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Titanium containing inorganic–organic hybrid mesoporous materials with exceptional activity in epoxidation of alkenes using hydrogen peroxide

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Titanium containing ethane bridged hybrid mesoporous materials with uniform hexagonal arrangement are prepared by two different routes and characterized using several analytical techniques. The effect of substitution of bridged silsesquioxane precursors for siloxane precursors on the properties of resultant mesoporous bulk materials are also evaluated and discussed in term of mesoscopic order and oxidation catalysis. The materials are highly hydrophobic and selectively epoxidize the α-pinene to α-pinene oxide (with >99% selectivity) and display high hydrogen peroxide efficiencies.

Introduction

The preparation, characterization, and application of organic–inorganic hybrid materials have become a rapidly expanding area of research in material science. Recently, a novel sol–gel approach for the synthesis of organic–inorganic hybrid mesoporous materials comprising bridged bonded organic groups integrated into silica, *i.e.*, the surfactant cast structures of organic silsesquioxanes has been reported.[1–3] The major driving force behind this discovery are the fascinating new and useful properties of nanocomposites, which the traditional mesoporous silica materials do not have. Thus, functionalized mesoporous materials are of great interest in their range of potential applications especially in electronic, optical, catalysis, separation and adsorption functions.[4] These new hybrid materials offer well-ordered mesoporous structures, exceptionally high surface area, which allows the binding of a large number of surface chemical moieties *via* classical organic reactions. Only few stable hybrid mesoporous materials have been reported to date. Among them only the ethane derivatives can be easily manipulated by common organic reactions. It is also possible to manipulate the composition, the chemical and mechanical properties as well as the hydrophobicity and hydrophilicity of these materials.

Incorporation of an active metal species would be useful to modify the catalytic properties; this would need to be into the channel wall of the hybrid materials. Our research is focused to on the modification of the catalytic properties of this class of nanocomposite materials. Titanium incorporation in several silicalites, such as silicalite-1(2), ZSM-12, ZSM-48 and zeolite-β, is well documented and has been found to be effective for the selective oxidation of alkanes, the hydroxylation of phenols and epoxidation of alkenes using peroxides as an oxidant.[5–7] Also, titanium containing siliceous mesoporous materials (Ti-MCM41 and Ti-MCM48) have been reported with remarkable activities in liquid phase oxidation catalysis using aqueous H_2O_2 or *tert*-butyl hydrogen peroxide (TBHP) as oxidants.[8] In addition, the synthesis and catalytic activity of titanium containing aluminophosphate molecular sieves, such as TAPO-5, -11, -31, and -36, has been reported.[9] Titanium incorporated into mesoporous aluminophosphate materials thereby providing an improved catalytic activity for the epoxidation of alkenes has also been described.[10]

In this work we present the synthesis of an ethane bridged silica hybrid mesoporous material with titanium incorporated. The material necessarily incorporates the titanium along with the organic constituents into the framework (channel wall) as molecularly dispersed bridging ligands, while maintaining the structural integrity and order of the mesoporous organosilica material intact. Different possible routes for the synthesis as well as various methods to incorporate the titanium into the framework of the inorganic–organic hybrid mesoporous materials were adopted. Samples were also prepared with varied titanium loadings. Since the material is highly hydrophobic, improved catalytic hydrophobic surface properties are anticipated. The materials selectively epoxidized bulky aromatic alkenes and displayed high hydrogen peroxide efficiencies.

Experimental

Materials

The organosilane compound, 1,2-bis(trimethoxysilyl)ethane [$(CH_3O)_3Si–CH_2–CH_2–Si(CH_3O)_3$; BTMSE] was used as received (specially ordered from Shin-Etsu Chemical Co. Ltd.). The 1,2-bis(triethoxysilyl)ethane [$(C_2H_5O)_3Si–CH_2–CH_2–Si(C_2H_5O)_3$; BTESE] was purchased from Aldrich Chemicals. Cationic surfactants, alkyltrimethyl ammonium chloride [C_nTMACl], where n denotes the carbon number of the alkyl chain (C_{18} and C_{16}) were obtained from Tokyo Chemical Industries. Titanium butoxide (TBOT), tetraethyl orthosilicate (TEOS), ethanol, hydrochloric acid (HCl), tetramethyl ammonium hydroxide (TMAOH) and sodium hydroxide (NaOH) were purchased from Wako Chemicals. α-Pinene was obtained from Aldrich Chemicals.

