

Titanium-rich highly ordered mesoporous silica synthesized by using a mixed surfactant system

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Abstract

A new titanium-rich highly ordered 2-D hexagonal mesoporous titanium silicate has been synthesized using a mixture of cationic (cetyltrimethylammonium bromide, CTAB) and non-ionic (Brij-35, $C_{12}H_{25}-(OC_2H_4)_{23}-OH$, a polyether and aliphatic hydrocarbon chain surfactant) mixed surfactant system as the supramolecular structure directing agent (SDA) in the presence of tartaric acid (TA) as a mineralizer of Ti(IV). XRD, N_2 adsorption and TEM data suggested the presence of mesophase with hexagonal pore arrangements and the UV–visible, FT IR and XPS studies suggested the incorporation of mostly tetrahedral titanium (IV) species in the highly ordered silica network. This mesoporous titanium silicate material showed excellent catalytic activity and selectivity in the epoxidation of styrene using dilute aqueous H_2O_2 as oxidant.

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1. Introduction

Syntheses of titanium silicate with novel framework structures have attracted widespread attention because of their applications in eco-friendly, selective and industrially important catalytic oxidative organic transformations in the presence of dilute aqueous H_2O_2 as oxidant [1]. Medium pore titanium silicates, TS-1 and TS-2 have been known over a decade for their outstanding catalytic activity in a wide range of eco-friendly oxidation reactions, e.g. oxidation of C–H, N–H, S–H, epoxidation, hydroxylation, ammoximation, etc [1–4]. However, their catalytic activities were limited to smaller organic molecules only (C_2 – C_7) due to their pore size constraints. With the discovery of highly ordered mesoporous silica [5,6] and its titanium silicate analog [7] it was expected that these mesoporous materials would overcome this difficulty in catalyzing bulky organic molecules. However, mesoporous titanium silicates synthesized in the presence of the self-assembly of cationic

surfactants alone are found to be catalytically less active in partial oxidation reactions using dilute aqueous H_2O_2 as oxidant because of the surface hydrophilicity in these materials due to the presence of excessive surface Si–OH groups. In the supramolecular assembly of cationic surfactant the polar head groups are oriented toward the edge of the micelle and thus responsible for excessive surface silanol density. Moreover, these Ti-containing mesoporous silicas showed relatively better activity if organic peroxides were used as oxidants, which reduces the environmental and economic advantages of titanium silicate, since the management of the organic by-products is a major drawback. Again, the loading of titanium in highly ordered titanium silicate mesoporous materials synthesized by using cationic surfactants were relatively low [7,8]. Hence, mesoporous titanium silicates (preferably Ti-rich) [9], which can be active in the liquid phase partial oxidation reactions in the presence of a dilute aqueous H_2O_2 as oxidant are very important for their practical applications in organic fine chemical synthesis [10–15]. Very recently ordered silicas have been synthesized using a combination of cationic/non-ionic [16], cationic/anionic surfactant

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mixtures [17], or microemulsion [18], some of them having well-defined particle sizes and morphologies. Due to partial charge neutralization or decrease in charge density of the micelle in the mixed-surfactant systems [19–23] these materials should have more hydrophobic surface than the mesoporous silica synthesized using ionic surfactant alone [20]. Since frameworks of these mesoporous materials synthesized by using mixed surfactant routes are composed of inactive silica only, an active transition metal has to be incorporated in these mesoporous frameworks in order to achieve the desired catalytic activity in a liquid phase partial oxidation reaction. Here, we first report the synthesis of a highly ordered Ti-rich mesoporous titanium silicate using the mixture of cetyltrimethylammonium bromide (CTAB) and Brij-35 ($C_{12}H_{25}-(OC_2H_4)_{23}-OH$) as supramolecular structure directing agent (SDA) in the presence of tartaric acid (TA) and tetramethylammonium hydroxide (TMAOH) under alkaline condition. This material showed excellent catalytic activity in the liquid phase partial oxidation reaction of styrene to styrene oxide using dilute aqueous H_2O_2 as oxidant.

