
303	1.38	3.54	0.35	1.67	0.52	0.67	0.49
333	1.30	3.17	0.30	1.17	0.22	0.94	0.58
373	1.08	1.87	0.18	0.89	—	1.63	0.76
393	0.93	1.52	0.12	0.80	—	1.57	0.72

[a] The intensity of $960\,cm^{-1}$ was calculated from the ratio of the integrated areas of $960\,cm^{-1}$ band with $800\,cm^{-1}$ band.

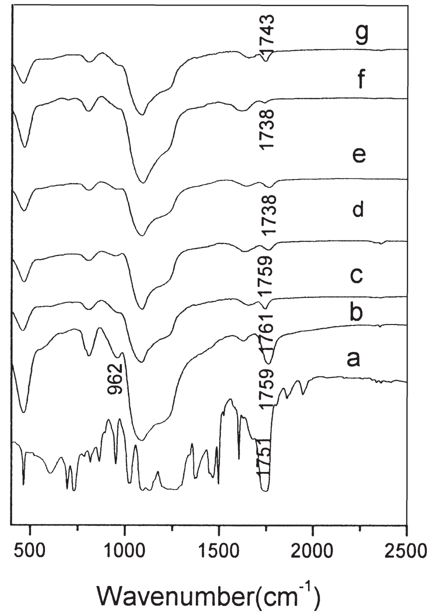


Figure 5. FT-IR spectra of various assembled HMS samples with Ti complex. (a) $Ti(O^iPr)_4$ + DET, (b) HMS(c)−TA, (c) HMS(c)−TA-Ti, (d) HMS(c)–TA–$TiCl_4$, (e) HMS(c)−Ti-DET, (f) HMS(m)−Ti-DET, (g) HMS(c) + Ti + DET.

3.4. Epoxidation of styrene

The catalytic properties of the above-assembled HMS materials were tested and compared with those of Ti-substituted HMS (Ti-HMS) catalysts in the epoxidation of styrene with TBHP. The results listed in tables 2 and 3 indicated that styrene was selectively oxidized to styrene oxide ($PhCHOCH_2$), phenylacetaldehyde ($PhCH_2CHO$) and a small quantity of benzaldehyde (PhCHO) over these catalysts. Among them, the HMS(c)−Ti prepared at 393 K showed the best catalytic activity (30% conversion of styrene), which was slightly better than the reaction results of silica-$Ti(OiPr)_4$ catalyst reported previously by Cativiela [7]. Ti−HMS also possessed a high catalytic activity (20% conversion of styrene). If using a convenient hydroperoxide (31% aq. H_2O_2) instead of TBHP as an oxidant, these catalysts would be less active. For example, a very poor conversion of styrene was obtained on the HMS(c)−Ti (see table 2). It may be because a large amount of water in H_2O_2 can enhance the hydrolysis of Ti compound-anchored HMS and lead the catalysts to loss of activity. Comparisons of these assembled catalysts might show that the used HMS supports, Ti compounds and DET ligand, as well as the exchange temperature and assembled methods for the preparation of these catalysts, all affected their catalytic properties to a different degree. In the following sections, we will describe these influencing factors respectively.

3.4.1. Effects of HMS supports

Among the $Ti(O^iPr)_4$ assembled HMS catalysts, HMS(c)−Ti families had a higher activity and lower selectivity for the epoxides than HMS(m)−Ti and especially HMS(u)−Ti families (see table 2). We propose that the Lewis acid of the Ti sites anchored on the supports may be the main factor affecting their catalytic properties; $Ti(O^iPr)_4$ with a strong Lewis acid alone is not used as an oxidative catalyst, and this may be confirmed by the fact that $Ti(O^iPr)_4$ only catalyzes the polymerization of styrene (see table 2). When $Ti(O^iPr)_4$ is bound to HMS(c) by exchange reaction, its Lewis acidic intensity would be reduced, and then HMS(c)−Ti samples would become the effective oxidative catalysts. But the Lewis acid sites of the HMS(c)−Ti catalysts could further catalyze the rearrangement of the epoxides and lead to the decrease in epoxidative selectivity. This may be confirmed from their efficient catalyzation of this rearranged reaction (table 2, about 70% styrene oxide can be rearranged to $PhCH_2CHO$ and a small of PhCHO over HMS(c)−Ti). When $Ti(O^iPr)_4$ was bound to both supports containing the surface NH_2 groups, its Lewis acid was abruptly decreased because of the positioning of the surface NH_2 groups of the supports on the Ti sites. It is reasonable that they show a low oxidative activity and a high epoxidative selectivity. A further comparison of HMS(u)−Ti and HMS(m)−Ti catalysts might show that the former with a high Ti loading had inversely a lower activity but higher selectivity than the latter with a low Ti loading, which

Table 2
Effects of exchanged temperature on catalytic properties of Ti compounds–assembled catalysts for epoxidation of styrene