Substituted titanium containing ethane bridged mesoporous materials: BTESE–TEOS–TMAOH–surfactant–H_2O system

First, in order to evaluate the effect of the substitution of bridged silsesquioxanes for siloxanes on the properties of the resultant mesoporous bulk materials, a series of samples were prepared with varying ratios of TEOS and silsesquioxane

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precursor (BTESE). In a typical synthesis procedure, the requisite amount of BTESE and TEOS were added to an aqueous solution of surfactant, C_{16}TMACl. This was followed by the addition of TMAOH, (~26% aq) and a diluted solution of TBOT in propan-2-ol. The mixture was stirred initially at ambient temperature for 36 h and the white precipitate obtained was filtered off, washed with distilled water and re-dispersed in alkaline C_{16}TMACl solution (pH ~ 10.5) followed by hydrothermal aging at 85–90 °C for 12 h. The material was recovered by filtration, washed with distilled water and finally dried under vacuum at room temperature. For the series of samples prepared using the BTESE–TEOS–TMAOH–surfactant–H_2O system, the represented molar ratios of starting compositions are (0.9–0.7) TEOS : (0.1–0.3) BTESE : 0.3 surfactant : 0.15 TMA : (0–0.04) TBOT : 36 H_2O.

Synthesis of titanium containing ethane bridged mesoporous materials: BTMSE–NaOH–surfactant–H_2O system]

Highly ordered titanium containing inorganic–organic hybrid materials were synthesized as follows: BTMSE (8 g) was first added to a mixture of C_{18}TMACl (6 g), NaOH (2.9 g) and water (194 g) under continuous stirring at room temperature. The requisite amount of TBOT was than introduced very slowly with vigorous stirring. The clear suspension was stirred for 18 h at ambient temperature followed by refluxing and heating for 30 h at 92 °C. The precipitate obtained was filtered and washed with distilled water and finally dried under vacuum. Materials were also prepared using C_{16}TMACl as surfactant.

Removal of surfactant

Surfactant was removed from the as-synthesized material by HCl/ethanol extraction.[11] 1.0 g of sample was stirred in a mixture of ethanol (150 ml) and 36% HCl (2.0 g) for 8 h at 40 °C. The solids were recovered by filtration and repeatedly washed with an excess of ethanol. The process was then repeated until the surfactant was extracted completely. The materials were further dried under vacuum and kept in sealed bottles.

Titanium incorporation by grafting procedure

For comparison, the catalyst was also prepared by direct grafting of titanium butoxide[8] onto mesoporous organic–inorganic hybrid silica. The desired amount of titanium butoxide was first dissolved in methanol and the ethane bridged hybrid mesoporous sample was added to the solution and kept for 6 h at 50 °C. Samples were recovered by filtration and dried under vacuum at 70 °C for 5 h. Finally the material was calcined overnight at 200 °C.

Catalysis

The catalytic activity was evaluated by the liquid phase epoxidation of α-pinene with H_2O_2 and the results were compared to traditional titanium containing mesoporous silica (Ti-MCM41). The details of the reaction procedure are described elsewhere.[8]

Characterization

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku D-Max VC X-ray diffractometer using nickel filtered Cu-Kα (λ = 1.5406 A) radiation, operating at 40 kV and 30 mA. The BET specific areas and average pore diameter were determined by N_2 adsorption–desorption isotherm recorded at 77 K using a Bellsorp system (Bell Japan Inc.). Diffuse reflectance UV–Vis spectra were recorded using a Varian double beam spectrometer. The Ti content was determined using a PerkinElmer ICP instrument. The ^{29}Si and ^{13}C NMR were recorded on Bruker spectrometer and the chemical shifts were referenced to trimethylsilane (TMS) at 0 ppm. Transmission electron microscopy (TEM) analysis was performed using a Hitachi H-9000.

