One-pot incorporation of titanium catalytic sites into mesoporous true liquid crystal templated (TLCT) silica

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A one-pot synthesis procedure is described for the production of catalytically active titanium-incorporated mesoporous silica; the nature and accessibility of Ti(IV) sites derived from two different Ti sources was elucidated by means of catalytic tests, UV–VIS and photoluminescence spectroscopy.

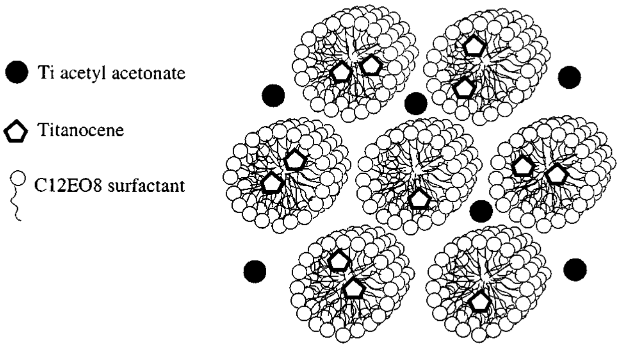
Titanosilicates are of great interest for various catalytic applications.[1] TS-1, a microporous titanium silicate containing catalytically active tetrahedral Ti(IV) sites, was first synthesised by Taramasso *et al.*[2] and was found to catalyse a wide range of low-temperature oxidations with hydrogen peroxide. In 1994, Corma *et al.*[3] and Pannavaia and coworkers[4] published their work on introducing titanium into the silica framework of MCM-41, and since then a considerable number of papers have been written dealing with various aspects of Ti-incorporated MCM-41, reviewed by Maschmeyer.[5] These materials can be prepared in principally two ways: (i) Grafting titanium species to the mesopore surfaces *via* a post-synthetic procedure[6] and (ii) substituting Ti into the silica framework by adding a titanium alkoxide precursor to the MCM-41 synthesis gel.[3,4]

Here, we describe a novel 'one-pot' method for the synthesis of titanium-incorporated mesoporous silica *via* a true liquid crystal templating (TLCT) process.[7] The advantage of this method over those previously described for Ti-MCM–41 is that no post-synthetic, and potentially damaging, treatment of the mesoporous silicates is required, and the disordered side products often associated with classical MCM-41 formation are avoided. Two types of titanium precursor were used for comparison: titanium cyclopentadienyl dichloride (Aldrich) and Tilcom TAA (Tioxide Specialities Ltd). Tilcom TAA consists of a 75 wt% solution of diisopropoxy bis(pentane-2,4-dionato)titanium(IV), or titanium acetylacetonate, in isopropanol. The titanium content of Tilcom TAA is 9.9 wt%. The precursors were dissolved directly in the synthesis gel consisting of a 1 : 1 : 2.1 weight ratio of octaethylene glycol monododecyl ether ($C_{12}EO_8$, Fluka), 10^{-2} M HCl and tetramethoxysilane (TMOS, Aldrich), respectively. For 1.5 g of surfactant template, 0.06 g of titanocene dichloride or 150 μl of Tilcom TAA were added.

The hexagonal mesoporous product formed overnight, under constant vacuum (to remove the methanol TMOS hydrolysis by-product), at room temperature. The deep orange colour of the titanocene-doped as-synthesised material suggested that the titanocene complex remained unhydrolysed throughout the synthesis (hydrolysis products would have been light orange/yellow). It is also supposed that owing to the hydrophobic nature of the cyclopentadienyl ligands, the transition metal was located primarily in the central hydrocarbon regions of the polyoxyethylene (POE) cylindrical micelles (Scheme 1), *i.e.* on the internal surfaces of the mesopores once the materials were calcined. The POE micelles therefore protected the complex from the aqueous regions of the synthesis mixture, pointing to a potentially general method for mesopore functionalisation.

