The epoxidation of allyl alcohol on Ti-complex/MCM-48 catalyst

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Abstract

The heterogeneous sharpless-type catalyst was prepared by an in situ method using MCM-48 as the support. The influence of the incorporation process on the structure of MCM-48 was studied by the XRD, FT-IR, ²⁹Si MASNMR and N₂ adsorption–desorption. The obtained materials showed the definite catalytic activity on the epoxidation of allyl alcohol under the system of acetone (solvent) and peroxydicarbonate (oxidant).

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1. Introduction

Since the introduction of the sharpless asymmetry epoxidation reaction in 1980 [1], it has been attracting many researchers to prepare the heterogeneous sharpless-type catalyst to resolve the problem of deactivation and separation related to the homogenous catalyst [2,3]. Recently, the discovery of the M41s family that has a large and regular channel structure, the OH-rich inner surface and the stability in organic solvent provided a better support material for the preparation of the organic–inorganic hybrid heterogeneous catalyst and enabled the incorporation of large active centers into the channel of these materials. Based on this, Johnson et al. [4], Bae et al. [5] and Xiang et al. [6] had successfully incorporated the different chiral reagents into the channel of MCM-41. However, similar reports of MCM-48 having more advantages of three-dimensional channel system over MCM-41 having the one-dimensional channel system are very few [7–9]. Additionally, in their reports, the influence of the incorporation process on the structure of support was not studied in detail. Here, we introduced a convenient in situ method to incorporate the sharpless-type catalyst into the channel

of MCM-48 and studied the influence of the incorporation process on the structure of MCM-48.

2. Experimental

2.1. Synthesis

The synthesis method of MCM-48 used in this work had been described elsewhere [10–12]. Typically, MCM-48 was prepared as follows: tetraethylorthosilicate (TEOS, Chemical Co., Beijing) was added to the mixture of cetyltrimethylammonium bromide (C₁₆H₃₃Me₃NBr, CTAB, Chemical Co., Beijing), sodium laurate (C₁₁H₂₃COONa, SL, Chemical Co., Beijing), NaOH (Chemical Co., Beijing) and H₂O. The molar composition of the above mixture was 1.0SiO₂:0.153CTAB:0.017SL:0.25Na₂O:100H₂O. This solution was stirred at 30 °C for 1 h. After that, the mixture was placed in a static autoclave at 100 °C for 4 days. The solid product was recovered and calcined at 550 °C in air (5 °C/min) for 4 h.

The incorporation procedure was as follows: 0.5 g MCM-48 was activated by heating under vacuum at 300 °C for 2 h. Then 1.25 ml of 1 M solution of the titanium tetraisopropoxide (Ti(OⁱPr)₄, Fluka Co.) or 1.56 ml of 0.8 M solution of the titanium tetrachloride (TiCl₄, Fluka Co.), 0.31 g D-(+)-diethyl-tartrate (DET, Fluka

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Co.) and 10 ml dry toluene (Chemical Co., Beijing) were added to the activated solid under N_2 protection at rt. The resulted mixture was stirred under the atmosphere with the solvent protection device (see the [supporting material](#)) at 15 °C for 12 h. Finally, toluene was eliminated via the syringe and the solid was repeatedly washed by dry toluene and dry acetone (5 ml per time) under N_2 protection until the lotion (the washed toluene and acetone) had no optical activity (this step will eliminate the influence of unbound DET in solution in the next optical activity tests). The obtained solid was dried and placed into desiccators.

2.2. Characterization

The MCM-48 samples were characterized by the powder X-ray diffraction (XRD), TEM, FT-IR, ^{29}Si MAS-NMR and sorption studies systematically. The XRD patterns were recorded on a Rigaku D/Max-IIA X-ray powder diffractometer (Ni-filtered $\text{Cu K}\alpha$ radiation with $\lambda = 1.542 \text{ \AA}$) operated at 30 kV and 20 mA. The TEM images were obtained on the JEM-2010 transmission electron microscope operated at 200 kV. FT-IR spectra were obtained on the Bruker Vector22 with KBr as reference. ^{29}Si MAS-NMR was recorded on the Bruker DSX-300 Spectrometer (the magnetic field is 7.05 T and the resonance frequency is 59.63 MHz). N_2 adsorption–desorption isotherms were determined at 77 K on a Micromeritics TriStar 3000 instrument using nitrogen as the adsorbent. The pore size distribution curve came from the analysis of the adsorption branch of the isotherm by the BJH (Barrett-Joyner-Halenda) method. The Ti loading was measured by the chemical analysis with EDTA and ZnCl_2 solution. Optical activities were measured by the WZZ-2A automatic digital display polarimeter.

