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Research Note

Formation of better catalytically active titanium species in Ti-MCM-41 by vapor-phase silylation

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Abstract

Calcined Ti-MCM-41 was silylated by trimethylchlorosilane in the vapor phase for 2–9 h. ^{29}Si MAS NMR spectroscopic study showed that Ti-MCM-41 silylated for 2–5 h exhibited a peak at 11 ppm, which was assigned to $(CH_3)_3SiOSi(OSi)_3$ species. Further silylation of Ti-MCM-41 for 5–9 h gave an additional peak at 5.1 ppm, which was assigned to novel titanium species of $(CH_3)_3SiOTi(OSi)_3$. Ti-MCM-41 silylated for 5 h showed relatively high activity in hydroxylation of benzene and epoxidation of 1-octene compared with calcined Ti-MCM-41. More important, Ti-MCM-41 silylated for 9 h gave much higher activity than Ti-MCM-41 silylated for 5 h. ^{29}Si MAS NMR spectra showed the presence of the titanium species of $(CH_3)_3SiOTi(OSi)_3$ in Ti-MCM-41 silylated for 5–9 h, and these can be better catalytically active sites than conventional titanium species in Ti-MCM-41.

Keywords: Mesoporous titanosilicate; Catalytically active titanium species; Silylation; Hydroxylation; Epoxidation; ^{29}Si MAS NMR spectroscopy

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1. Introduction

Selective catalytic oxidation is an important industrial process in the production of fine chemicals in organic reactions [1–6]. After the synthesis of microporous TS-1 by Enichem Company [1], the catalysts for selective oxidation have focused mainly on titanium-substituted microporous zeolites, such as Ti-ZSM-12, Ti-ZSM-48, and Ti-Beta [7–9]. All of these microporous titanosilicates show remarkable catalytic performance however, they cannot effectively catalyze bulky molecules, because of the limitations of micropore size. The discovery of titanium-containing mesoporous silicates, typically Ti-MCM-41, offers an opportunity to use titanosilicates as versatile catalysts for the conversion of bulky molecules [10]. Unfortunately, when compared with TS-1, the catalytic activities of mesoporous titanosilicates for oxidations are relatively low, which severely hinders their practical application [11]. Therefore, the mesoporous titanosilicates with better catalytically active titanium species are always desirable.

There are a number of approaches for preparing mesoporous titanosilicates with catalytically active titanium species [12–21]. For example, MCM-41 grafted by an organic titanium source (titanocene dichloride) shows much higher catalytic activity than conventional Ti-MCM-41 [22]. Ti-substituted SBA-15 materials through fluoride-accelerating hydrolysis show high activity in the epoxidation of styrene [23]. An ordered mesoporous titanosilicate with Ti species similar to those in TS-1 can be synthesized by the assembly of preformed titanosilicate precursors with surfactant micelle. It exhibits high activity in the oxidation of both smaller molecules, such as phenol and styrene, and bulky molecules like trimethylphenol [11,24,25]. Notably, the mesoporous titanosilicates prepared by these routes are somewhat complex.

Recently, it has been found that a simple silylation of Ti-MCM-41 can effectively increase catalytic activity and selectivity in oxidations [26–30]. According to Notari [27], postsynthetic silylation of titanium-containing molecular sieve results in a significant increase of catalytic activity and selectivity in

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oxidation. Corma et al. [28] observed that silylation of the surface of Ti-MCM-41 produces a very hydrophobic catalyst, increasing the activity of epoxidation of cyclohexene. Tatsumi et al. [29] also reported that titanium-containing mesoporous materials modified by trimethylsilane showed enhanced catalytic activity in the oxidation of alkenes and alkanes with H_2O_2. Sever et al. [30] described vapor-phase silylation processes that were more cost-effective than liquid-phase processes. But all of these studies focused mainly on improving hydrophobicity in ordered mesoporous titanosilicates through the formation of surface groups of $(CH_3)_3SiOSi(OSi)_3$ during silylation.

In the present study, it is very interesting to note that Ti-MCM-41 silylated for 9 h exhibited much higher activity and selectivity in the hydroxylation of benzene and epoxidation of 1-octene than provided by conventional Ti-MCM-41. ^{29}Si MAS NMR spectroscopy suggested the formation of better catalytically active titanium species in Ti-MCM-41 by vapor phase silylation for 5–9 h.