Samples	Exchange temp. (K)	Ti loading ($\mathrm{mmol\,g^{-1}}$)	Conversion of styrene (mol%)	Product distribution[a] (%)		
				PhCHO	$\mathrm{PhCH_2CHO}$	$\mathrm{PhCHOCH_2}$
HMS(c)−Ti	303	1.38	17.4	26.1	73.9	—
	373	1.08	24.6	18.7	69.2	12.1
	393	0.93	30.1	14.7	64.6	20.7
HMS(u)−Ti	303	0.67	4.9	14.2	41.5	44.3
	373	1.63	12.9	4.2	19.4	75.4
	393	1.57	12.2	4.7	23.6	71.7
HMS(m)−Ti	303	0.49	4.1	19.3	58.9	21.8
	373	0.76	18.4	16.1	59.4	24.5
	393	0.72	17.9	13.9	61.9	24.2
HMS(c)−$\mathrm{TiCl_4}$	393	0.80	10.2	8.4	70.0	21.6
Ti−HMS[b]	—	0.33	21.3	10.9	62.7	26.4
HMS−Ti[c]	393	0.93	2.9	75.1	24.9	—
HMS(c)−Ti[d]	393	0.93	—	6.3	63.7	30.0

[a] Reaction was carried out at 323 K; Product distributions included benzaldehyde (PhCHO), phenylacetaldehyde ($\mathrm{PhCH_2CHO}$) and styrene oxide ($\mathrm{PhCHOCH_2}$).
[b] Ti-HMS was prepared on the basis of reference [22].
[c] Use of 31% aq. $\mathrm{H_2O_2}$ instead of TBHP as an oxidant.
[d] 3.6 mmol of styrene oxide, 0.1 g of catalyst and 2 mL of $\mathrm{CH_2Cl_2}$ as solvent at 323 K for 7 h.

was mainly because the former with high surface $\mathrm{NH_2}$ groups had a stronger positioning to the Ti sites than the latter with low surface $\mathrm{NH_2}$ groups.

3.4.2. *Effects of exchange temperature*

The influences of the exchange temperature on the catalytic properties of the above catalysts were the same, namely, the activities of these catalysts were continuously increased as the increase in their exchange temperature (see table 2). It is very reasonable that the catalytic activities of a series of catalysts of HMS(u)−Ti and HMS(m)−Ti correspond well with their Ti loading. On the contrary, the catalytic activities of a series of catalysts of HMS(c)−Ti correspond inversely with its Ti loading. This abnormal phenomenon may be explained as follows: the exchange temperature affects the exchange model of HMS(c) with Ti compounds by modifying the numbers of surface hydroxyls of HMS(c) occupied by one Ti compound, and results in the varieties of the coordination environment of Ti active sites on HMS(c)−Ti. This is consistent with the above-described characterization results.

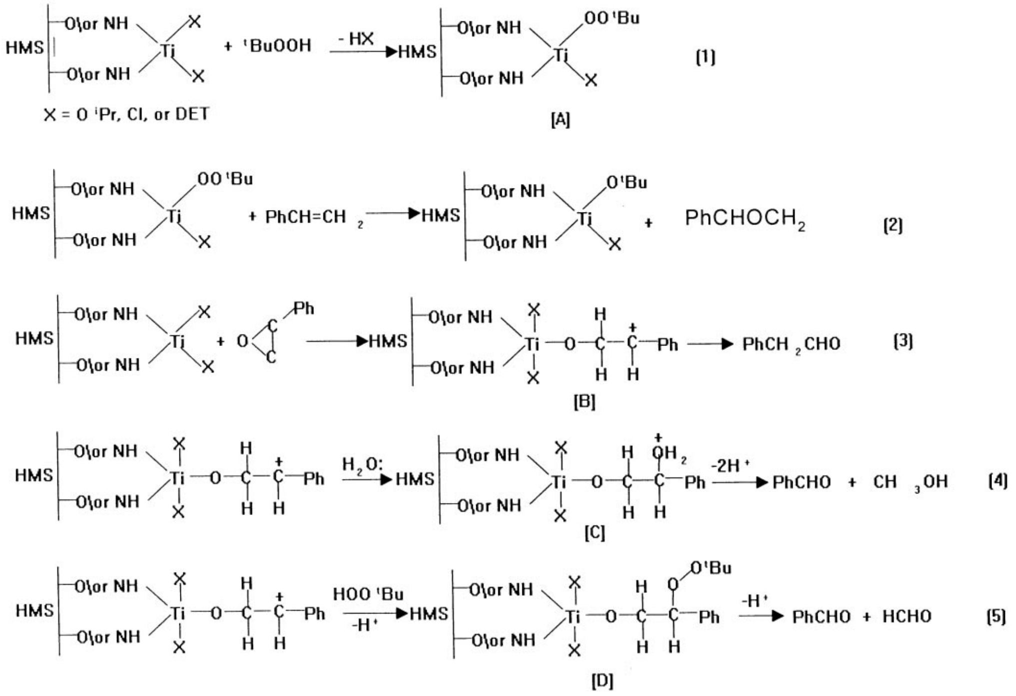
3.4.3. *Effects of DET ligand and assembled methods*

