One-Step Synthesis of a Highly Active, Mesoporous, Titanium-Containing Silica by Using Bifunctional Templating

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Abstract: A highly active, three-dimensional, mesoporous titanosilica, Ti-TUD-1, with comparable properties to Ti-grafted mesoporous silica MCM-41, has been prepared in a one-step synthesis. A non-surfactant chemical, triethanolamine, was used as a template molecule. Triethanolamine easily forms complexes with titanium alkoxides, yielding titanatrane complexes, which together with free triethanolamine form meso-sized aggregates that template mesopores upon increasing the temperature of the synthesis mixture. Triethanolamine served as both mesopore template and ligand for the titanium complexes, which represent the majority of the catalytic-site precursors. The formation of the silica network and the titanium insertion were followed by a combination of diffuse reflectance UV/Vis/NIR and FTIR spectroscopy. A titanium-rich phase was obtained on the mesopore surfaces during calcination, allowing for easy accessibility of the reactants to the catalytic sites. Ti-TUD-1 is about six times more active than framework-substituted Ti-MCM-41 and has similar activity to Ti-grafted MCM-41.

Keywords: complexation · epoxidation · mesoporous materials · template synthesis · titanosilica

Introduction

The development of solid catalysts for selective oxidation has drawn much attention.[1] Until the late seventies, ion exchange was the principle method for the introduction of transition metals into microporous matrices; this raises the major problem of metal leaching in liquid-phase oxidation.[2] A breakthrough was made with the discovery of titanium(IV) silicate-1 (TS-1),[3, 4] in which titanium is substituted into the silicate framework. TS-1 displayed remarkable activity due to the unique atomic architecture of the titanium centers, which are isolated, four-coordinated Ti located in the hydrophobic pores of the silicate.[5] Based on this understanding of TS-1, many microporous titanosilicates, such as TS-2,[6] Ti-ZSM-48,[7] Ti-β,[8], and titano-aluminophosphates, TAPO-5,[9] TAPO-11,[9] TAPO-36,[10] and TAPO-34,[11] with tetrahedrally substituted Ti centers have been prepared. The common drawback of these materials lies in their small pores, which restrict access for important, but bulky substrates.

The initial discovery of the M41S family[12] opened the way to prepare mesoporous titanosilicas and extended the scope to much larger substrates for selective oxidations. A number of mesoporous titanosilicas, such as Ti-MCM-41,[13, 14] TiHMS,[14, 15] Ti-MCM-48,[16] and silylated Ti-MCM-41,[17] have been prepared by introducing titanium into the initial synthesis mixtures, but a significant fraction of the Ti^{IV} centers lie buried inaccessibly in the framework. However, this drawback can be overcome by grafting an organometallic titanium catalytic-site precursor onto the inner surfaces of the mesoporous host after synthesis.[18] This method yields efficient catalysts for epoxidation with organic hydroperoxide, owing to the presence of a high concentration of accessible, well-spaced, and structurally well-defined, tetrahedral Ti surface sites,[19] and is a successful example of controlling the atomic architecture of active sites in catalysts.[20] The influence of various types of Ti precursor on the catalytic performance have also been investigated.[21] Furthermore, it has been reported that germanium can enhance the catalytic performance of Ti-grafted MCM-41.[22]

A MCM-41-type catalyst with a Ti-rich phase on the inner wall has been prepared by a one-pot synthesis by using the

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true liquid-crystal template route and titanocene dichloride as the precursor;[23] in this catalyst titanium is located primarily in the central hydrocarbon regions of the micelles owing to the hydrophobic nature of the ligands of the Ti precursor. However, this only produces a one-dimensional channel system and is a very expensive synthesis method.