2. Experimental

Tetraethyl orthosilicate (TEOS, Aldrich) and titanium (IV) tetrabutoxide (TBOT, Aldrich) were used as a silica and titanium sources, respectively. TA (Loba Chemie) was used because of the stability of its complex with Ti(IV) in aqueous medium, which could help the incorporation of more active Ti-centers in the internal surface of the mesopores. In a typical synthesis, 2.96 g CTAB (Loba Chemie) (0.00814 mol) and 0.8 g (for sample 1) or 1.5 g (for sample 2) Brij-35 (Loba Chemie) were dissolved in the acidic aqueous solution of TA (0.78 g TA in 60 g H_2O) under vigorous stirring at room temperature for 0.5 h. Then 3.5 g TEOS (0.0168 mol) was added to the mixture under continuous stirring for 0.5 h. After 6 h continuous stirring, 0.2287 g TBOT (0.000672 mol), taken in 5 g of isopropyl alcohol was added slowly to the mixture. Finally tetramethylammonium hydroxide (TMAOH, 25% aqueous, Demi Chem) was added dropwise and pH was maintained at ca. 11.0. The resulting mixture was aged for overnight under stirring at room temperature and then heated at 353 K for 72 h without stirring. The solid product was recovered by filtration, washed several times with water and dried under vacuum. The resulting powders were calcined in the flow of air at 703 K for 8 h to remove the organic surfactants. The molar ratios of the constituents in the synthesis gels were:

25TEOS : 1.0TBOT : 12.5CTAB(Brij-35) : 2.5TA : 5556 H_2O .

All the samples were identified by powder XRD using a Seifert 3000P X-ray diffractometer on which the small- and wide-angle goniometers are mounted. The X-ray source was CuK_α radiation ($\alpha = 0.15406$ nm) with an applied voltage and current of 40 kV and 20 mA, respectively.

Mesophases of different samples were analyzed using a JEOL, JEM 2010 TEM at an accelerating voltage of 200 kV. N_2 adsorption measurements were carried out using a Belsorp 28 NA at 77 K. Pre-treatment of the sample was done at 473 K for 3 h under high vacuum. Jeol JEM 6700F field emission scanning electron microscopy with an EDS attachment was used for the determination of surface morphology and chemical composition. UV–visible diffuse reflectance spectra were recorded on a Shimadzu 2401PC UV–visible spectrophotometer with an integrating sphere attachment using $BaSO_4$ as background standard. For the Fourier transform infrared (FT IR) measurement a Nicolet Magna IR 750 Series II was used. X-ray photoelectron spectroscopic (XPS) measurements were conducted on an Omicron Multiprobe (Omicron NanoTechnology GmbH., UK) spectrometer fitted with an EA125 (Omicron) hemispherical analyzer. Monochromatic AlK_α source operated at 150 W was used and the pass energy of the analyzer was kept fixed at 40 eV. A low-energy electron gun (SL1000, Omicron) with a large spot size was used for sample neutralization. The voltage of the electron gun was fixed at -3 V. A Perkin Elmer 2380 AAS was used for wet chemical analysis. Liquid phase oxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and placed in an oil bath at 333–353 K under stirring. Dilute aqueous H_2O_2 (25% aqueous) was added immediately before the start of the reaction. At different time intervals the products were collected from the reaction mixture and analyzed by capillary gas chromatography (Agilent 4890D, FID). The products were identified by using known standards.

3. Results and discussion

Chemical analysis data for samples 1 and 2 revealed that the Si/Ti mole ratios of 28.1 and 25.2, respectively. Small-angle X-ray diffraction patterns of these samples are shown in Fig. 1(a–c). All four peaks for 100, 110, 200 and 210 planes of the 2-D hexagonal mesophase [6,7] were observed for the as-synthesized and calcined samples indicating highly ordered structures. Samples synthesized in the absence of TA are mostly disordered mesophases. This result suggested that the presence of TA helps in the incorporation of a large amount of Ti in the ordered hexagonal mesophase. In Fig. 2 the N_2 sorption isotherms for sample 2 at 77 K are shown. Typical type IV isotherm with steep rise due to capillary condensation, characteristic of the other mesoporous materials [5–7] was seen. BET surface area and average pore diameter for samples 1 and 2 were 951.7 and 967.4 $m^2 g^{-1}$ and 2.24 and 2.45 nm, respectively. In the inset of Fig. 1 the unit cell (2D-hexagonal) parameters and wall thickness are also shown. Pore wall thickness is quite slim, suggesting the active titanium sites are mostly located at the surface of the catalyst. TEM image for as-synthesized sample 2 is shown in Fig. 3. Hexagonal arrangement of the pores with different contrast than that of the pore walls was very