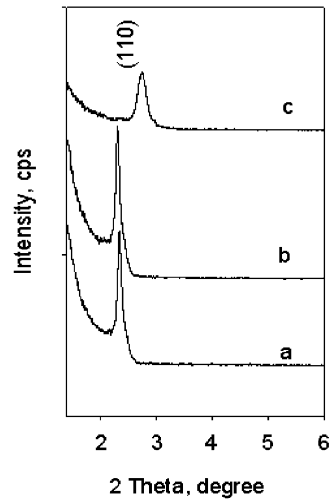

Fig. 1 PXRD patterns of titanium containing organic–inorganic hybrid mesoporous materials prepared with different BTESE to TEOS ratio: a, 10 : 90; b, 20 : 80; and c, 30 : 70. [BTESE–TEOS–TMAOH–surfactant–H_2O system].

Results and discussion

The PXRD patterns of the series of titanium containing ethane bridged mesophases prepared for this study are given in Fig. 1. It reveals that the structure of these mesophases was very sensitive to the BTESE : TEOS ratio. The titanium containing mesophases derived from the mixture with BTESE : TEOS ratios of 10 : 90, 20 : 80 and 30 : 70 using C_{18}TMACl surfactant showed peaks at low angle $2\theta \sim 1$–5°, which can also be indexed as a highly ordered 2dH (*p*6*mm*) mesophase with a unit cell (a = ~44 Å). Beyond these ratios, a collapse in ordering with >15% shrinkage was observed (a = 37.4 Å). In addition, titanium incorporation into the mesophase framework could not occur when only BTESE was used along with TMAOH for the synthesis of the titanium containing ethane bridged organosilica described in the Experimental section, only, mesophases with occluded titanium species {TiO_2} were obtained.

In another approach NaOH was used instead of TMAOH for enhanced hydrolysis and condensation reactions. Interestingly, substituted titanium containing ethane bridged hybrid mesoporous materials using the TEOS and BTESE mixture could not be obtained when NaOH was used. BTMSE as silica precursor is useful for rapid and complete condensation of silica as described under the BTMSE–NaOH–surfactant–H_2O system section. The PXRD patterns of surfactant free titanium incorporated into ethane bridged mesoporous organosilica prepared with different surfactants are shown in Fig. 2. All hybrid materials showed clear diffraction peaks characteristic of a 2D hexagonal phase (typical of Ti-MCM41 type materials) with lattice constants a = 57.6, and 56.1 for the materials prepared using surfactants with C_{18} and C_{16} alkyl chain lengths, respectively. The d-spacings were slightly lower compared to the ethane bridged hybrid mesoporous materials.[1] Also the intensity of the d_{100} reflection was considerably lower with titanium incorporation but the materials showed a high degree of mesoscopic order. The wall thickness was in the range 23–27 Å for all samples studied.

The diffuse reflectance UV spectra (Fig. 3) indicate that most of the titanium is present as isolated tetrahedral {TiO_4} units in the solid framework prepared within Si : Ti = ~45, whose

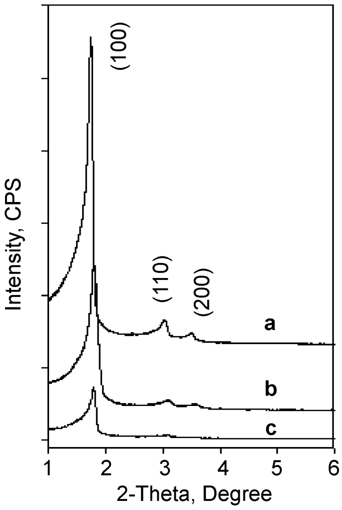

Fig. 2 PXRD patterns of titanium containing ethane bridged hybrid mesoporous materials prepared with different surfactants: a, without titanium, $C_{18}TMACl$; b, Ti-$C_{18}TMACl$; and c, Ti-$C_{16}TMACl$. [BTMSE–NaOH–surfactant–H_2O system].

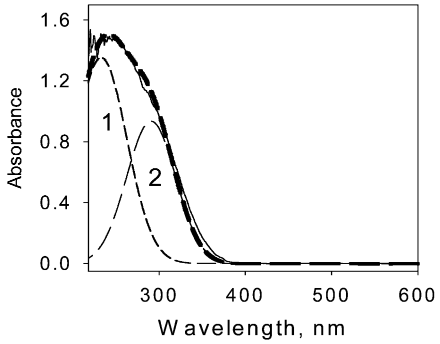

Fig. 3 Deconvoluted diffuse reflectance UV–Vis spectrum of titanium containing ethane bridged mesoporous materials prepared using $C_{18}TMACl$ surfactant. [BTMSE–NaOH–surfactant–H_2O system].

intensity is mainly due to the electronic transition from O^{2-} (2p) to Ti^{4+} (3d) orbitals. The samples containing higher titanium Si : Ti = 30 show a small hump at 440–480 nm confirming the presence of occluded or extra framework titanium $\{TiO_2\}$.