The novel templating method for the synthesis of TUD-1 (without surfactant or liquid-crystal template, but with triethanolamine (TEA) instead)[24, 25] provides an opportunity to design a new one-pot grafting methodology, because triethanolamine can act as both a template in the mesopore formation and a metal-complexing agent. Initially, the appropriately selected active metal forms complexes with triethanolamine, which together with free triethanolamine template the mesopores. During calcination these complexes decompose and any organic species are removed. Consequently, the metals are grafted onto the surface of the mesopores as oxide species. Depending on the loading these can be highly disperse monomeric sites or small oxide clusters. Here, we demonstrate the viability of this new methodology by introducing titanium into the mesopores of siliceous TUD-1 and report the synthesis, characterization, and comparative performance evaluation of the three-dimensional mesoporous titanosilica, Ti-TUD-1.

Results and Discussion

Structural properties of Ti-TUD-1: Figure 1 shows a typical powder X-ray diffraction (XRD) pattern of Ti-TUD-1 after calcination at 700 °C in air for 10 h, in which an intense peak around 1.0–2.0° in 2θ indicates that Ti-TUD-1 is a mesostructured amorphous material. The TEM image shows the foamlike structure of Ti-TUD-1. It has been shown previously that TUD-1 has uniform mesopores,[25] which are connected randomly in three dimensions, distinguishing it from the one-dimensional MCM-41. The mesopore sizes can be tuned from 25 to 250 Å and the surface areas from 400 to 1000 m^{2}g^{-1}, depending on the synthesis conditions.

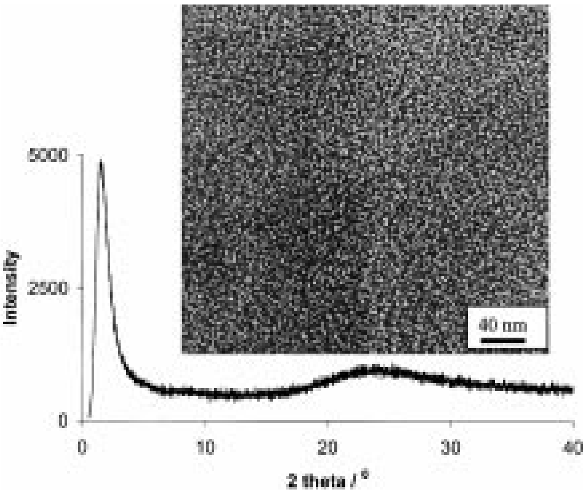

Figure 1. XRD pattern of Ti-TUD-1 calcined at 700 °C for 10 h. Inset: TEM image of the corresponding Ti-TUD-1.

Complexation of titanium with triethanolamine: It is well known that Ti^{IV} easily forms titanatranes with triethanolamine (TEA). Verkade and co-workers have studied these compounds by single-crystal X-ray crystallography and by solution NMR spectroscopy.[26] Both monomeric and (fluxional) dimeric behaviors have been observed for these complexes. Bulky substituents at the axial position seem to destabilize the dimeric form.[26] For example, with O-*i*Pr at the axial position, the NMR spectra indicated that the compound was predominantly monomeric in solution. To investigate the interaction of TEA and titanium(IV) *n*-butoxide, the latter compound was added step-wise to a sample of TEA (100.6 mg) in $CDCl_3$ (0.5 mL). After each addition ^{1}H and ^{13}C NMR spectra were recorded. At a low molar ratio of Ti to TEA, a large number of new resonances were observed in the ^{13}C NMR spectrum near the signals of free TEA (cf. Figure 2); this suggests that asymmetric oligomeric or polymeric Ti–TEA complexes were formed. Increasing the molar ratio of Ti to TEA simplified the spectra to two broad resonances for the TEA nuclei (cf. Figure 3). This may be ascribed to a dimeric complex undergoing fluxional motion around the *n*Bu-Ti-N axis as expressed schematically in Figure 4.[26a]