The various Ti tartrate–assembled catalysts exhibited higher activity and selectivity for the epoxide than unloading Ti tartrate complex in the epoxidation of styrene (only 7.0% conversion and 16.5% selectivity could be obtained over $\mathrm{Ti(O^iPr)_4}$ + DET complex). A further comparison of them might show that the used support affected their catalytic performances; when the HMS(c)−Ti (prepared at 393 K) further bonded DET

Table 3
Adjusting effects of DET ligand on catalytic properties of various assembled catalysts in epoxidation of styrene with TBHP

Samples	Ti loading ($\mathrm{mmol\,g^{-1}}$)	Conversion of styrene (mol %)	Product distribution (%)		
			PhCHO	$\mathrm{PhCH_2CHO}$	$\mathrm{PhCHOCH_2}$
HMS(c)−Ti−DET	0.93	15.7	5.8	49.8	44.4
HMS(c)+Ti+DET	1.33	22.0	3.7	56.7	43.6
HMS(c)−TA−Ti	0.94	15.4	—	70.2	29.8
HMS(c)−TA−$\mathrm{TiCl_4}$	1.49	7.8	5.8	50.6	43.6
HMS(m)−Ti−DET	0.76	23.2	5.6	55.2	39.2
$\mathrm{Ti(O^iPr)_4}$[a]	—	100	—	—	—
$\mathrm{Ti(O^iPr)_4}$ + DET[b]	—	7.0	28.2	55.3	16.5

[a] 0.1 mmol of $\mathrm{Ti(O^iPr)_4}$ as catalyst. Styrene was completely polymerized.
[b] 0.1 mmol of $\mathrm{Ti(O^iPr)_4}$ plus 0.12 mmol of DET as catalyst.



Scheme 4.

ligand, its activity was abruptly decreased from 30.1 to 15.1% and its selectivity was significantly increased from 20.7 to 44.4% (HMS(c)–Ti-DET sample), which might be due to the strong adjusting of DET to the Ti sites on HMS(c). Adversely, the adjusting of DET to the Ti sites on the HMS(m) could slightly increase its catalytic activity from 17.6 to 23.2%, indicating a weak adjusting (see tables 2 and 3). The assembled pathways for HMS(c) binding Ti tartrate complex also affected the catalytic properties, HMS(c) + Ti + DET catalyst prepared by the third pathway showed the best activity (ca. 22.0% conversion), in agreement with its high Ti loading. HMS(c)–TA–Ti catalyst prepared by the second pathway exhibited an activity similar to HMS(c)–Ti-DET but a low selectivity (only 29.8% styrene oxide) similar to HMS(c)–Ti, which is mainly because it has a Ti coordination environment similar to HMS(c)–Ti.

On the basis of the 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 the replacement of TBHP to one ligand on the Ti sites–anchored HMS supports and then it oxidizes styrene to form the epoxides (see equations 1 and 2 in scheme 4). 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 [B] is further rearranged to form $PhCH_2CHO$ (see equation 3 in scheme 4); another [B] combines with water or TBHP to form the unsteady intermediates ([C] and [D]), following which [C] and [D] are further cracked into PhCHO, HCHO, and CH_3OH (see equations 4 and 5 in scheme 4).

3.4.4. Reuse testing

Table 4 lists the reused results of the recovered HMS(c)–Ti catalyst (prepared at 393 K) for the epoxidation of styrene. The results that the measured Ti leaching of the first and second recovered catalysts was only 0.97 and 0.22%, respectively, and the fact that the recovered catalysts could be repeatedly used many times with little loss of activity indicated that our prepared Ti-grafted HMS catalyst had excellent reusability.

Table 4
Reused results of recovered HMS(c)–Ti catalyst

No	Ti loading ($mmol\,g^{-1}$)	Conversion of styrene (mol %)	Product distribution (%)		
			PhCHO	$PhCH_2CHO$	$PhCHOCH_2$
1	0.932	30.3	13.2	68.7	18.1
2	0.923	29.7	4.6	69.2	26.2
3	0.921	30.1	4.4	63.0	32.6

4. Conclusions

Ti compounds and their complexes can be successfully assembled on HMS supports by binding them with the surface OH or NH_2 groups of the supports. The binding of the surface hydroxyls of the support with Ti compounds occurs more easily than that of the surface NH_2 groups of the supports with Ti compounds. The measured Ti loading of HMS(c)−Ti corresponds inversely with the exchanged temperature, indicating that the exchanged temperature probably affects the number of surface hydroxyls of HMS(c) exchanged by one Ti compound. The UV–vis reflection spectra indicate that most of Ti species in our HMS(c)−Ti and HMS(c)−Ti-DET are highly dispersed onto the surfaces of HMS(c).

In catalyzing epoxidation of styrene with TBHP, the assembled catalysts have higher activity and selectivity for the epoxides than unloading $Ti(O^iPr)_4 + DET$ complexes, Ti-substituted HMS catalysts. The HMS(c)−Ti catalyst prepared with $Ti(O^iPr)_4$ at 393 K possesses the best catalytic activity and can be reused many times with little loss of activity. The adjusting of DET and NH_2 groups to the Ti-active sites anchored on the supports leads to the decrease in the catalytic activity and the increase in the epoxidative selectivity.

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