The UV-Vis spectrum was deconvoluted into two separate peaks. Peak 1 at lower wavelength (Abs = 220–245 nm) is assigned to the tetrahedral coordination of titanium in the framework (~62%), while the higher wave number peak 2 (Abs > 300 nm) is typical of the titanium present in the extra framework (~38%) of the material (*i.e.* five- and six-coordinated). The IR band at 962 cm^{-1} also confirms the presence of tetrahedral framework titanium, which can be attributed to SiO^- defects in the silica patches, indicating the substitution of Ti^{4+} for Si^{4+} in the SiO_2 domain.[12]

The two signals at −57.8 ppm [corresponding to trifunctional (T^2) silicons; $SiC(OH)(OSi)_2$] and −66.7 ppm [T^3 silicons; $SiC–(OSi)_3$] in the ^{29}Si MAS NMR spectrum of the organic–inorganic hybrid material reveal that the organic fragment (ethane) is covalently bonded to Si on both sides as in the $SiO_{1.5}–CH_2CH_2–SiO_{1.5}$ network. There was no evidence of tetra-functional Q silicons at −102 or −108 ppm, implying complete retention of the bridging ligands after extraction (Fig. 4a). On the other hand, materials prepared using the TEOS–BTESE mixture showed peaks for T^2 and T^3 (−57 to −68 ppm) as well as Q3 and Q4 silicon (−100 to −110 ppm) species indicating that the ethane fragment could remain intact (Fig. 4b). The ^{13}C NMR spectrum shows a signal at 5.2 ppm corresponding to the $Si–CH_2CH_2–Si$ fragment. Also, that no carbon signal for the surfactant was detected in the ^{13}C NMR spectrum indicates the complete removal of surfactant during the extraction process (Fig. 5).

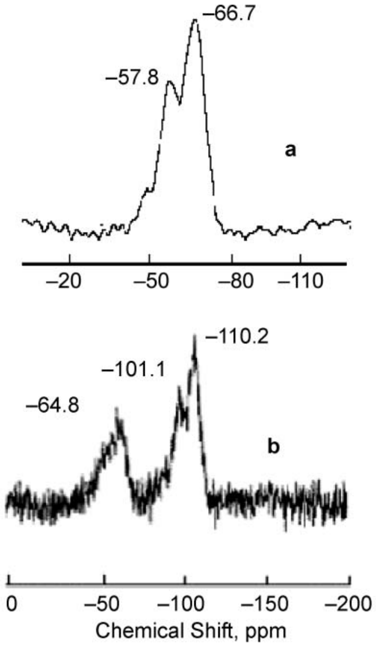

Fig. 4 ^{29}Si MAS NMR spectra of titanium containing ethane bridged mesoporous materials prepared from: a, BTMSE–NaOH–surfactant–H_2O system; b, BTESE–TEOS–TMAOH–surfactant–H_2O system.

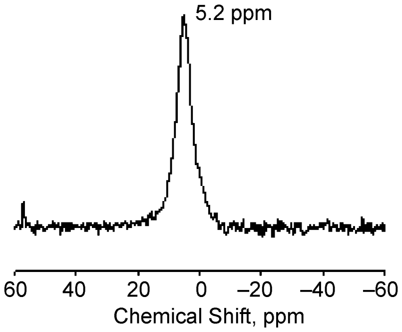

Fig. 5 ^{13}C CP MAS NMR spectrum of titanium containing ethane bridged mesoporous materials prepared from BTMSE–NaOH–surfactant–H_2O system.