2. Experimental

2.1. Preparation of samples

2.1.1. Ti-MCM-41

Ti-MCM-41 was synthesized from the template of cetyltrimethylammonium bromide (CTAB) in titanosilicate gels formed by tetraethyl orthosilicate (TEOS) and tetrabutyl orthotitanate (TBOT) under ammonia aqueous solution (molar ratio of $SiO_2/TiO_2/CTAB/NH_3H_2O/H_2O = 40/1.0/5.1/525/2372$). After calcination at 550 °C for 4 h, the template in as-synthesized Ti-MCM-41 was removed, and the molar ratio of Si to Ti for calcined Ti-MCM-41 was 65.

2.1.2. Silylation of Ti-MCM-41

The silylation was carried out in a fixed reactor. After the fixed reactor was heated to 200 °C, the vapors of trimethylchlorosilane (TMCS) in N_2 were passed through the bed of Ti-MCM-41 for 2–9 h. The silylated Ti-MCM-41 samples with various silylation times were denoted as Ti-MCM-41(SN), where N represents silylated hours. After silylation, the samples were washed with methanol and deionized water until no chloride was detected.

For comparison, silylated pure silica MCM-41 and Ti-MCM-41(Si/Ti = 100, molar ratio) samples were prepared by a silylation method similar to that for Ti-MCM-41(S9). The samples were denoted as Si-MCM-41(S9) and Ti-MCM-41(100)(S9), respectively.

2.1.3. Titanation of silylated MCM-41

Titanation of silylated MCM-41 was done by postsynthesis using TBOT as a Ti source [19]. The product was denoted as Ti-MCM-41-S.

2.2. Characterization

X-ray powder diffraction measurements were performed on a Siemens D5005 instrument with Cu-K$_\alpha$ radiation, scanning speed of 2° min^{-1}, and scanning regions of 1°–10°. Infrared (IR) spectra of the samples were recorded on a Perkin–Elmer FT-IR spectrometer (PE 430) with a resolution of 1 cm^{-1}. ^{29}Si MAS NMR spectra were recorded on a Bruker MSL-400WB spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS).

2.3. Catalytic tests

Hydroxylation of benzene and epoxidation of 1-octene were carried out in a 50-mL glass reactor and stirred with a magnetic stirrer. In a typical experiment, 12.8 mmol of benzene (or 8.9 mmol of 1-octene), 50 mg of catalyst, and 5 mL of solvent were mixed, followed by addition of 12.8 mmol of H_2O_2 (or 8.9 mmol of H_2O_2). After the reaction for 4 h at 60 °C, the products were analyzed by gas chromatography (GC-14C, Shimadzu) with a flame ionization detector.

3. Results and discussion

3.1. X-ray diffraction (XRD) and infrared spectroscopy (IR)

Fig. 1 shows XRD patterns and IR spectra of calcined Ti-MCM-41, Ti-MCM-41(S9), and Ti-MCM-41-S. Notably, after vapor phase silylation by TMCS in N_2 at 200 °C for 9 h, Ti-MCM-41(S9) and Ti-MCM-41-S still show three diffraction peaks, indexed as (100), (110), and (200) reflections, indicating that the ordered hexagonal mesostructure of Ti-MCM-41 was stable for vapor phase silylation (Figs. 1B and 1C). However, compared with calcined Ti-MCM-41 ($d_{100} = 4.16$ nm), the value of $d(100)$ for Ti-MCM-41(S9) and Ti-MCM-41-S shifted to 3.84 nm, indicating a decrease in mesopore size. Possibly, the shift of d_{100} is related to the connection of trimethylsilyl groups on the surface of mesopores in Ti-MCM-41. IR spectra show that Ti-MCM-41(S9) and Ti-MCM-41-S exhibit obvious bands at 760 and 845 cm^{-1} (Figs. 1E and 1F), which are assigned to characteristics of trimethylsilyl groups [31]. These IR results indicate that trimethylsilyl groups of TMCS are really anchored on the surface of mesopores in Ti-MCM-41, in good agreement with XRD results.

