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Improvement in thermal stability and catalytic activity of titanium species in mesoporous titanosilicates by addition of ammonium salts

Xiangju Meng[a], Weibin Fan[a], Yoshihiro Kubota[b], Takashi Tatsumi[a,*]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[b] Division of Materials Science & Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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Abstract

Mesoporous titanosilicates (MTS-9A) with thermally stable titanium species were synthesized by adding ammonium salts in the preparation procedure. Characterization results show that hexagonal mesoporous titanosilicates (MTS-9A) contain primary and secondary structural building units of zeolite in the framework, in a similar manner to MTS-9. The promoted condensation of Ti-containing silica network in MTS-9A leads to higher thermal stability of four-coordinated titanium species compared with MTS-9, as evidenced by UV–vis and ^{29}Si NMR spectra. Catalytic tests indicate that MTS-9A samples show high activity in hydroxylation of both small (phenol) and bulky reactants (2,3,6-trimethylphenol) before and after calcination. Moreover, the recycled catalyst retains high conversion, confirming the high thermal stability of titanium species.

Keywords: Mesoporous titanosilicates; Four-coordinated titanium; Thermal stability; Hydrothermal stability; Ammonium salts

1. Introduction

Since the discovery of microporous crystal of TS-1 by Enichem Company [1], a series of microporous titanosilicates has been prepared in expectation of excellent catalytic activity in oxidation reactions for fine chemical production [2–8]. However, one disadvantage of these titanosilicate catalysts is that their pore sizes (generally <0.7 nm) are too small to allow access of bulky reactants to the active sites in the micropores, and such bulky reactants dominate most of the chemical transformations of importance in the fine chemical and pharmaceutical industries. Therefore, titanosilicates with relatively large pore size have always been sought. Mesoporous silica materials developed by Mobil scientists opened up a new route for preparing ordered mesoporous materials with large pore sizes of 2–20 nm [9–13].

Much attention has been paid to mesoporous titanosilicates in the last decade because of their potential use as catalysts for bulky substrates in the chemical industry. Some successful examples, including Ti-MCM-41 [14–16], Ti-HMS [17], Ti-MCM-48 [18], and Ti-SBA-15 [19,20], have shown remarkable catalytic activities in various reactions. However, for small substrates, the catalytic activities of these mesoporous titanosilicates are still low compared with those of microporous zeolite of TS-1 [1,16], which can be attributed to the amorphous nature of the mesoporous wall. Therefore, novel mesoporous titanosilicates with TS-1-like titanium species and high catalytic oxidation ability are still desirable.

Ordered mesoporous titanosilicate (MTS-9) prepared by the assembly of preformed titanosilicate precursors with triblock copolymers (P123) have been reported to show remarkable catalytic activity in a series of oxidations [21–23]. However, the thermal stability of titanium in MTS-9 is relatively low, and calcination results in the transformation of the coordination environment of titanium species, leading to decreased catalytic activity in oxidation [23]. The relatively low thermal stability of titanium has been attributed to the imperfectly condensed mesoporous walls formed at relatively low temperature (100 °C). Thus, Yang et al. prepared Ti-JLU-20 by assembling preformed titanosilicate precursors with a mixture of fluorinated surfactant (FC-4) and triblock copolymer (P123) at high temperature

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[*] Corresponding author. Fax: +81 45 9245282.
E-mail address: ttatsumi@cat.res.titech.ac.jp (T. Tatsumi).

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(180 °C) [24]. Ti-JLU-20 has high thermal stability and active four-coordinated titanium species for oxidation, which is assigned to the well-condensed mesoporous walls; however, its surface area is small ($<400\ \mathrm{m}^2/\mathrm{g}$), much lower than that of most mesoporous materials. As a result, Ti-JLU-20 is catalytically less active than either TS-1 or as-synthesized MTS-9 samples. Consequently, mesoporous titanosilicates with relatively large surface area and high thermal stability are always sought.

Recently, the effect of ammonium salts on the synthesis and catalytic properties of TS-1 has been investigated in our laboratory [25]. Some ammonium salts can be used as crystallization-mediating agents to promote the condensation of framework as well as the catalytic activities of samples [25]. Here we show that thermal stability and catalytic activities of titanium species in MTS-9 are greatly improved by the addition of ammonium salts in the gel preparation procedure.