2.3. Catalytic test

The catalytic tests were carried out in a 25 ml two-necked flask equipped with a condenser and a thermometer. Allyl alcohol (1 g), peroxy carbamide (0.5 g), catalyst (0.1 g), acetone (5 ml) and a few molecular sieves, 5A (these were used to absorb the water of the reaction system during the catalytic test and showed no activity for the reaction) were added to the flask. This mixture was stirred at 15 °C for 2 h. The reaction products were analyzed by gas chromatography (GC) on a column packed with 10% di-isobutyl phthalate with an FID.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern of as-synthesized MCM-48 sample. One can see that the four typical diffraction peaks of (211), (220), (420) and (332), which correspond to the Ia3d space group, are well resolved in this sample. Fig. 2 shows the TEM image of calcined MCM-48 sample on the (110) plane. It shows that the cubic (Ia3d) textural structure is uniform. The powder

Fig. 1. XRD pattern of as-synthesized MCM-48 sample.

Fig. 2. TEM image of calcined MCM-48 sample on the (110) plane.

X-ray diffraction patterns of the incorporated MCM-48 samples are shown in Fig. 3. It was found that sample b (using TiCl_4 as Ti-source) still retains the four diffraction peaks attributed to the cubic Ia3d structure although the intensity of the peaks decreased. On the contrary, the diffraction peaks of (420) and (332) disappeared completely in the case of sample c (using $\text{Ti}(\text{O}^i\text{Pr})_4$ as Ti-source) and the intensity of (211) and (220) peaks decreased much more. This result showed that the incorporation of Ti-complexes into the channel of MCM-48 leads to a substantial loss in scattering contrast between the channel and the wall, and then reduces the intensity of the scattered X-ray in the powder diffraction experiment [13]. Due to the larger volume of $\text{Ti}(\text{O}^i\text{Pr})_4$, this change was more obvious for sample c. In addition, the diffraction peak corresponding to the bulk TiO_2 ($2\theta = 25.5$) in the high degree region does not appear for both treated MCM-48 samples (not shown here) and their UV–visible spectra (see the [supporting](#)

Fig. 3. XRD patterns of MCM-48 samples: (a) Untreated MCM-48, (b) MCM-48 + TiCl_4 + DET and (c) MCM-48 + $\text{Ti}(\text{PrO})_4$ + DET.

material, Fig. 1) also do not have the characteristic peaks of bulk TiO_2 [14]. Both of these suggested that the hydrolyzation of Ti-source happens rarely during the incorporation process.

Fig. 4 shows the FT-IR spectrum of the different MCM-48 materials. The peak near 960 cm^{-1} was usually assigned to the stretch vibration of Si–O–H, while the peak near 801 cm^{-1} was attributed to the symmetry stretch vibration of Si–O–Si [15]. We thought the intensity contrast between these two peaks may reflect the inflection of the SiO_4 tetrahedral configuration in the framework. On observation of Fig. 4, we found (1) The 953 cm^{-1} peak of the incorporated samples (c and d) shifts toward the low wave number region compared to the 958 cm^{-1} peak of untreated MCM-48 sample (b). This could be explained by that the

Fig. 4. FT-IR spectrum of MCM-48 samples: (a) Free DET, (b) Untreated MCM-48 ($I_{960}/I_{801} = 1.31$), (c) MCM-48 + TiCl_4 + DET ($I_{960}/I_{801} = 1.01$) and (d) MCM-48 + $\text{Ti}(\text{PrO})_4$ + DET ($I_{960}/I_{801} = 0.575$).