3.2. ^{29}Si MAS NMR spectroscopy

Fig. 2 shows ^{29}Si MAS NMR spectra of calcined Ti-MCM-41, Si-MCM-41(S9), Ti-MCM-41(S5), Ti-MCM-41(S9), Ti-MCM-41(100)(S9), and Ti-MCM-41-S samples. Calcined Ti-MCM-41 exhibits two peaks, at −112 and −102 ppm (Fig. 2A), which are attributed to Q^4 [$Si(OSi)_4$] and Q^3 [$Si(OSi)_3OH$ or $Si(OSi)_3OTi$], respectively [32]. Notably, after silylation by TMCS in N_2 at 200 °C for 9 h, Si-MCM-41(S9) had a new peak at 11 ppm in addition to the peaks at −112 and −102 ppm (Fig. 2B), which was assigned to $(CH_3)_3SiOSi(OSi)_3$ species [33,34]. Very interestingly, after silylation by TMCS in N_2 at 200 °C for 5 h, Ti-MCM-41(S5) exhibited another new peak, at 5.1 ppm, that was quite different from the peak at 30.9 ppm associated with ^{29}Si NMR spectrum of liquid TMCS (Fig. 2C). To our knowledge, the peak at 5.1 ppm has not been observed

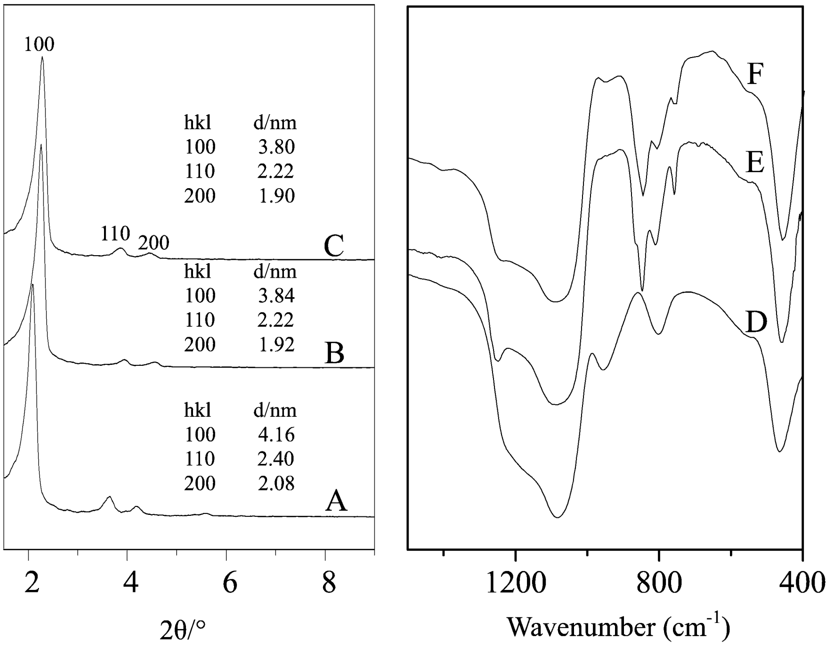


Fig. 1. XRD patterns of (A) Ti-MCM-41, (B) Ti-MCM-41(S9), (C) Ti-MCM-41-S, and IR spectra of (D) Ti-MCM-41, (E) Ti-MCM-41(S9), and (F) Ti-MCM-41-S.

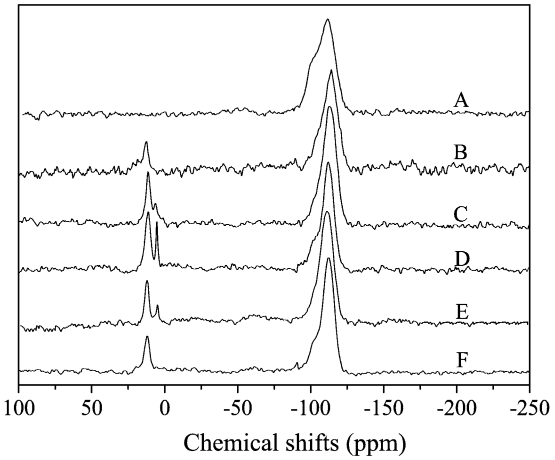
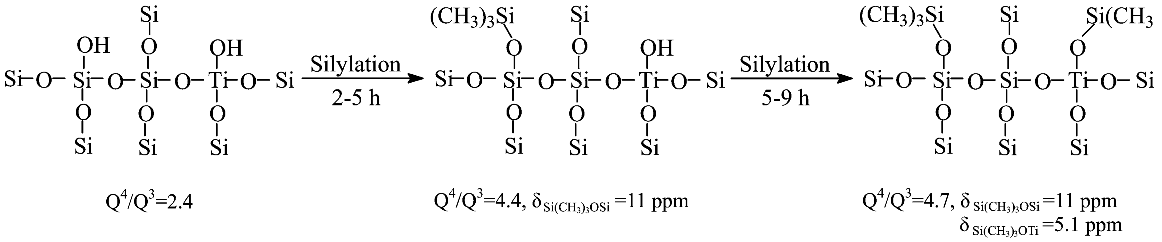