2. Experimental

2.1. Materials

The TCI products were titanium tetrabutoxide (TBOT), tetraethyl orthosilicate (TEOS), ethanol, acetonitrile, tetrapropylammonium hydroxide (TPAOH), hydrochloric acid, ammonium chloride, phenol, catechol, hydroquinone, benzoquinone, 2,3,6-trimethylphenol, trimethylhydroquinone, trimethylbenzoquinone, and H_2O_2 (30%). $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was purchased from Aldrich.

2.2. Synthesis

Mesoporous titanosilicates were synthesized from assembly of surfactant with preformed titanosilicate precursors [21–23] in strongly acidic media. As a typical example, MTS-9A was synthesized as follows:

1. The zeolite precursor solution with zeolite TS-1 primary structure units were prepared by mixing 6 mL of TPAOH aqueous solution (25%) with 12 mL of H_2O, followed by adding 0.3 mL of $Ti(OC_4H_9)_4$ and 5.6 mL of TEOS under stirring ($TiO_2/SiO_2/TPAOH/H_2O$ molar ratios of 1.0/30/8/1500). The mixture was then aged at 100 °C for 4 h. The final product was also a clear solution.
2. A 0.8-g sample of $EO_{20}PO_{70}EO_{20}$ was dissolved in 20 mL of H_2O containing the required amount of NH_4Cl mixed with 3 mL of HCl (10 M/L), followed by adding 9.0 mL of precursor solution (containing 8 mmol of SiO_2) obtained in step 1. The mixture was stirred at 40 °C for 20 h, then transferred into an autoclave for additional reaction at 100 °C for 24 h.
3. The products were collected by filtration, washed, and dried in air. Such products are defined as as-synthesized samples.
4. As-synthesized samples were treated in ethanol/HCl solution at 333 K overnight, to remove the templates.

By this procedure, the surfactant of P123 in the mesopores was removed completely, but a small amount of TPA^+ remained in the mesopores of extracted samples. The as-synthesized samples were calcined at 500 °C for 4 h to remove the residual TPA^+; the calcined samples had no organic templates. The products were designated as MTS-9A-x, where A represents ammonium chloride (NH_4Cl) and x is the amount of NH_4Cl added.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded by a MAC Science M3X 1030 X-ray diffractometer with Cu$K\alpha$ radiation (40 kV, 20 mA). The isotherms of nitrogen were measured at the temperature of liquid nitrogen using a Belsorp 28SA system. The samples were outgassed for 10 h at 250 °C before the measurements. The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. The diffuse reflectance UV/vis spectra (DRS) were measured on a Jasco V-550 UV/vis spectrophotometer. Infrared (IR) spectra were acquired on a PE-1600 FTIR spectrometer. Scanning electron microscopy (SEM) experiments were performed on a Hitachi S-5200 electron microscope. ^{29}Si MAS NMR measurements were performed on a JEOL LA400WB 400-MHz nuclear magnetic resonance spectrometer at ambient temperature. The chemical shift was referenced to an external standard of polydimethylsilane. The spin rate of the rotor was 5.0 kHz. A pulse length of 7 ms was applied, and approximately 3000 scans were accumulated with a repetition time of 30 s. The spectra were deconvoluted with a Gaussian–Lorentzian mixed equation. The chemical composition of the samples was determined with an inductively coupled plasma–atomic emission spectrometer (Shimadzu ICPS-8000E).

2.4. Catalytic tests

Phenol hydroxylation experiments were run in a 50-mL glass reactor. In a standard run, 13.6 mmol of phenol, 50 mg of catalyst, and 10 mL of water were mixed, followed by addition of 4.53 mmol of H_2O_2 (30% aqueous). After reaction for 4 h at 353 K with magnetic stirring, the products were taken out from the system and analyzed by a Shimadazu GC-14B gas chromatograph, equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined by titrating with 0.1 m of $Ce(SO_4)_2$ aqueous solution.

The hydroxylation of 2,3,6-trimethylphenol was performed in a 50-mL glass reactor and stirred with a magnetic stirrer. In a standard run, 7.3 mmol of 2,3,6-trimethylphenol, 2.5 mL of acetonitrile as solvent, and 50 mg of catalyst were mixed in the reactor and heated to a given temperature. Then 2.78 mmol of H_2O_2 (30% aqueous) was added into the reactor. After the reaction for 2 h at 353 K with magnetic stirring, the products were removed from the system and analyzed as described above.

In catalyst recycling, the used catalysts were calcined at 550 °C for 6 h to remove the residual tar after being collected from the reaction solution before being reused in the next run.