bond length of O–Ti is longer than that of O–H ($k_{\downarrow}$) and the atomic weight of Ti is larger than that of H ($\mu_{\uparrow}$), so the $\nu(\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}})$ will decrease when the H^+ is substituted by Ti^{4+} . (2) The ratio of I_{960}/I_{801} for the incorporated samples decreases compared to that of the untreated MCM-48 sample, and moreover, this ratio of sample c is higher than that of sample d. It was reasonable to analyze that the binding process between the guest molecule (Ti-complex) and the host (OH in the inner surface) will cause the distortion of the SiO_4 tetrahedral configuration in the framework. As a result, the ratio of I_{960}/I_{801} will decrease. In other words, the more the distortion increases, the lower the ratio of I_{960}/I_{801} will be. In the case that the DET binds with the anchored Ti-compound (the OH in the inner surface will prefer to react with the Ti-compound when it simultaneously meets with the Ti-compound and DET), the C–O–Ti bond between the DET and the Ti-compound will weaken the Si–O–Ti bond between the OH and Ti-compound (see Eq. (1)). So, the inductive effect of Ti-complex to the SiO_4 tetrahedral configuration will impair, and then the distortion of SiO_4 tetrahedral configuration in the framework will decrease. Consequently, the ratio of I_{960}/I_{801} in this case (1.01) will be higher than that of the other case (0.575) that DET does not bind with the anchored Ti-compound further. (3) In the case of sample c (using the TiCl_4 as Ti-source), a new peak appears at 1738 cm^{-1} , the position of which is somewhat “red shifting” compared to the position of C=O belonging to free DET (1743 cm^{-1}). Since the blank test results excluded the possibility that some factors, such as the system error of the instrument, the space limit of MCM-48 channel for DET (the case of physical adsorption), and the interaction between the free Ti-compound and free DET, cause this change, we thought the DET probably binds with the anchored Ti-compound by its OH rather than its C=O. Then the vibration of C=O cannot be affected sharply by the incorporation process (see Eq. (1)) [16]. In the case of sample d (using $\text{Ti}(\text{O}^i\text{Pr})_4$ as Ti-source), a peak appears at 1743 cm^{-1} , the position of which is the same as the position of C=O belonging to free DET. This fact suggests that the DET does not bind with the anchored Ti-compound further in this case.

The ^{29}Si MASNMR results (Fig. 5) of untreated MCM-48 and incorporated MCM-48 sample (using TiCl_4 as Ti-source) show that the amount of $\text{Q}^2((\text{SiO})_2\text{Si}(\text{OH})_2)$ units and $\text{Q}^3((\text{SiO})_3\text{SiOH})$ units of incorporated MCM-48 sample decreases obviously compared to that of the untreated MCM-48. It meant that some OH groups belonging to Q^2 or Q^3 have bound with the Ti-complex during the incorporation process. This is in good response to the above FT-IR results.

Fig. 5. Deconvoluted ²⁹Si MASNMR of MCM-48 samples: (a) MCM-48 + TiCl₄ + DET and (b) Untreated MCM-48.

The N₂ adsorption–desorption isotherms and the corresponding BJH pore size distributions based on the adsorption branch for the MCM-48 samples are shown in Fig. 6. Both the isotherms of the incorporated samples are typically irreversible IV adsorption isotherms with two separate H1 and H4 hysteresis loops as defined by IUPAC [17]. Compared to the untreated MCM-48 sample, the H1 hysteresis loops of the incorporated MCM-48 samples shift toward low p/p_0 region, and among them, the hysteresis loop of sample c (using the Ti(O^{*i*}Pr)₄ as Ti-source) not only shifted further toward low p/p_0 region but also looked more smooth than that of sample b (using TiCl₄ as Ti-source). All of these suggested that the introduction of Ti(O^{*i*}Pr)₄ into the channel will cause a great change in the pore structure of the support during the incorporation process. One can see these changes more clearly from Table 1. Both the pore volume and pore diameter of the incorpo-

Fig. 6. N₂ adsorption and desorption isotherms of MCM-48 samples. The inset shows the pore size distribution calculated from the analysis of the adsorption branch of the isotherm (a) Untreated MCM-48, (b) MCM-48 + TiCl₄ + DET and (c) MCM-48 + Ti(O^{*i*}Pr)₄ + DET.

rated MCM-48 samples decrease compared to those of untreated MCM-48 samples and these two values of sample c are much lower. The loss of pore volume and pore diameter suggested that the Ti complex had actually been introduced into the channel of MCM-48. Meanwhile, since the anchored/filled Ti-complex did not distribute orderly in the whole channel, so the pore diameter of some part of the channel became narrow while other parts did not. As a result, the average pore diameter (the fourth column of Table 1) of the incorporated MCM-48 samples would also decrease accompanying the decrease of the pore volume. And furthermore, their FWHM (the fifth column of Table 1) would become wider because of the broadening of the pore size distribution.