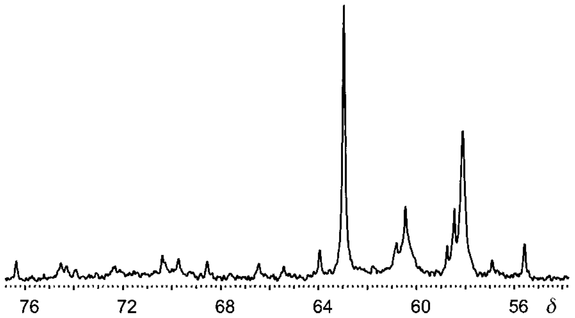

Figure 2. ^{13}C NMR (75 MHz) of the mixture of titanium(IV) *n*-butoxide, and triethanolamine with a TEA/Ti molar ratio of 2.59. Measuring conditions: a mixture containing titanium(IV) *n*-butoxide (100 mg) and TEA (100.6 mg) in $CDCl_3$ (0.5 mL) at 25 °C.

In the synthesis mixture (TEA/Ti molar ratio of 50), both the silicon and titanium alkoxides are expected to form complexes with TEA. Ti does so more easily than Si due to the interaction of the lone electron pair on the nitrogen atom with the empty *d* orbital of the titanium.

The synthesis gel was dried and then extracted with ethanol in a Soxhlet apparatus for three days. The elemental analysis of the washings then showed that about 10 % of the total Ti used was extracted and that the Si/Ti atom ratio in the washings was about 22 instead of 50 in the initial synthesis mixture. This shows that the TEA phase, in as far as it could be separated, is enriched in titanium. As a result of the hydrolysis and subsequent condensation reactions, involving not only tetraethyl ortho silicate (TEOS) and Ti–butoxide, but also Ti–TEA complexes, these last are, in part, connected to the silica framework and, hence, could not be extracted. Extraction of a gel after heating it in an autoclave at 190 °C for 24 h (i.e., the inorganic condensation is almost completed) resulted in an extract with 0.62 % Ti of total Ti used and Si within the margins of detectability. This indicates that even

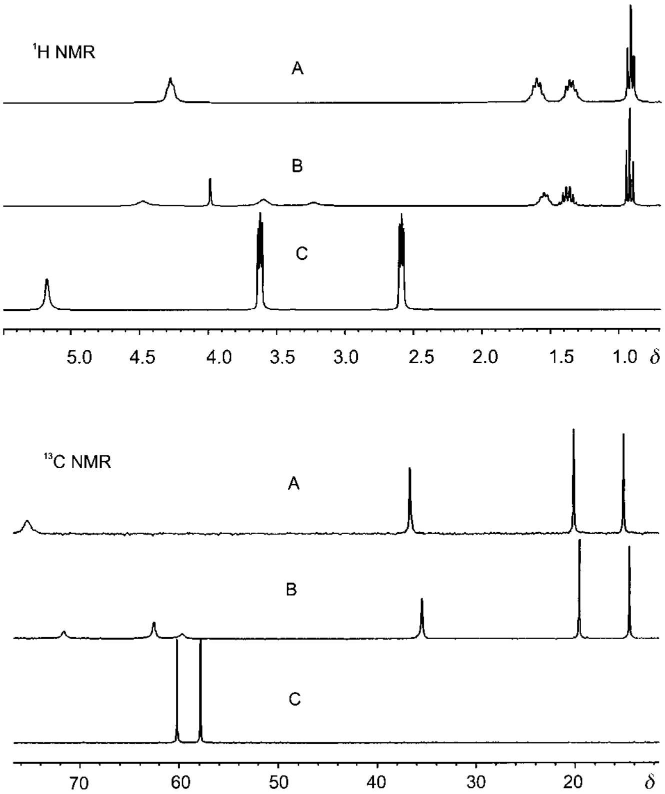

Figure 3. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) of A) titanium(IV) *n*-butoxide, B) a TEA/Ti mixture with a molar ratio of 0.86, and C) TEA. Measuring conditions: a mixture containing titanium(IV) *n*-butoxide (300 mg) and TEA (100.6 mg) in $CDCl_3$ (0.5 mL) at 25 °C.