Fig. 2. ^{29}Si MAS NMR spectra of (A) Ti-MCM-41, (B) Si-MCM-41(S9), (C) Ti-MCM-41(S5), (D)Ti-MCM-41(S9), (E) Ti-MCM-41(100)(S9), and (F) Ti-MCM-41-S.

before. Considering the composition of Ti-MCM-41(S5) and Si-MCM-41(S9), the peak at 5.1 ppm can be reasonably assigned to $(CH_3)_3SiOTi(OSi)_3$ species (Scheme 1). When the silylation time was increased to 9 h, Ti-MCM-41(S9) showed a relatively strong peak at 5.1 ppm (Fig. 2D), compared with Ti-MCM-41(S5) (Fig. 2C). These results indicate that the species associated with 5.1 ppm in silylated Ti-MCM-41 were formed mainly at the silylation time of 5–9 h (Scheme 1). In contrast, the 5.1-ppm peak in Ti-MCM-41-S formed by titanation of silylated MCM-41 cannot be observed (Fig. 2F). Moreover, Ti-MCM-41(100)(S9) with a high Si/Ti ratio exhibits a relatively weak peak at 5.1 ppm in the ^{29}Si MAS NMR spectrum compared with Ti-MCM-41(S9) (Fig. 2E). These results further confirm that the peak at 5.1 ppm is strongly related to the Ti concentration in the samples, and it can be reasonably assigned to $(CH_3)_3SiOTi(OSi)_3$ species.

It is worth mentioning the change in Q^4/Q^3 ratios for various samples. The Q^4/Q^3 ratio in Ti-MCM-41 was estimated as 2.4. When Ti-MCM-41 was silylated for 5 h, Ti-MCM-41(S5) exhibited a Q^4/Q^3 ratio of 4.4. These results indicate that partial Q^3 species are transformed into Q^4 species during silylation, which means that partially terminal OH groups in mesoporous walls [$Si(OSi)_3OH$, Q^3] react with TMCS to form $(CH_3)_3SiOSi(OSi)_3$ species (Q^4). When Ti-MCM-41 was silylated for 9 h, Ti-MCM-41(S9) also showed a Q^4/Q^3 ratio (4.7) similar to that of Ti-MCM-41(S5). This phenomenon may be related to the fact that silylation for 5–9 h in Ti-MCM-41(S9) occurs mainly between titanol [$(OH)Ti(OSi)_2OSi(OSi)_3$, Q^3] and TMCS, and this kind of silylation cannot affect the Q^4/Q^3 ratio (Scheme 1). Ti-MCM-41-S also exhibited almost the same



Scheme 1. Proposed silylation of silanols and titanols with trimethylchlorosilane in Ti-MCM-41.

Table 1
Activities and selectivities in oxidations over various catalysts

Catalyst	Si/Ti (mol)	Reactions	Conversion (%)	TOF[a] (h^{-1})	Selectivity (%)
Ti-MCM-41	65	Benzene hydroxylation[b]	4.3	10.9	59.5
Ti-MCM-41(S9)	71	Benzene hydroxylation[b]	18.7	51.9	92.6
Ti-MCM-41-S	79	Benzene hydroxylation[b]	8.9	27.5	89.9
Ti-MCM-41(S5)	70	Benzene hydroxylation[b]	10.8	30.0	86.9
Ti-MCM-41(S2)	68	Benzene hydroxylation[b]	7.1	18.9	79.3
Ti-MCM-41	65	1-Octene epoxidation[c]	5.3	9.4	69.2
Ti-MCM-41(S9)	71	1-Octene epoxidation[c]	9.7	18.7	90.4
Ti-MCM-41-S	79	1-Octene epoxidation[c]	5.9	12.7	79.9
Ti-MCM-41	65	1-Octene epoxidation[d]	4.8	8.5	88.5
Ti-MCM-41(S9)	71	1-Octene epoxidation[d]	13.8	26.6	98.6
Ti-MCM-41-S	79	1-Octene epoxidation[d]	5.2	11.2	95.5

[a] Turnover frequency is moles of substrate converted per mole Ti active site of the catalyst per hour. The active site numbers of various catalysts are estimated on the basis of the amount of Ti (moles) determined by ICP and chemical analysis.