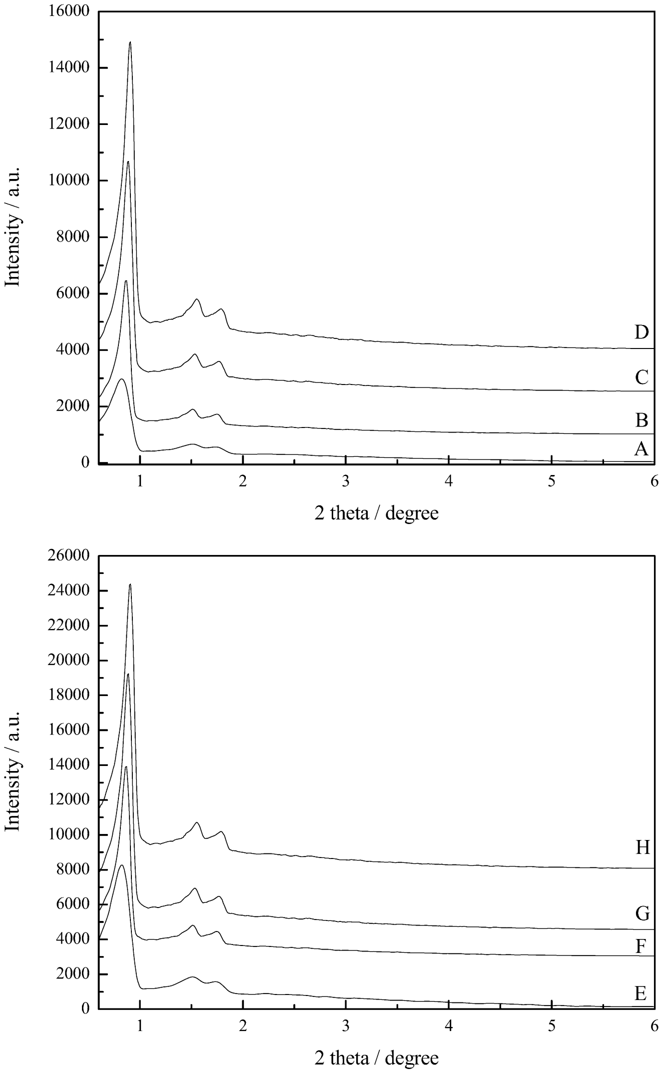

Fig. 1. The XRD patterns of as-synthesized MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C), MTS-9A-0.12 (D) and calcined MTS-9 (E), MTS-9A-0.6 (F), MTS-9A-0.9 (G), MTS-9A-1.2 (H).

3. Results and discussion

3.1. XRD and FE-SEM

Fig. 1 shows the small-angle X-ray diffraction patterns of various as-synthesized and calcined mesoporous titanosilicates. All samples clearly show three peaks, indexed as (100), (110), and (200) associated with the hexagonal symmetry, as previously reported for MTS-9 [21–23]. The (100) peak reflects d spacing in the range of 9.8–10.8 nm and a_0 in the range of 11.3–12.5 nm. Notably, the reflection intensity of MTS-9A samples is much higher than that of the MTS-9 sample, and the intensity increases with increasing amounts of NH_4Cl, suggesting that adding NH_4Cl results in the formation of a well-condensed, highly ordered structure, in good agreement with a previous report [26].

FE-SEM images of these mesoporous titanosilicates are given in Fig. 2. All samples exhibit hexagonal arrays of mesopores with uniform pore size. From the high-dark contrast in the images of the samples, the distance between mesopores is estimated to be about 12 nm, which is consistent with the estimation from XRD patterns.

3.2. N_2 adsorption

Fig. 3 shows N_2 adsorption–desorption isotherms of calcined mesoporous titanosilicates, and Table 1 gives their structural parameters. Obviously, all samples show similar isotherms of type IV, and a step increase occurs in the adsorption curve at a relative pressure of $0.7 < P/P_0 < 0.8$, due to the mesoporous structures. Correspondingly, these mesoporous titanosilicates have narrow uniform mesopores in the range of 7.1–7.9 nm. Notably, the surface area of MTS-9A samples synthesized in the presence of NH_4Cl (853–907 m^2/g) is much larger than that of Ti-JLU-20 (398 m^2/g) [24]. The relatively larger surface area would give them superiority in potential use as catalysts.