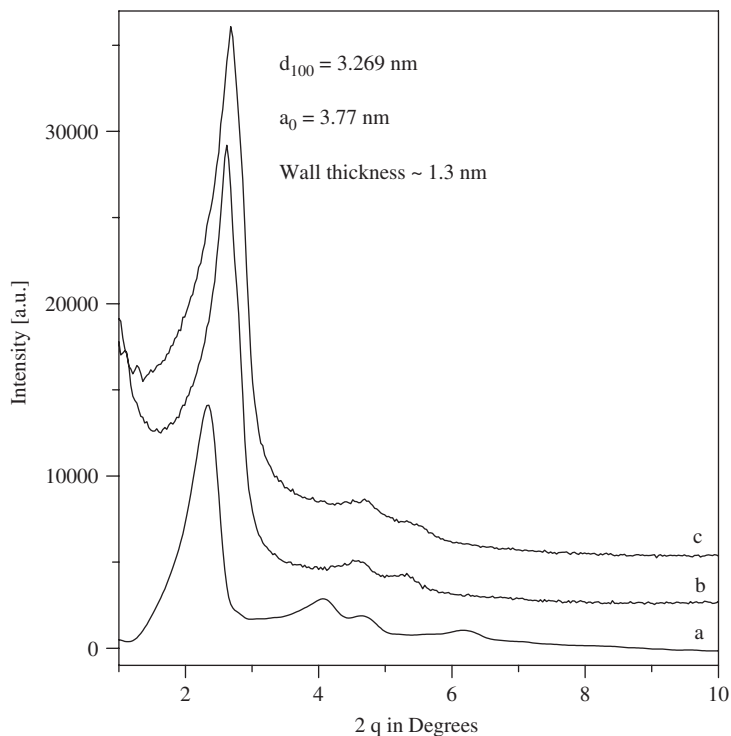


Fig. 1. XRD patterns of as-synthesized sample 1 (a) and calcined samples 1 (b) and 2 (c).

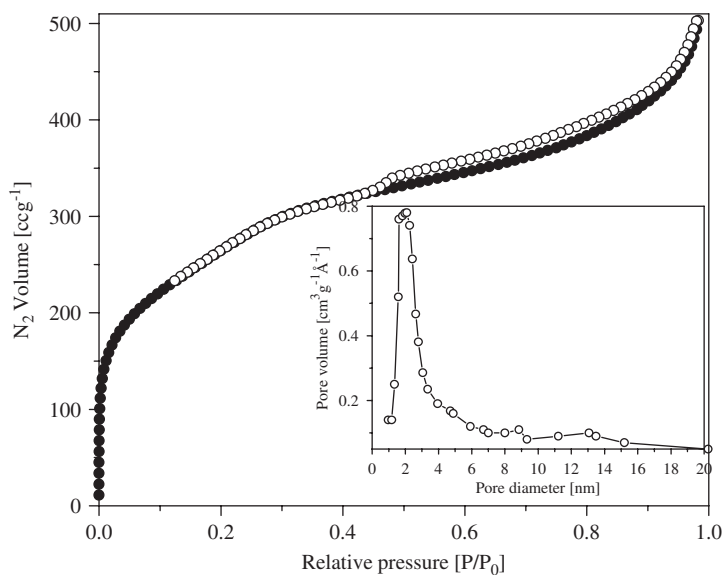


Fig. 2. N_2 adsorption/desorption isotherm for sample 2. Adsorption points are marked by filled cycles and desorption points are marked by open cycle. BJH pore size distribution given in the inset.

clear. Selected area electron diffraction pattern shown in the inset of this image suggested the hexagonal ordering of the channels. The average pore diameter for this sample was ca 2.8 nm, which agrees well with the N_2 sorption data (2.45 nm) on the calcined sample 2, considering the fact that considerable contraction of the unit cell occurs during calcinations as seen from the respective XRD pattern (Fig. 1).

Fig. 4 illustrates the UV–visible diffuse reflectance spectra of the different mesoporous titanium silicate samples after the removal of surfactant. Strong UV–visible absorption band in 200–290 nm was observed for all samples. This band was due to the electronic transition from O^{2-} to Ti^{4+} . Similar high-energy absorption edges due to tetrahedral coordination of Ti have been observed for other titanium-containing mesoporous molecular sieves