[b] Reaction conditions: 10 mL of H_2O as a solvent, reaction temperature at 60 °C, benzene/$H_2O_2 = 1/1$ (molar ratio), reaction time at 4 h, catalyst/benzene = 5% (weight ratio), selectivity for phenol.

[c] Reaction conditions: 5 mL of methanol as a solvent, reaction temperature at 60 °C, 1-octene/$H_2O_2 = 1/1$ (molar ratio), reaction time at 4 h, catalyst/1-octene = 5% (weight ratio), selectivity for 1,2-epoxyoctane.

[d] Reaction conditions: 5 mL of methanol as a solvent, reaction temperature at 60 °C, 1-octene/TBHP = 1/1 (molar ratio), reaction time at 4 h, catalyst/1-octene = 5% (weight ratio), selectivity for 1,2-epoxyoctane.

Q^4/Q^3 ratio (4.5), suggesting similar silylation of silanols with TMCS in these samples.

3.3. *Catalytic tests*

Table 1 presents activities and selectivities in the hydroxylation of benzene epoxidation of 1-octene over various catalysts with H_2O_2. In benzene hydroxylation, Ti-MCM-41 showed low conversion (4.3%) and selectivity (59.5%). However, a series of silylated Ti-MCM-41 samples exhibited relatively higher activities (7.1–18.7%) and selectivities (79.3–92.6%). Interestingly, conversion and selectivity in the reaction increased with silylated time from 2 h to 9 h. The hydrophilic/hydrophobic property of Ti-MCM-41 plays a very important role in the catalytic performance in oxidation [26–30]. However, the highest conversion (18.7%) for Ti-MCM-41(S9) cannot be simply assigned to the change in hydrophilic/hydrophobic property for the sample, because Ti-MCM-41-S with the same silylated time showed a conversion of only 8.9%. The big difference in catalytic conversion between Ti-MCM-41(S9) and Ti-MCM-41-S suggests that there may be new catalytically active titanium species in Ti-MCM-41(S9). As observed on ^{29}Si MAS NMR spectroscopy (Fig. 2), there was a unique peak at 5.1 ppm assigned to $(CH_3)_3SiOTi(OSi)_3$ in Ti-MCM-41(S9). The highest conversion and selectivity in benzene hydroxylation possibly could be attributed to both an increased hydrophobicity on the mesopore surfaces and the formation of better catalytically active titanium species in Ti-MCM-41(S9). In comparison, Ti-MCM-41(S5) (10.8%) with very weak peak at 5.1 ppm showed a conversion similar to that of Ti-MCM-41-S (8.9%), confirming that the titanium species recorded at 5.1 ppm in ^{29}Si MAS NMR spectroscopy is very important for benzene hydroxylation with H_2O_2.

In the epoxidation of 1-octene, Ti-MCM-41 showed low activities (5.3% for H_2O_2 and 4.8% for TBHP), whereas Ti-MCM-41-S exhibited slightly higher activities (5.9% for H_2O_2 and 5.2% for TBHP). However, Ti-MCM-41(S9) gave much higher activities (9.7% for H_2O_2 and 13.8% for TBHP) than Ti-MCM-41-S and Ti-MCM-41. Similar to hydroxylation of benzene, the high activity for Ti-MCM-41(S9) can also be attributed to the unique species of $(CH_3)_3SiOTi(OSi)_3$ appearing at 5.1 ppm in the ^{29}Si MAS NMR spectrum.

It is also interesting to note that Ti-MCM-41(S9) was very active in the epoxidation of 1-octene with TBHP, indicating that 1-octene easily reacts with the bulky oxidant of TBHP. In contrast, TS-1 catalyst was completely inactive for this reaction for the limitation of pore size [5]. These results suggest that Ti-MCM-41(S9) is a potentially active catalyst for the oxidation of both bulky reactants and bulky oxidants.

4. Conclusions

Hexagonal mesoporous titanosilicate [Ti-MCM-41(S9)] with better catalytically active titanium sites was successfully synthesized by vapor phase silylation (9 h). The ^{29}Si MAS NMR spectrum of Ti-MCM-41(S9) exhibited a unique peak appearing at 5.1 ppm that was assigned to $(CH_3)_3SiOTi(OSi)_3$ species formed by the interaction of titanols with TMCS. Based on the catalytic activity in the hydroxylation of benzene and epoxidation of 1-octene, we propose that the titanium species ($\delta = 5.1$ ppm) in Ti-MCM-41(S9) are more catalytically active than those in conventional Ti-MCM-41.

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