3.3. IR spectra

Fig. 4 shows the mid-infrared spectra of various mesoporous titanosilicates. All samples exhibit an obvious band at about 550 cm^{-1} in addition to the band at 460 cm^{-1}, similar to what was reported previously [23]. The band at about 550 cm^{-1} is similar to that of 5-membered rings of T–O–T (T = Si or Al) in microporous zeolites [27]. These results suggest that MTS-9A samples also have zeolite primary and secondary building units.

All of the results of XRD, FE-SEM, N_2 adsorption, and IR spectra analyses suggest that the textural properties of the MTS-9A samples are similar to those of MTS-9, but more highly ordered.

3.4. UV–vis spectra

UV–vis spectroscopy is a very common method for characterizing the coordination environment of Ti species in the zeolite framework [16,23,28–30]. Fig. 5 shows the spectra of various samples before and after calcination. Obviously, all of the as-synthesized samples exhibit a band in the range of 214–217 nm, suggesting the presence of four-coordinated titanium species similar to those in TS-1. After calcination, MTS-9A samples give a band in the range of 219–222 nm; every band is distinguishable from the band at 226 nm for MTS-9. It is well known that titanosilicates containing only framework titanium shows an optical transition at about 212 nm, which is assigned to a charge transfer (CT) in $[TiO_4]$ and $[O_3Ti–OH]$ moieties (e.g., Ti species in the TS-1 sample), and that isolated extra-framework Ti exhibits a CT band at about 225 nm (e.g., those in Ti-SBA-15) [16,23]. It was reported previously that the Ti species in MTS-9 samples are similar to those in TS-1 before calcination and transformed into ones similar to Ti-SBA-15 after calcination [23], indicating the relatively low thermal stability of titanium species in MTS-9. In contrast, MTS-9A samples show a very small shift to high wavelength even after calcination at 550 °C; in particular, MTS-9A-1.2 shows a nearly identical band (219 nm) compared with the as-