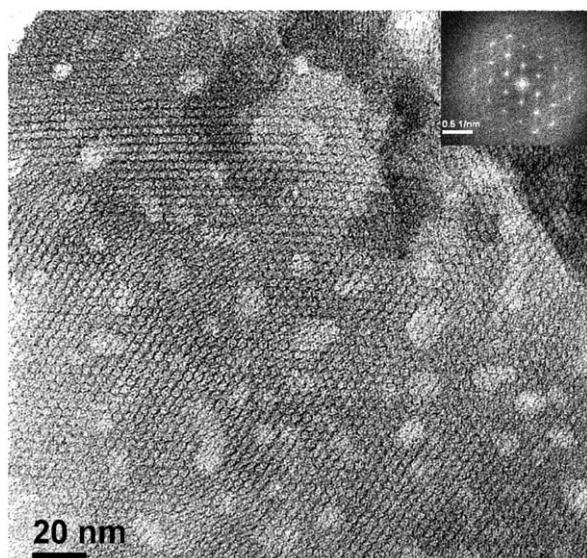


Fig. 3. TEM image of sample 2. Electron diffraction pattern is shown in the inset.

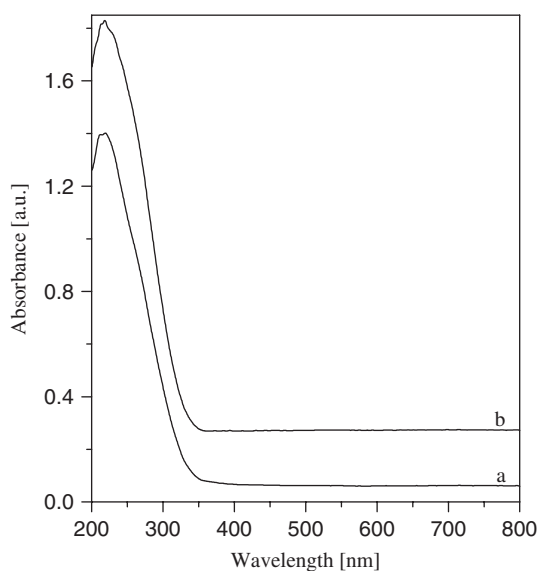


Fig. 4. UV-visible spectra of calcined samples 1 (a) and 2 (b).

[4,11,12,24]. The high-energy absorption band for titanium silicate material suggested that highly dispersed tetrahedral Ti(IV) in an isolated silica environment dominated in this material. FT IR spectra of different template-free samples are shown in Fig. 5. Strong bands at $960\text{--}965\text{ cm}^{-1}$ have been observed for both the calcined samples, which could be attributed to the Si–O–Ti stretching vibration [8,15]. Peaks at ca. 790 , 1084 and 3344 cm^{-1} , respectively could be attributed to the different characteristic Si–O–Si vibrations and defect Si–O–H stretching vibrations. Peaks at ca. 1630 cm^{-1} could be attributed to the adsorbed residual water. These spectra suggested the presence of Si–O–Si and Si–O–Ti bonding in the mesoporous titanium silicate samples.

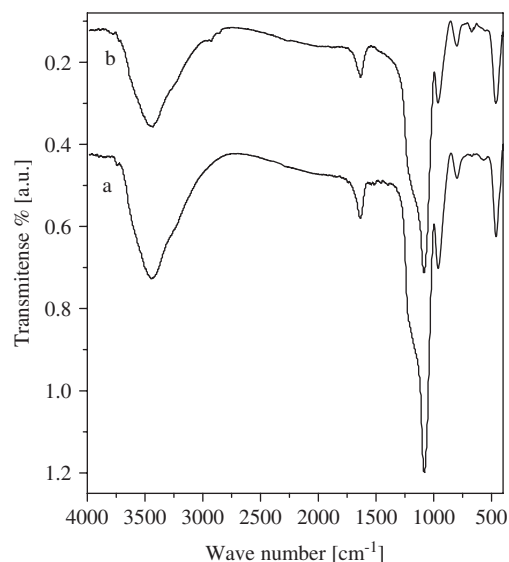


Fig. 5. FT IR spectra of calcined samples 1 (a) and 2 (b).