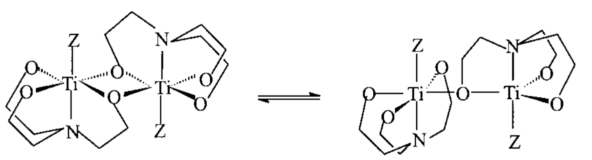

Figure 4. The fluxional motion of a dimeric Ti-TEA complex, Z = 1-butanol (the titanium concentration in the TUD-1 synthesis mixture is about 50 times below that used for the NMR investigations reported here, hence, any dimerization is suppressed).

after this severe treatment some Ti–TEA complexes remain in the TEA-dominated phase, although effectively all silica species condensed to form the silica framework. This is consistent with the Ti–TEA complexes decomposing more slowly than the Si–TEA complexes, leading to the preferential location of titanium species at the interface of the inorganic framework and organic-dominated TEA aggregates.

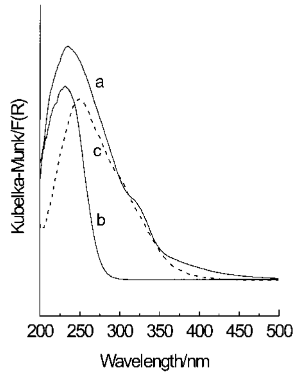

Figure 5. Diffuse reflectance UV/Vis spectra of a) the dried synthesis mixture, b) calcined Ti-TUD-1, and c) the mixture of Ti-butoxide/TEA.

Ti incorporation: The diffuse reflectance UV-Vis spectrum (Figure 5a) of the dried synthesis mixture showed a broad absorption centered at 235 nm, which is clearly formed by a band at 220–230 nm and other components at higher wavelengths (250–350 nm). Whilst the band at lower wavelength can be assigned to an electronic charge-transfer transition (LMCT) of tetrahedral Ti ions in a siliceous environment,[19] the components at 250–350 nm are due to electronic transitions of Ti–TEA complexes (see for comparison the spectrum of the Ti–butoxide/TEA mixture, Figure 5c).

After calcination, these complexes decomposed, depositing the titanium on the surface as grafted species to form a titanium-rich phase. The diffuse reflectance UV/Vis spectrum of the Ti-TUD-1 (Figure 5b) shows a band centered at 225 nm, indicating that Ti centers in Ti-TUD-1 are isolated and tetrahedrally coordinated,[19] that is, the environment of the titanium(IV) centers is comparable to that in Ti-grafted MCM-41.[19, 27]

Figure 6 shows the FTIR spectra of the dried synthesis mixture of Ti-TUD-1, TEA, and TEOS. The dried gel and TEA have very similar IR spectra; however, some new IR features in the spectrum of Ti-TUD-1 are significant. Broad bands (marked *) at 1200, 950 (shoulder), and 785 cm^{-1} can be assigned to oligomeric silica species.[28, 29] The weak intensity of these bands suggests that the silica polymerization is rather incomplete. The weak band at 950 cm^{-1} is due to Ti-O-Si species,[27] indicating that some Ti condensation with the siliceous species occurred at this stage; this is in good agreement with titanium extraction results and diffuse reflectance UV results (vide supra). This confirms that some Ti–TEA complexes are chemically bonded to silica and, thus, could not be extracted. However, the majority is still not incorporated into the framework; this is consistent with our proposed mechanism. The IR spectrum of TEOS is reported for comparison. The doublet at 1105 and 1080 cm^{-1} due to Si-O-C stretching vibrations[28] is not present in the spectrum of Ti-TUD-1, in which, beside bands of oligomeric silica species,

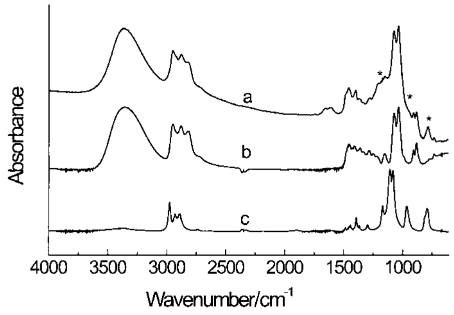

Figure 6. FTIR spectra of a) the dried synthesis mixture , b) TEA, and c) TEOS.

only absorptions due to TEA molecules are observed. This means that, although the silica polymerization is largely incomplete, hydrolysis of TEOS and some subsequent condensation has occurred.