In substituted ethane bridged mesoporous hybrid materials prepared with various ratios of TEOS and BTESE, the BET surface areas depended on the amount of substitution while the post-synthesis titanium grafted sample showed the least BET surface area. The textural properties of all the titanium containing hybrid mesophases are given in Table 1. The N_2 adsorption isotherms of the representative titanium hybrid mesoporous material (Ti-HMM) sample (Fig. 6a) are qualitatively consistent with those previously obtained for the corresponding Ti-MCM-41 and ethane bridged hybrid mesoporous materials,[1,8] which are typical of surfactant-templated mesophases in general. The BET surface area and pore diameter were decreased when the C_{16} surfactant was used. A further decrease was observed with an increase in titanium content. Some textural properties of such mesophases are listed in Table 2. All the materials have a completely uniform distribution of the organic fragment along with the titanium incorporated within the inorganic oxide framework at the

Table 1 Textural properties of titanium containing organic–inorganic HMM prepared from the BTESE–TEOS–TMAOH–surfactant–H_2O system

Material description	BTESE : TEOS	Si : Ti ratio	Ti in product[a] (%)	Wall thickness/Å	BET/m^2g^{-1}	D_p/Å	V_p/Å
HMM	10 : 90	100	—	11.7	1023	30.4	0.46
Ti-HMM	10 : 90	47	2.03	13.7	891	29.3	0.51
Ti-HMM	20 : 80	45	2.11	14.9	822	28.1	0.58
Ti-HMM	30 : 70	46	2.02	13.0	749	26.6	0.41
Ti-HMM-Cal[b]	10 : 90	47	2.03	14.8	1092	29.2	0.59
Ti-HMM-grafted[c]	10 : 90	~45	2.07	ND	804	25.9	0.37
Ti-MCM41	0 : 100	49	1.93	9.7	1230	32.7	0.58

[a] Determined by ICP. [b] Calcined at 550 °C for 6 h. [c] Grafted using TBOT, as per ref. 8.

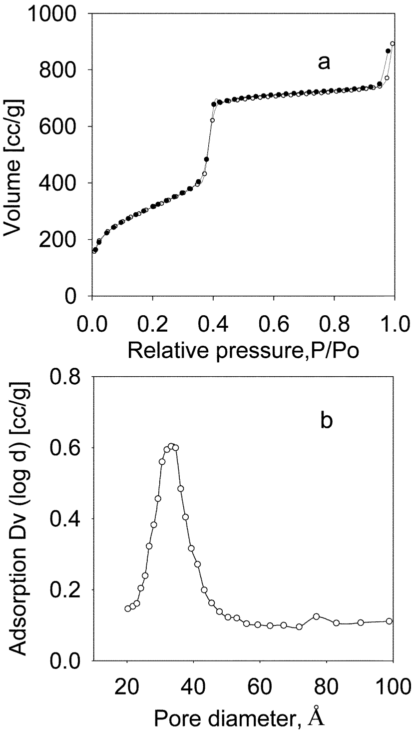

Fig. 6 a, Nitrogen adsorption isotherm; and b, pore size distribution of titanium containing ethane bridged mesoporous material.

molecular level, with a periodic pore arrangement structure (Fig. 6b). The results agree with the pore dimension estimated from the TEM image, which shows a clear hexagonal arrangement of pores with uniform size (Fig. 7). A 3D hexagonal mesophase was not observed, as reported earlier for mesophases obtained with TMOS and silsesquioxanes mixtures.[13] The rich hydrophobic nature of the materials was confirmed by water vapor adsorption measurements. At the monolayer adsorption level little uptake was monitored compared to Ti-MCM41.

Table 3 lists the results of the epoxidation of α-pinene over various titanium containing hybrid mesoporous materials synthesized with various BTESE : TEOS ratios. α-Pinene oxide was the major product with >99% selectivity. The conversion of α-pinene greatly depended on the BTESE : TEOS ratio. Catalysts prepared with 10 : 90 ratios of silica precursors (BTESE : TEOS) showed higher conversion and better efficiency of H_2O_2 utilization (18.6 mol% and 43.2%, respectively). The H_2O_2 efficiencies and conversions decreased with increasing BTESE content. Interestingly, the Ti-hybrid mesoporous materials exhibited >3-fold conversion and

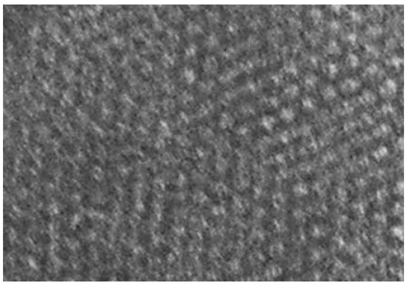

Fig. 7 TEM image of titanium containing ethane bridged mesoporous material.