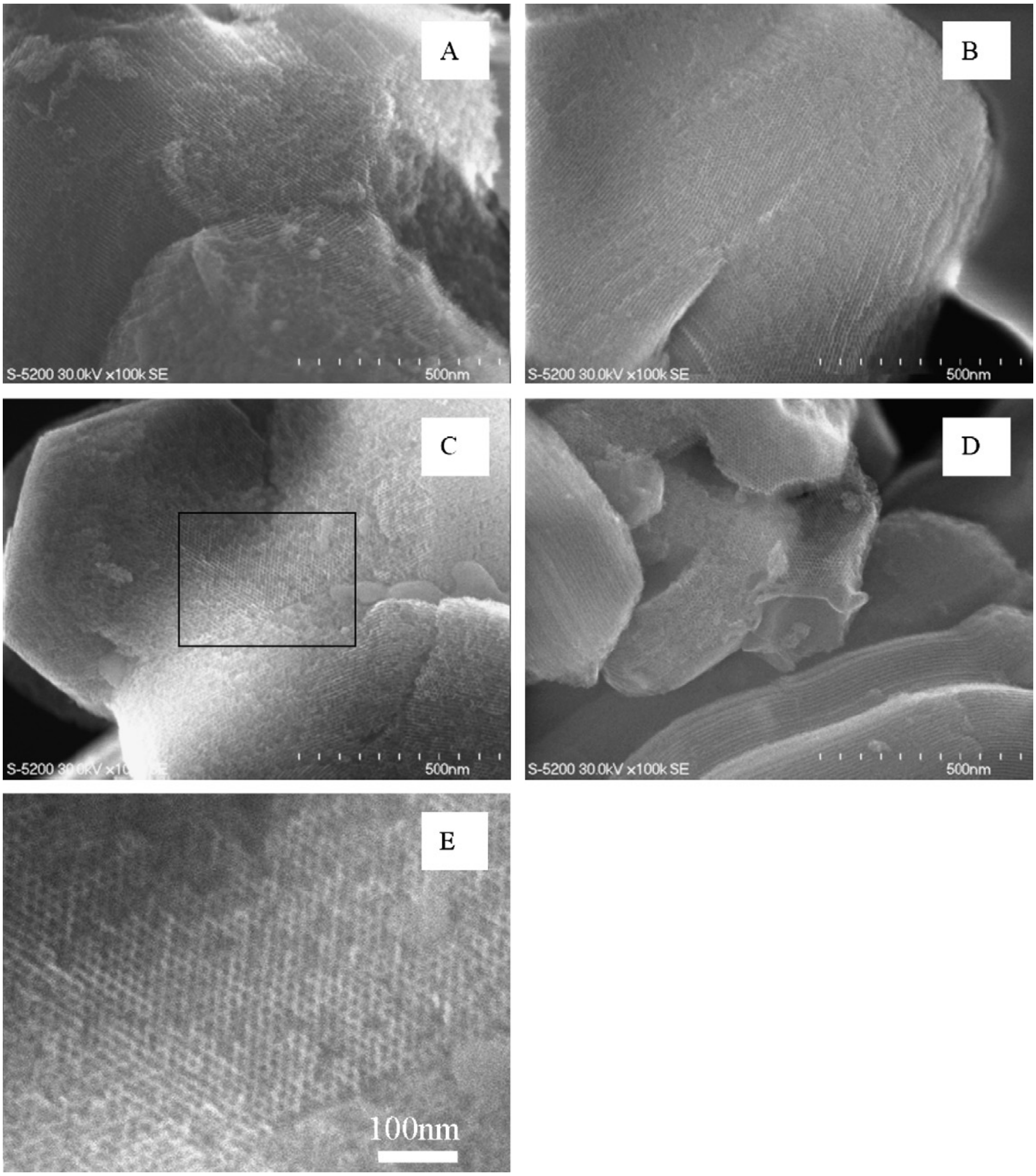

Fig. 2. The FE-SEM images of calcined MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C), MTS-9A-0.12 (D) and (E) Enlarged image of MTS-9A-0.9, corresponding rectangle area in (C).

synthesized sample (217 nm), exhibiting high thermal stability of the titanium species. These results indicate that the thermal stability of titanium species of the MTS-9A samples has been greatly enhanced by the addition of NH_4Cl into the mother gel.

3.5. ^{29}Si MAS NMR

The improved thermal stability of titanium species for MTS-9A can be attributed to the well-condensed framework of mesoporous structure, which has been confirmed by ^{29}Si NMR, as shown in Fig. 6. As-synthesized MTS-9A-1.2 is composed primarily of fully condensed Q^4 silica units ($\delta = -112$ ppm) with a small contribution from incompletely cross-linked Q^3 ($\delta = -102$ ppm) and Q^2 ($\delta = -92$ ppm), giving a relatively high $Q^4/(Q^3 + Q^2)$ ratio of 3.7. The high degree of silica condensation for mesoporous walls likely prevents the transformation of four-coordinated titanium species to five- or six-coordinated titanium species [24,31,32]. In contrast, MTS-9 has typical peaks assigned to Q^2, Q^3, and Q^4 silica species in a $Q^4/(Q^3 + Q^2)$ ratio of 1.5. These results suggest that the addition of NH_4Cl has promoted condensation of the framework. It must be noted that Xiao et al. recently reported that MTS-5 prepared by the assembly of TS-1 precursors facilitated by cetyltrimethylammonium bromide in NH_3 aqueous solution has a more condensed framework [$Q^4/(Q^3 + Q^2)$ of 2.5] and better thermal stability

Table 1
The structure parameters of various mesoporous titanosilicates

Sample	Si/Ti	d (nm)	a_0 (nm)	Pore size (nm)	Wall thickness (nm)	PV[a] (cm^3/g)		Surface area (m^2/g)	$Q^4/(Q^3+Q^2)$
						Meso-	Micro-		
MTS-9	38	10.8	12.5	7.9	4.6	1.20	0.15	980	1.5
MTS-9A-0.6	40	10.2	11.8	7.5	4.3	1.12	0.13	907	2.3
MTS-9A-0.9	39	10.0	11.5	7.3	4.2	1.01	0.14	879	3.1
MTS-9A-1.2	40	9.8	11.3	7.1	4.2	0.98	0.12	853	3.7

[a] PV: pore volume; Meso-: volume of mesopores; Micro-: volume of micropores.