Figure 7 shows the IR spectra of Ti-TUD-1 after different thermal treatments (curves a–c) and of a pure silica TUD-1 after calcination (curve d) for comparison. These spectra suggest that during the hydrothermal treatment the polymerization proceeded, but not completely. Only after calcination was the siliceous matrix fully condensed. Bands at 1200 and 1080 cm^{-1} due to asymmetric stretching of SiO_4 tetrahedral units in silicate structures, and at 805 cm^{-1} due to the symmetric vibration of the same units[29] fully developed only after this treatment. It is of note that the incorporation of Ti ions in the silica matrix, as witnessed by the appearance of the band at 955 cm^{-1} due to a Ti-O-Si vibration,[27] occurred to a significant extent only after calcination as expected from our mechanism. This Ti-O-Si band is absent in the spectra of the pure siliceous TUD-1 material.

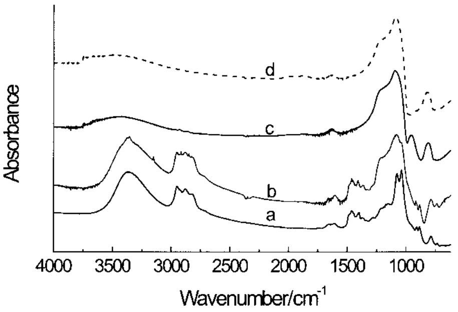

Figure 7. FTIR spectra of the synthesis mixture of Ti-TUD-1: a) dried, b) after being heated in an autoclave to 190 °C, c) after calcination at 700 °C, and d) calcined siliceous TUD-1.

We have also followed the formation of the Ti-TUD-1 catalyst in situ by starting from the dried gel and heating it under vacuum at increasing temperatures (Figure 8). We chose the temperatures according to the main weight loss steps of the material obtained by thermal gravity analysis (TGA), as reported in the inset of Figure 9.

After degassing at 250 °C (Figure 8b) there was a partial decomposition of the organics and further condensation of silica (bands at 1190 and 1100 cm^{-1}). Only after degassing at 400 °C (Figure 8c) was the TEA completely decomposed and the siliceous structure well formed; this is suggested by the formation of the bands of the SiO_4 units in the 1250–900 cm^{-1} range and at 805 cm^{-1}. The band at 960 cm^{-1}, due to a vibration involving the Ti ions within the siliceous structure, also developed at this temperature. The degassing at 600 °C and the following calcination served to burn residual organic compounds and to clean up the silica surface.

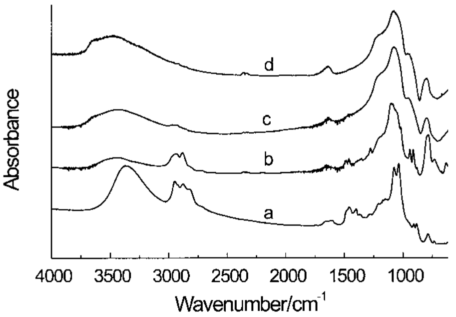

Figure 8. FTIR spectra of the synthesis mixture degassed at different temperatures: a) 100 °C, b) 250 °C, c) 400 °C, and d) 600 °C.