Table 3 Catalytic performance of titanium containing ethane bridged hybrid mesoporous materials prepared from the BTESE–TEOS–TMAOH–surfactant–H_2O system in α-pinene epoxidation[a]

Material	BTESE : TEOS	α-Pinene conversion/ mol%	H_2O_2/mol% Conversion	Efficiency
Ti-HMM	10 : 90	18.6	36.2	43.2
Ti-HMM	20 : 80	15.3	40.6	31.7
Ti-HMM	30 : 70	12.1	46.1	22.1
Ti-HMM-Cal[b]	10 : 90	8.2	42.1	16.4
Ti-HMM-grafted[c]	10 : 90	12.9	33.5	32.4
Ti-MCM41	0 : 100	6.1	44.2	11.6

[a] Reaction conditions: catalyst, 0.1 g; α-pinene, 0.037 mol; H_2O_2 (30% aq sol), 0.044 mol; reaction temp., 328 K; reaction duration, 5 h. [b] Calcined at 550 °C for 6 h. [c] Grafted using TBOT, as per ref. 8.

Table 2 Textural properties of titanium containing organic–inorganic HMM prepared from the BTMSE–NaOH–surfactant–H_2O system

Material description	Si : Ti ratio in gel	Ti in product[a] (%)	Wall thickness/Å	BET/m^2g^{-1}	D_p/Å	V_p/cc g^{-1}
HMM	100	—	25.9	889	34.7	0.83
Ti-HMM	48	1.96	23.8	860	33.1	0.76
Ti-HMM[b]	48	1.87	24.2	822	32.4	0.68
Ti-HMM-Cal[c]	48	1.91	22.6	766	29.8	0.65
Ti-HMM-grafted[d]	~46	1.99	ND	729	28.2	0.69
Ti-HMM	39	2.37	24.7	802	31.6	0.61
Ti-HMM	30	3.13	26.8	771	30.9	0.54

[a] Determined by ICP. [b] Prepared using $C_{16}TMACl$ surfactant. [c] Calcined at 550 °C for 6 h. [d] Grafted using TBOT, as per ref. 8.

Table 4 Catalytic performance in α-pinene epoxidation of titanium containing ethane bridged hybrid mesoporous materials prepared from the BTMSE–NaOH–surfactant–H_2O system[a]

Material	Ti in product (%)	α-Pinene conversion/ mol%	H_2O_2/mol%	
			Conversion	Efficiency
Ti-HMM	1.96	22.9	33.2	49.8
Ti-HMM[b]	1.87	18.7	36.6	42.9
Ti-HMM-Cal[c]	1.91	11.3	42.1	20.4
Ti-HMM-grafted[d]	1.99	15.4	34.1	34.7
Ti-HMM	2.47	16.1	39.7	31.4
Ti-HMM	3.23	10.8	40.2	19.6

[a]Reaction conditions: catalyst, 0.1 g; α-pinene, 0.037 mol; H_2O_2 (30% aq sol), 0.044 mol; reaction temp., 328 K; reaction duration, 5 h. [b]Prepared using C_{16}TMACl surfactant. [c]Calcined at 550 °C for 6 h. [d]Grafted using TBOT, as per ref. 8.

peroxide efficiency compared with a traditional Ti-MCM41 sample (Table 3).

Catalyst prepared by direct grafting of titanium to the ethane bridged hybrid mesoporous materials prepared under similar conditions (BTESE : TEOS = 10 : 90), named Ti-HMM-grafted, showed an enhanced activity for α-pinene epoxidation, this is probably owing to the presence of surface sites that could be highly dispersed isolated and tetrahedral in nature. Again, α-pinene oxide was the major product with >99% selectivity. In addition, materials calcined at 550 °C for 6 h also showed somewhat higher conversions and H_2O_2 efficiency to those observed for Ti-MCM-41 (Table 3). Although the ethane fragment was completely decomposed at 550 °C, the more hydrophobic features remained and led to improved catalytic activity. These features were further confirmed by a noticeable uptake of H_2O vapor during water adsorption experiments.