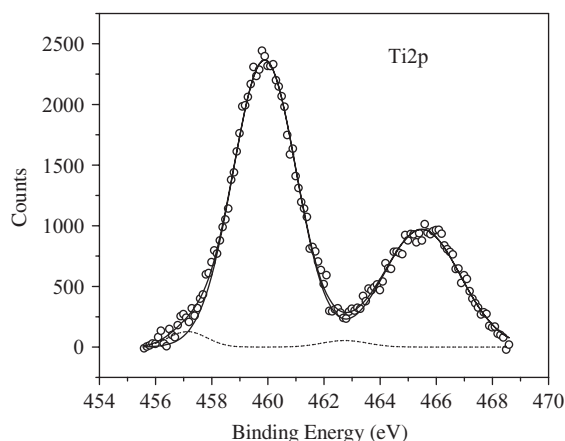


Fig. 6. X-ray photoelectron spectra of sample 1. Solid lines correspond to the tetrahedrally coordinated framework Ti(IV) and broken lines refer to the octahedrally coordinated extra framework Ti(IV).

XPS data could be a direct measure of the loading of framework tetrahedral Ti(IV) [25–27] in these mesoporous titanium silicate materials. In Fig. 6 the X-ray photoelectron spectrum of Ti $2p$ electron in sample 1 is shown. The energy positions of the peaks were calibrated by fixing the position of the C $1s$ peak at 285.0 eV . From the XPS measurement the atomic percentage ratios for Ti/Si and O/(Ti+Si) were 4.1 and 2.79% , respectively. This result suggested in the surface there is little higher concentration of Ti than that in the bulk. The peak positions for Si $2p$ and Ti $2p_{3/2}$ were 103.35 and 459.9 eV , respectively. Titanium (IV) ions located at the tetrahedral position in the titanium silicalite framework of TS-1 have Ti $2p_{3/2}$ and Ti $2p_{1/2}$ binding energies of 460 and 466 eV , respectively [25–27], whereas for the octahedrally coordinated Ti(IV) attributed to extra-framework titanium atoms with a Ti $2p_{3/2}$ binding energy of 458 eV and Ti $2p_{1/2}$ of 464 eV [25]. Presence of

Ti2p_{3/2} and Ti2p_{1/2} peaks in our sample at 459.9 and 465.7 eV thus confirmed that most of the titanium species present in our sample is Ti(IV) having tetrahedrally coordinated with silica in the mesostructure. Deconvoluted pattern (Fig. 6) suggested that out of the total Ti(IV), 97% are tetrahedrally coordinated (solid line) in the framework, whereas 3% are octahedrally coordinated (broken line) extra-framework Ti(IV).

Mesoporous titanium silicate samples 1 and 2 were used for the liquid phase epoxidation of styrene using dilute aqueous H₂O₂ as oxidant under mild condition (333 K).

Table 1
Oxidation of styrene over mesoporous titanium silicates using H₂O₂ as oxidant^a

| Sample | Reaction time (h) | Conversion (%) | Epoxide sel. (%) | TOF ^b |
|----------------|-------------------|----------------|------------------|------------------|
| 1 | 30 | 95.7 | 68.2 | 2.71 |
| 2 | 24 | 100.0 | 61.0 | 3.20 |
| 3 ^c | 30 | 16.2 | 54.0 | 0.91 |
| 2 ^d | 24 | 94.6 | 69.2 | 3.02 |

^aStyrene/H₂O₂ = 1(mol/mol), solvent acetone, reaction temperature 333 K, catalyst 20 wt% with respect to the substrate.

^bTurn over frequency = moles of substrate converted per mol of Ti per h.

^cTi-MCM-41 (Si/Ti = 57.4, surface area 1020 m² g⁻¹) synthesized using CTAB only [15].

^dSample 2 was re-used as catalyst in the third cycle.

Styrene oxide has been observed as main product together with some hydrolyzed diols and minor amount of over oxidized products. Conversion, epoxide selectivity and turn over frequencies (TOF) for the samples are given in Table 1. Catalytic data for a reference Ti-MCM-41 sample synthesized using CTAB only (sample 3) [15] has been shown here for comparison. Interestingly, samples 1 and 2, synthesized with cationic–nonionic mixed surfactant systems showed much better conversion, epoxide selectivity, and TOF compared to Ti-MCM-41 (sample 3) with a relatively better surface area suggesting the presence of more active Ti-sites at the surface of the formers. A possible mechanistic pathway for the oxidation of styrene over these mesoporous titanium silicate in the presence of dilute aqueous H₂O₂ has been shown in Fig. 7. The titanium-hydroperoxo species (I) generated in-situ in the presence of H₂O₂ helped to form the styrene oxide as the major product. No leaching of Ti has been observed in either of the reaction mixtures after the reactions. This result suggested that the liquid phase oxidation of styrene over the mesoporous titanium silicate synthesized by using mixed surfactant systems is purely catalytic in nature and the presence of active Ti-sites in this mesoporous titanium silicate material. After the reaction the catalyst was filtered, washed with water, dried and calcined at 773 K. Regenerated catalyst obtained by this method was repeatedly used for two cycles more and in both cases high conversion and