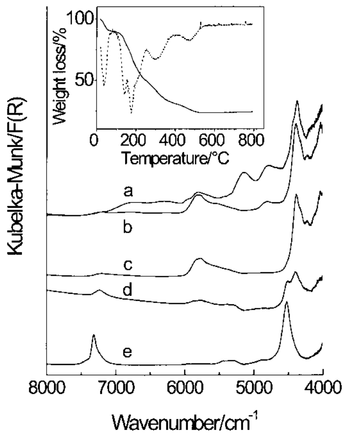

Figure 9. Diffuse reflectance NIR spectra. a) Dried synthesis mixture, and after being degassed at: b) 130 °C, c) 300 °C, d) 400 °C, and e) 600 °C. Inset: thermogravimetric analysis (TGA) of the dried synthesis mixture. Dotted line refers to the differential curve (DTG).

Silanols are also formed after thermal treatments, as demonstrated by means of diffuse reflectance NIR spectroscopy. Uncalcined material (Figure 9a) showed bands at 5140 cm^{-1} due to a combination mode of water molecules, at 5000–4000 cm^{-1} due to combination modes of CH stretching with bending vibrations of hydrocarbons, and at 6000–5000 cm^{-1} due to overtones of CH stretchings of hydrocarbons.[30] Water was completely removed after degassing at 130 °C (Figure 9b), whereas only at 400 °C (curve d) was there a substantial decrease of the bands due to organic compounds; these completely disappeared after calcination at 600 °C (curve e). These results are in good agreement with the TGA data (inset of Figure 9). At 400 °C there was a formation of some silanols, indicated by bands at 7320 and 4525 cm^{-1} due to the overtone and combination vibrations, respectively,[30] which increased after calcination at 600 °C.

Accessibility of Ti centers: The coordination states of the Ti centers were studied by diffuse reflectance UV/Vis spectra in Figure 5; this indicated that the Ti centers in TUD-1 are isolated and tetrahedrally coordinated. The change of coordination of Ti centers was studied by NH_3 adsorption. Figure 10a shows the shift of the band at 225 nm, after exposure to NH_3, due to the expansion in the coordination sphere of the Ti centers.[29b, 31]

After evacuation at room temperature, the adsorption is not completely reversible (Figure 10b), indicating that many Ti centers are available to strongly coordinate NH_3 molecules. This clearly indicates that most isolated, tetrahedrally coordinated Ti centers are accessible to form hydroperoxo-type species during epoxidation.

Catalytic performance: Four different catalysts were compared with regard to their catalytic performance in the

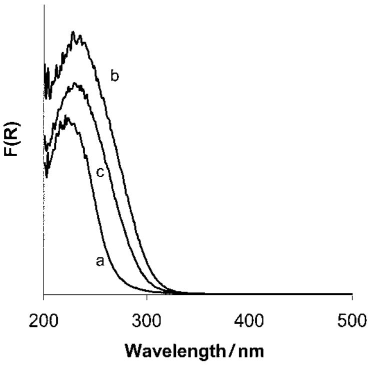

Figure 10. Diffuse reflectance UV/Vis spectra of Ti-TUD-1 after a) calcination, b) exposure to 50 Torr NH_3, and c) evacuation at room temperature for 30 min.

epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP): Ti-TUD-1 and Ti-MCM-41 (both synthesized in one step), Ti-grafted TUD-1, and Ti-grafted MCM-41. Their physical properties and activities are presented in Table 1, and the catalytic testing details are given in the Experimental Section. The turn-over frequency (TOF, moles of cyclohexene converted per mole of Ti per hour) of Ti-TUD-1 is about 5.6 times higher than that of the framework-substituted Ti-MCM-41,[32] and similar to that of Ti-grafted MCM-41 under our testing conditions. The selectivity of TBHP to cyclohexene epoxide was about 94% after six hours of reaction. It is attractive that titanosilica with activity similar to Ti-grafted MCM-41 can be prepared in such a one-pot synthesis.

Table 1. Comparison of catalytic activities for cyclohexene epoxidation over Ti-TUD-1, Ti-MCM-41, Ti-grafted TUD-1, and Ti grafted MCM-41.