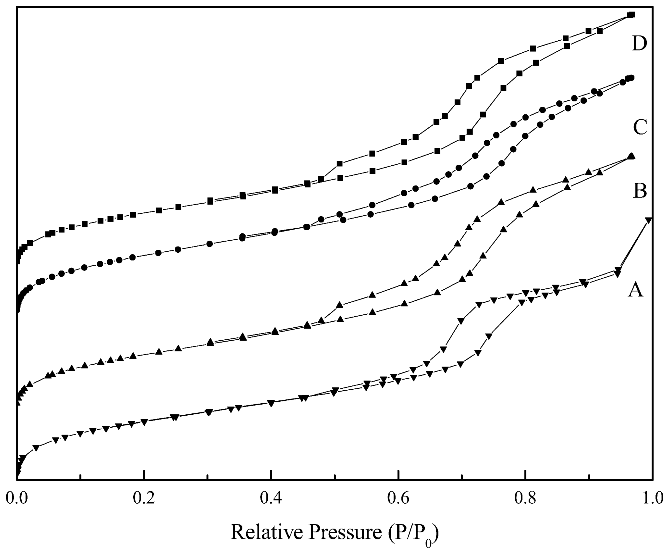

Fig. 3. Nitrogen adsorption–desorption isotherms of calcined MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C) and MTS-9A-0.12 (D).

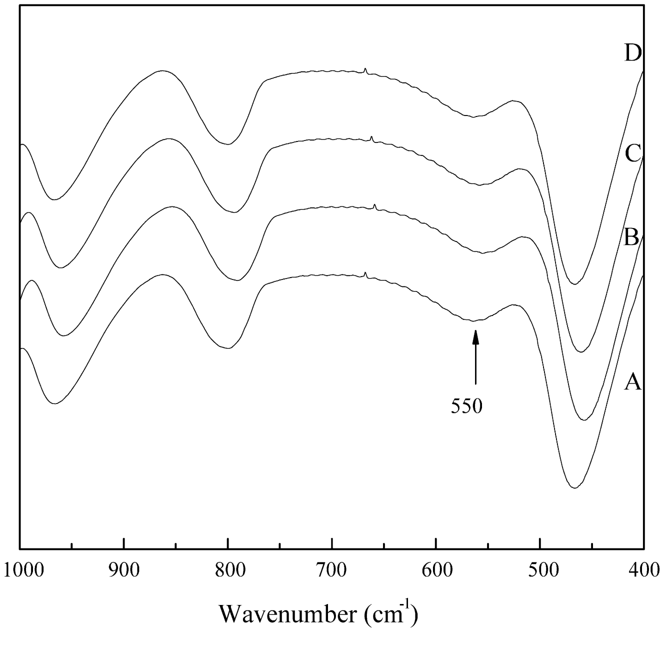

Fig. 4. IR spectra of calcined MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C) and MTS-9A-1.2 (D).

of titanium species than MTS-8 [$Q^4/(Q^3 + Q^2)$ of 1.6] when prepared in HCl solution [33]. However, the addition of NH_4Cl resulted in a more condensed framework.