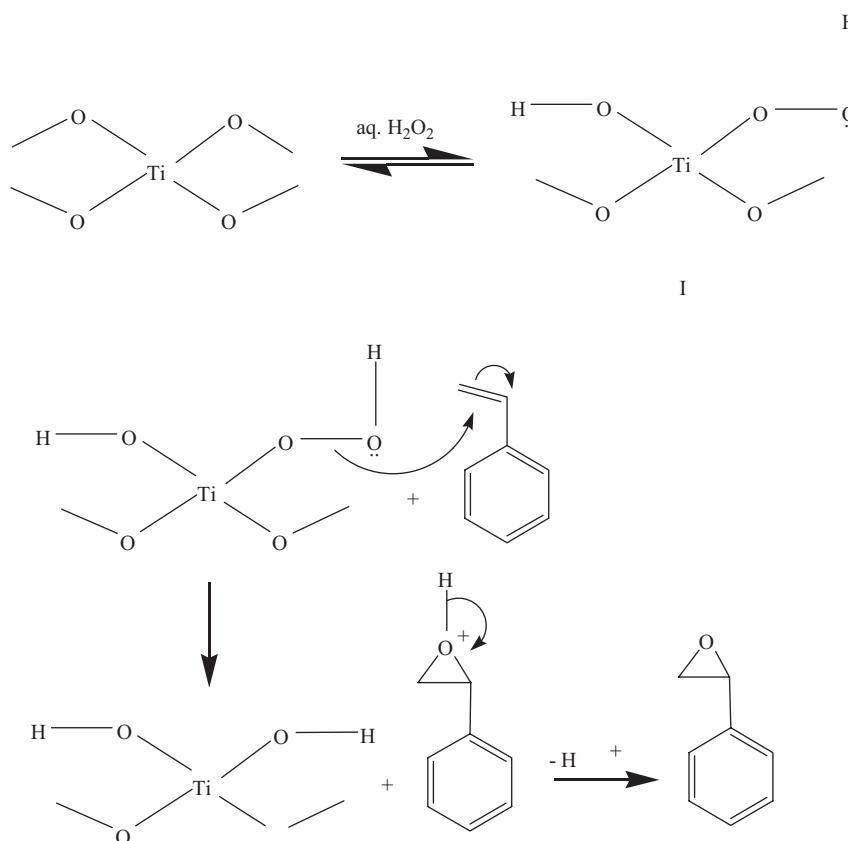


Fig. 7. Reaction scheme for the oxidation of styrene over mesoporous titanium silicate.

selectivity was obtained. In third cycle on sample 2 as high as 94.6% conversion of styrene and 69.2% selectivity for styrene oxide was obtained (Table 1). This data clearly suggested that our titanium silicate is efficient catalyst for repeated uses.

Interestingly this highly ordered 2D-hexagonal mesoporous titanium silicate has been synthesized by using much higher concentration of Ti in the synthesis gel. Under conventional synthesis condition using a cationic surfactant alone as supramolecular assembly such high loading of Ti usually leads to wormhole-like disordered mesostructure [9]. Here possibly due to the decrease in charge density of the self-assembled mixed surfactant micelle [20] may help to incorporate high loading of Ti, which in-turn may be responsible for high efficiency of these mesoporous titanium silicate samples in liquid phase partial oxidation reactions using dilute H_2O_2 as oxidant.

4. Conclusions

Highly ordered 2-D hexagonal mesoporous titanium silicate has been synthesized using the self-assembly of cationic surfactant CTAB and non-ionic surfactant Brij-35 mixtures under alkaline pH conditions. Characterization results suggested the 2D-hexagonal arrangement of the channels with mesopores of dimension 2.2–2.45 nm in these samples. Spectroscopic results suggested that most of the titanium present in these samples are tetrahedrally coordinated Ti(IV). High loading of Ti(IV) in the ordered mesoporous titanium silicate network could be achieved by using the mixed-surfactant system as the SDA in the presence of TA as mineralizer. This material showed much higher catalytic activity and selectivity in the epoxidation of styrene using dilute aqueous H_2O_2 as oxidant vis-à-vis mesoporous titanium silicate synthesized using cationic surfactant alone.

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