Catalysts	Ti[a] [wt%]	S_{BET}[b] [m^2g^{-1}]	D[c] [nm]	TOF[d] [h^{-1}]	S[e] [%]
Ti-TUD-1	1.50	917	4.5	20.2	90
Ti-MCM-41[32]	1.82	921	3.1	3.6	–
Ti grafted TUD-1	1.87	561	10.1	27.7	81
Ti grafted MCM-41	1.79	1015	3.0	23.4	82

[a] Titanium loading. [b] Surface area obtained from nitrogen adsorption. [c] Mesopore diameter at maximum peak calculated by using the BJH model. [d] Turnover frequency after 6 h reaction. [e] Selectivity of TBHP after 6 h reaction.

It is also noteworthy that Ti-grafted TUD-1 showed an even higher activity than Ti-grafted MCM-41. To highlight this performance enhancement, we used Ti-grafted TUD-1 with a much lower surface area than the Ti-grafted MCM-41; this illustrates that the three-dimensional connectivity of mesopores reduced diffusion limitations and enhanced the activity of TUD-1. In both cases the particle size is estimated by SEM to be in the micrometer range.

Discussion

The high activity of Ti-TUD-1 originates from both the high accessibility of the substrates to the catalytic site provided by the three-dimensional mesopore system and from the formation of a titanium-enriched phase on the surface of the mesopore wall, to give an optimum usage of Ti. The key aspect of the synthesis is the use of the non-surfactant chemical triethanolamine (TEA), which serves as both mesopore template and ligand for the in situ formation of titanium complexes: during mixing, aging, and drying. The complexes and free TEA were homogeneously dispersed in a flexible, silica-dominated inorganic framework. Upon heating, condensation ensued of both silica and some titanium species. In parallel, triethanolamine together with some of the titanium complexes was expelled from the inorganic framework to form mesosized organic-dominated aggregates. The aggregates templated a three-dimensional, inorganic, mesostructured framework. Meanwhile, some of Ti-O-C bonds of Ti–TEA complexes were hydrolyzed, with the resulting TiOH groups subsequently condensing with silanol groups to yield the more stable Ti-O-Si entities. These Ti species were strongly bonded to the silica framework at one side and penetrated into the organic-dominated TEA aggregates at the opposite side. Hence, two major types of Ti species could be observed: the free Ti–TEA complex in the TEA aggregates and the one strongly connected to the silica framework. The latter is situated at the interface of the inorganic-dominated silica phase and the organic-dominated TEA aggregates. The preferential dispersion of Ti species in TUD-1 can be schematically expressed as Figure 11b, which is different from the case of MCM-41 shown in Figure 11a. At elevated temperatures, all titanium complexes decomposed and the triethanolamine was removed, depositing titanium on the surface of the mesopores; this results in a three-dimensional mesoporous titanosilica with isolated, titanium species with a tetrahedral surface.

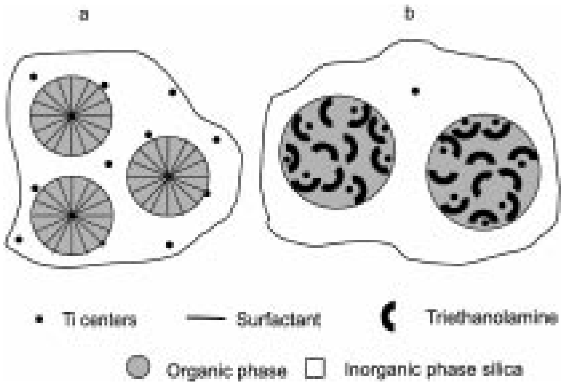

Figure 11. Comparison of the location of Ti centers in the as-synthesized form of a) Ti-MCM-41 and b) Ti-TUD-1.

Contrary to grafting onto a siliceous support in two-step synthesis approach,[33] a minority of titanium centers will be buried inside the silica walls, a process that occurs during the inorganic condensation; however, the three-dimensional mesopore structure enhances the efficiency of mass transfer, as indicated by the comparison of epoxidation activities between three-dimensional Ti-grafted TUD-1 and one-dimensional Ti-grafted MCM-41 (vide supra). So, the sum of various effects gives a similar activity of epoxidation as that of Ti-grafted MCM-41.