The results of the epoxidation of allyl alcohol are presented in Table 2. You can see that (1) When TiCl₄ is used as the Ti-source, the catalyst shows higher Ti loading and higher TON (turnover number, TON = converted allyl alcohol (mol)/Ti (mol)). The reason for the higher Ti loading might be that HCl (the product of the exchange reaction between TiCl₄ and OH in the inner surface) is an inorganic compound and it is easy to separate from the organic phase (toluene), so the exchange reaction can be

Table 1
Surface area and porous structure of MCM-48 samples under investigation

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (Å)	FWHM ^a (Å)
Untreated MCM-48	1159	1.38	26.5	3.53
MCM-48 + TiCl ₄ + DET	569	0.63	23.8	4.42
MCM-48 + Ti(O ^{<i>i</i>} Pr) ₄ + DET	415	0.45	20.2	6.01

^a The full-widths at half-maximum for the pore size distribution curves.

Table 2
The catalytic performance of the incorporated MCM-48 samples

Catalyst	Ti loading (mmol/g)	Allyl alcohol conv.	TON ^a	$[\alpha]_D^{25}$
Untreated MCM-48	0	0	0	0
TiCl ₄ /Ti(ⁱ OPr) + DET	0	0	0	0
MCM-48 + TiCl ₄ + DET	1.18	19.5%	28.8	+0.64
MCM-48 + Ti(ⁱ OPr) + DET	0.85	9.2%	18.4	0

Reaction conditions: allyl alcohol, 1 g; oxidant, 0.5 g; catalyst, 0.1 g; acetone, 5 ml; reaction temperature, 15 °C; and reaction time, 2 h.

^a TON = Converted allyl alcohol (mol)/Ti (mol).

carried through quickly; and that HCl can diffuse out of the channel more easily because of its small volume. On the contrary, the exchange reaction between Ti(ⁱPrO)₄ and OH in the inner surface processed slowly because isopropyl alcohol (its product) is an organic compound and has large volume. The reason for the higher TON could be explained by the fact that the DET can decrease the acid strength of the anchored TiCl₄ by substituting its other two Cl atoms and the DET could also change the electric and geometric environment of anchored TiCl₄, so the active center of this Ti-complex will be more advantaged to get the product (Glycidol). (2) The corresponding homogenous catalyst has no activity under this reaction system. We thought that the Ti-compound and DET cannot form a stable active center without the limit of the MCM-48 framework in this case. (3) Only for the catalyst to which the DET binds with the anchored Ti-complex (TiCl₄ is the Ti-source) does the product show some optical activity although the value is not high. Since the catalyst had been washed completely until the lotion had no optical activity before it was used, so the α (optical rotation) value would not come from the catalyst itself. Based on this, we thought that there are some chiral active centers in this catalyst. In addition, the reasons that we chose the cheap peroxycarbamide as oxidant was that this oxidant is a solid, so it is easy to be desiccated and separated; and that H₂O₂ could be released step by step.

4. Conclusions

Sharpless-type catalyst was introduced into the channel of MCM-48 successfully by an in situ method. When TiCl₄ was used as the Ti source, the DET could bind with the anchored Ti-compound by its OH and this caused a slight “red shifting” of the C=O belonging to free DET. The binding processes between Ti-complex and OH in the inner surface induced the distortion of the SiO₄ tetrahedral configuration in the framework and caused the decrease of the amount of Q² and Q³. The catalyst that was prepared by TiCl₄ showed better catalytic performance because of its higher Ti loading and better environment of active sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.micromeso.2007.09.020](https://doi.org/10.1016/j.micromeso.2007.09.020).

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