For the samples prepared with the BTMSE–NaOH–surfactant–H_2O system, the maximum conversion (22.9 mol%) with highest H_2O_2 utilization efficiency (49.8 mol%) was observed when the C_{18} surfactant was used. The conversion and efficiency of H_2O_2 utilization were somewhat lower with the C_{16} surfactant (Table 4). This clearly indicates that the higher mesoscopic ordered structure also influences the catalytic properties where the active species are readily available for reactants to diffuse easily into the pore channel. A decrease in conversion was noticed over the samples with higher titanium contents (Si : Ti = 39 and Si : Ti = 30). The materials also showed a lower efficiency of H_2O_2 utilization. Octahedrally coordinated titanium is usually inactive for the epoxidation of alkenes as it lacks free coordination of silica.[14,15] However, the presence of dimers and oligomers could be responsible for the decomposition of the peroxide. The reasonable activity of the titanium-grafted sample probably suggests that the average structure of the catalytic sites is mainly tetrahedral and/or the sites might be composed of mixtures of different tetrahedral species. While, the very low efficiency of H_2O_2 utilization upon calcination can be attributed to the high concentration of silanol and hydroxy groups generated on the wall surface after the hydrophobic component, ethane, was decomposed, which was responsible for the peroxide decomposition.

In some previously published literature[16,17] it was reported that the activity of V- and Cr-containing molecular sieves in liquid phase oxidation reactions was due to minor amounts of metal leaching out of the solid catalyst and being present in the reaction solution. A special kind of experiment was performed to check for any hypothetically leached Ti species under similar reaction conditions. The experimental details are given in ref. 18. We found no activity in the liquid phase alone after filtering out the catalyst from the reaction media. Fig. 8 shows the results of such a reaction. It is evident that no hypothetical Ti species leached out of the catalyst and the epoxidation reaction was stopped after catalyst removal. Thus it is concluded that the activity of the catalyst can be only due to the Ti atoms substituted in the framework of the ethane bridged hybrid mesoporous materials.

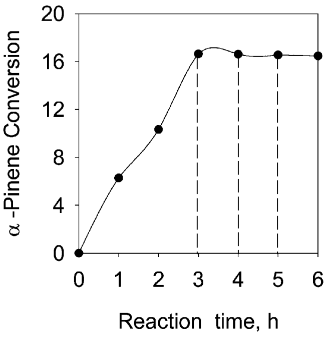

Fig. 8 Activity of reaction solution with titanium containing ethane bridged mesoporous materials as catalyst prepared by the BTMSE–NaOH–surfactant–H_2O system (up to 3 h) and after the removal of the catalyst from the reaction solution under the hot filtration test. (3–6 h).

Conclusion

Therefore, based on the results obtained, we can draw the conclusion that the improved catalytic performance of titanium containing ethane bridged hybrid mesoporous materials is due to the generation of active hydrophobic centers through an ethylene fragment that provides the possibility of incorporating more tetrahedrally coordinated titanium on the inner surface of the mesoporous silica. This also leads to a hexagonal arrangement of the pores which have a very uniform size. The structure–porosity relationship established using various BTESE : TEOS ratios is also important. A net decrease in charge density occurs when BTESE–TEOS mixtures were employed for the synthesis of the titanium containing hybrid mesophases.[13] The resulting decrease in the anion charge density increases the effective head group area of the surfactant counter-actions in accordance with the charge density matching at the organosilicate/surfactant interface.[19] Therefore, by varying the charge density in the system it is also possible to accommodate the large active tetrahedral titanium species at an easily accessable location, probably around the pore mouth. These titanium species [probably $Ti(O–Si)_3(OH)$ with a connectivity of ∼3] are supposed to occupy the interface of the inorganic (depends on geometry of the inorganic species) and surfactant micelle phase. Thus, a good structure–porosity relationship is responsible for the better catalytic properties of such materials.

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18 In order to check the leaching of Ti species during epoxidation reaction, an experiment performed under similar reaction conditions was interruped after 3 h. The hot two phase liquid medium was removed with a syringe equipped with a filter and immediately transferred to another reactor already at the same temperature. The compositions of the two phases were then monitored for another 3 h.

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