This synthesis opens a new way to effectively introduce active catalytic sites into a mesoporous host by the combination of mesopore formation and in situ organometallic complexation.

Experimental Section

Synthesis: Ti-TUD-1 can be obtained by aging, drying, and calcining a homogeneous basic synthesis mixture, mainly composed of titanium alkoxide, silicon alkoxides, such as tetraethyl ortho silicate (TEOS), and templates, such as triethanolamine (TEA). In a specific synthesis, first TEA (97%, ACROS) and then deionized water was added dropwise into a mixture of titanium(IV) *n*-butoxide (99%, ACROS) and TEOS (+98%, ACROS) while stirring. After about 1 h, tetraethylammonium hydroxide (TEAOH) (25%, Aldrich) was added dropwise into the above mixture. The final homogeneous mixture with a molar ratio composition of SiO_2/0.02 TiO_2/(0.1 – 0.3) TEAOH/(0.25 – 2) $C_6H_{15}O_3N$/11 H_2O was aged at room temperature for 24 h, dried at 100 °C for 24 h, and then calcined at 700 °C for 10 h in a ramp rate of 1 $^{\circ}C\,min^{-1}$ in air. In order to compare epoxidation activity, Ti-grafted MCM-41 and TUD-1 were prepared according to the method described by Maschmeyer et al.[18]

Characterization: X-ray powder diffraction (XRD) patterns were recorded by using $Cu_{K\alpha}$ radiation on a Philips PW 1840 diffractometer equipped with a graphite monochromator. The samples were scanned in the range of 0.5 – 40° 2θ with steps of 0.02°. Transmission electron microscopy (TEM) was performed using a Philips CM30T electron microscope with an LaB6 filament as the source of electrons operated at 300 kV. Nitrogen sorption isotherms were measured on the Quantachrome Autosorb-6B at 77 K. Mesoporosity was calculated using the BJH model.

Catalyric acivity measurements: Cyclohexene epoxidation was used as model reaction to test catalytic activity with *tert*-butyl hydroperoxide (TBHP) as an oxidant and was carried out at 40 °C under N_2.[32] The reaction mixture consisted of catalyst (0.1 g), cyclohexene (10 mmol, 99%, ACROS), TBHP (11 mmol, 70 wt% in water, ACROS, dried over anhydrous $MgSO_4$ before use) and dichloromethane (10 mL, 99%, Merck). Samples were analyzed by gas chromatography (WAX 52 CB). The turnover frequency is defined as moles of cyclohexene converted per mole of titanium per hour after reaction for 6 h.

Complexation of Ti with triethanolamine: The complexation of Ti with triethanolamine was investigated by means of ^{13}C and ^{1}H NMR spectroscopy with the use of a Varian-INOVA 300 spectrometer. To confirm the existence of titanium – triethanolamine (Ti – TEA) complexes, the synthesis gel was extracted before calcination with ethanol and a Soxhlet apparatus. The concentration of titanium in the ethanol solution was analyzed using ICP-OES.

Diffuse reflectance UV/Vis/NIR: Diffuse reflectance UV/Vis/NIR spectra were recorded using a Perkin – Elmer (Lambda 19) spectrometer equipped with an integrating sphere with $BaSO_4$ as reference. The samples, in the form of powders, were placed in quartz cells permanently connected to a vacuum line (ultimate pressure $\leq 10^{-5}$ Torr) for thermal treatments under in situ conditions. FTIR spectra on pellets of the samples mixed with KBr were recorded in air with a Bruker IFS88 spectrometer at a resolution of 4 cm^{-1}.

TGA analyses: TGA analyses were carried out on a TA instrument (SDT2960 model) by keeping sample (10 – 15 mg) under a constant flux of air and using a temperature ramp of 2 $^{\circ}C\,min^{-1}$.

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