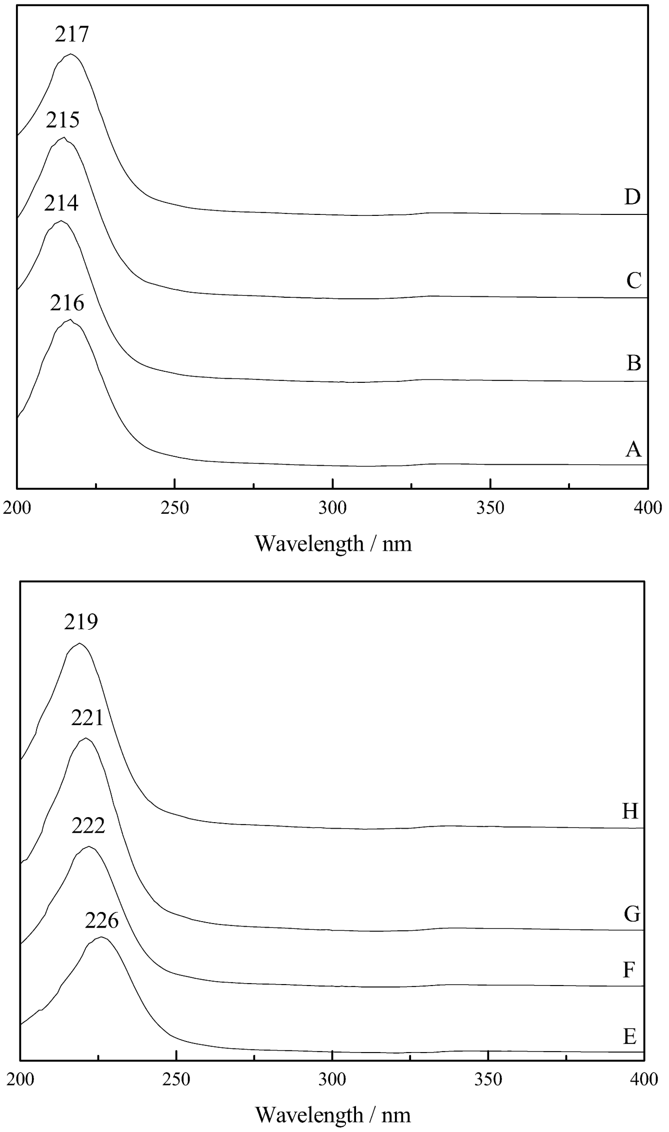

Fig. 5. UV–vis spectra of as-synthesized MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C), MTS-9A-1.2 (D) and calcined MTS-9 (E), MTS-9A-0.6 (F), MTS-9A-0.9 (G), MTS-9A-1.2 (H).

3.6. Catalytic tests

Catalytic activities in phenol hydroxylation by H_2O_2 over various titanosilicates before and after calcination are presented in Table 2. Obviously, all of the uncalcined mesoporous titanosilicates (surfactants have been extracted by ethanol) are very active and are of comparable activity to TS-1 [1,23], giv-

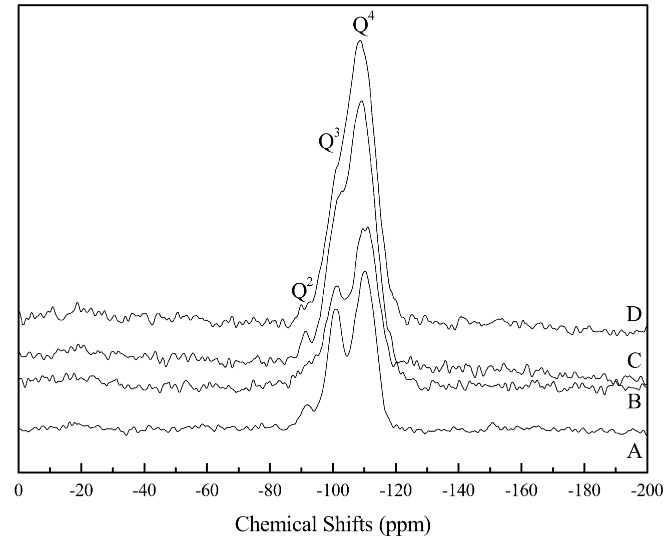

Fig. 6. ^{29}Si spectra of as-synthesized MTS-9 (A), MTS-9A-0.6 (B), MTS-9A-0.9 (C) and MTS-9A-1.2 (D).

Table 2
Catalytic activities of various titanosilicates in phenol hydroxylation before and after calcinations

Samples	Conversion (%)	TOF (h^{-1})	H_2O_2 efficiency[a] (%)	Product selectivity[b] (%)		
				CAT	HQ	BQ
MTS-9[c]	26.5	6.9	80.6	53.8	43.7	1.4
MTS-9[d]	14.8	3.8	44.9	54.2	44.6	1.2
MTS-9A-0.6[c]	25.5	7.0	78.2	53.1	44.7	2.2
MTS-9A-0.6[d]	20.7	5.7	63.8	50.0	47.2	2.8
MTS-9A-0.9[c]	24.8	6.8	75.8	53.0	45.1	1.9
MTS-9A-0.9[d]	22.2	6.1	69.0	48.2	48.1	3.6
MTS-9A-1.2[c]	25.3	7.0	76.7	54.0	44.9	1.1
MTS-9A-1.2[d]	24.6	6.8	74.8	53.6	45.1	1.3
MTS-9A-1.2[e]	23.9	6.6	73.6	52.6	44.8	2.6

[a] Efficiency of $H_2O_2 = H_2O_2$ converted into $(CAT + HQ + BQ)/H_2O_2$ added.

[b] CAT: catechol, HQ: hydroquinone, and BQ: benzoquinone.

[c] The sample was treated with ethanol to remove surfactant without calcination.

[d] The sample was calcined to remove surfactant.

[e] The catalyst was reused after calcination.

Table 3
Catalytic activities of mesoporous titanosilicates in 2,3,6-trimethylphenol hydroxylation before and after calcination

Samples	Conversion (%)	TOF (h^{-1})	H_2O_2 efficiency[a] (%)	Product selectivity (%)		
				Trimethylhydroquinone	Trimethylbenzoquinone	Others
MTS-9[b]	18.8	7.4	68.3	66.7	21.1	12.2
MTS-9[c]	10.8	4.3	41.6	57.2	28.5	14.3
MTS-9A-0.6[b]	18.4	7.2	67.7	65.1	22.6	12.3
MTS-9A-0.6[c]	14.7	5.8	55.2	59.0	25.2	15.8
MTS-9A-0.9[b]	18.2	7.1	66.1	67.0	21.1	11.9
MTS-9A-0.9[c]	16.6	6.5	58.8	64.2	18.1	17.7
MTS-9A-1.2[b]	18.1	7.1	67.8	64.0	24.9	11.1
MTS-9A-1.2[c]	17.9	7.0	67.1	63.6	25.1	11.3

[a] Efficiency of $H_2O_2 = H_2O_2$ converted into (trimethylhydroquinone + trimethylbenzoquinone)/H_2O_2 added.

[b] The sample was treated with ethanol to remove surfactant without calcination.

[c] The sample was calcined to remove surfactant.

ing high phenol conversions (24.8–26.5%). However, calcined MTS-9 gives relatively low conversion (14.8%), because of the transformation of titanium species coordination environment during calcination [23], which has been confirmed by UV–vis spectra as described above. On the other hand, calcined MTS-9A-1.2 still shows high conversion (24.6%), suggesting high thermal stability of titanium species thereon. Moreover, the catalytic activity of reused MTS-9A-1.2 is still very high (23.9%), confirming that the sample is recyclable, which is very important for industrial applications. MTS-9A-0.6 and MTS-9A-0.9 also give relatively high conversions (20.7 and 22.2%, respectively), in agreement with the findings from UV–vis and NMR spectra.

The catalytic activities of various titanosilicates in hydroxylation of 2,3,6-trimethylphenol are presented in Table 3. Like hydroxylation of phenol, as-synthesized MTS-9 shows high conversion (18.8%), and the calcined sample has a relatively low conversion of 10.8%. In contrast, the MTS-9A-1.2 sample shows high conversion before and after calcination (18.1 and 17.9%, respectively), indicating the thermally stable titanium species in MTS-9A samples. Obviously, MTS-9A samples can be used as effective catalysts for the oxidation of bulky molecules.

3.7. The role of NH_4^+

We have also used $(NH_4)_2SO_4$–H_2SO_4 (dilute), NH_4NO_3–HNO_3 (dilute), and $(NH_4)_3PO_4$–H_3PO_4 in place of NH_4Cl–HCl, obtaining similar results (data not shown here). The stability of titanium species was improved and the catalytic conversions were retained even after calcination. These results suggest that NH_4^+ plays an important role in improving the thermal stability of titanium species in mesoporous titanosilicates.

Mesoporous titanosilicate MTS-9A samples are prepared by the assembly of preformed titanosilicate precursors with surfactants. Their framework is composed of primary and secondary building units of zeolite, which is a distinct difference between MTS-9A samples and other conventional mesoporous titanosilicates, such as Ti-MCM-41 and Ti-SBA-15. It is well known that the alkali cation has a strong affect on the formation of zeolite and the incorporation of metal ions into the zeolite framework. We recently observed that the crystallization rate of TS-1 decreased but the crystallinity of final product increased by the addition of ammonium salts. Crystallization rate is one of the most important factors in the incorporation of titanium ions into the zeolite framework [1,25,34]. A too-rapid crystallization rate hinders the incorporation of titanium ions into the lattice sites, because the radii of titanium ions are larger that of Si^{4+}, resulting in instability of the framework. Adding ammonium salts during the preparation of MTS-9A would retard the crystallization but enhance the degree of condensation, thereby improving the thermal stability of titanium species.

4. Conclusion

Ordered mesoporous titanosilicates (MTS-9A) were synthesized by the addition of ammonium salts in the gel preparation procedure. Characterization results indicate that four-coordinated TS-1-like titanium species in MTS-9A sample exhibit high thermal stability, which can be attributed to promoted condensation of Ti-containing silica network. As a result, MTS-9A samples show excellent catalytic activity in the hydroxylation of both phenol and 2,3,6-trimethylphenol. Compared with previous mesoporous titanosilicates with the same structure, such as MTS-9 and Ti-JLU-20 prepared at high temperature, MTS-9A, with a relatively larger surface area and high thermal stability, is of potential use in industrial catalysis.

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