We propose that due to the high solubility of Tilcom TAA in the aqueous regions of the liquid crystalline synthesis gel, a large proportion of the titanium sites in the final calcined products were buried in the silica framework (Scheme 1). Calcination of the materials at 500 °C produced silicate structures consisting of hexagonal arrays of long channels of *ca.* 25 Å diameter (as determined by TEM and N_2 adsorption measurements with BJH calculation). The hexagonal symmetry of the materials was confirmed by polarising microscopy (characteristic optical texture under crossed polarisers) and small-angle X-ray diffraction. After calcination at 500 °C, the hexagonal structure remained intact (seen by X-ray diffraction), but the location of the titanium species remained to be determined. The Ti contents in the calcined materials were calculated from the initial gel compositions, assuming complete hydrolysis and condensation to SiO_2, and complete removal of the organic template by calcination. Assuming all of the titanium species remained implanted in the mesoporous structures after calcination, the titanium metal loading for the products were 0.92 wt% for the titanocene-doped material (Ti[CP]) and 1.18 wt% for the Tilcom TAA-doped product (Ti[ACAC]). The amount of titanocene dichloride lost during the calcination process by evaporation/sublimation is not actually known; this would of course affect the Ti content in the calcined material.

Catalytic tests (data not shown) on Ti[CP] showed that it was both active in the epoxidation of octene using *tert*-butylhydroperoxide (TBHP) as the source of oxygen,[8] and in the peroxidative bromination of phenol red (phenolsulfonephthalein) to tetrabromophenol blue (3′,3″,5′,5″-tetrabromophenolsufonephthalein).[9] No catalytic tests were done on Ti[ACAC], only on the calcined Ti[CP], as this appeared to be the most promising material from the spectroscopic studies. The epoxidation reaction was carried out at 80 °C under an inert argon atmosphere, and the reaction mixture consisted of 0.15 mol oct-1-ene, 0.0075 mol mesitylene, 0.0075 mol TBHP and 0.265 g Ti[CP] catalyst. Samples were taken from the reaction mixture at regular intervals and the reaction products were quantified by GC analysis. Octene was in large excess and acted as the solvent as well as reactant, mesitylene was the standard



Scheme 1 Representation of the assumed locations of the titanium precursors, Ti acetyl acetonate and titanocene dichloride within the hexagonal liquid crystal phase.

for GC analysis. The reaction rate calculated after the first hour of reaction was 84 mol epoxide per mole Ti per hour; this value was comparable (within 30%) with the reaction rates obtained for grafted Ti–MCM-41 materials[6] in a previous study. Our catalytic test results show that the material is active in the epoxidation of octene, with high selectivity for the epoxide (no other octene oxidation products were observed). The activity of the catalyst suggests that isolated tetrahedral Ti(IV) species were present.[1,5]

The peroxidative bromination test gave a qualitative indication of the catalytic activity of the catalyst, and the formation of bromophenol blue from phenol red was monitored by UV–VIS spectroscopy.† Our Ti[CP] catalyst again had slightly lower but comparable catalytic activity to the TiMCM materials described in the literature.[9]

The diffuse reflectance UV–VIS spectrum for calcined Ti[CP] had an intense maximum absorbance centred at 220 nm (Fig. 1). The electronic transition responsible for this absorption band in the UV diffuse reflectance spectrum is a ligand to metal charge transfer (LMCT) transition from oxygen to tetrahedral Ti(IV).[10–16] There were additionally two further much less intense absorption peaks at 330 and 460 nm, which may have been due to degradation products of the cyclopentadienyl ligands of the titanocene precursor.[17] Calcined Ti[ACAC] produced a somewhat different UV–VIS absorption spectrum from Ti[CP]. The maximum absorption peak had a similar intensity to that for Ti[CP], but was displaced to 240 nm and was somewhat broadened with respect to the Ti[CP] absorption band. The displacement of the main adsorption peak to longer wavelength for the framework-substituted Ti[ACAC] product was likely to be due to a somewhat different chemical environment for the tetrahedrally coordinated Ti atoms in the structure. The fact that the band was broadened with respect to the Ti[CP] material suggested that there was a greater number of chemically differing Ti sites within the Ti[ACAC] structure, absorbing at different wavelengths.

In the case of isolated tetrahedral Ti(IV) sites, photoluminescence is due to the reverse LMCT process to that responsible for the UV diffuse reflectance absorption.[10,11,18] The photoemission spectra for materials containing tetrahedral coordination Ti(IV) sites contain features in the range 400–600 nm. Photoluminescence spectra obtained for the Ti[CP] and Ti[ACAC] samples at 77 K were characterised by two main emission maxima at 440 and 490 nm. Both these emission bands had a maximum excitation at 250 nm. In agreement with the diffuse reflectance spectra, the excitation band for the Ti-[ACAC] material was broader than for Ti[CP].

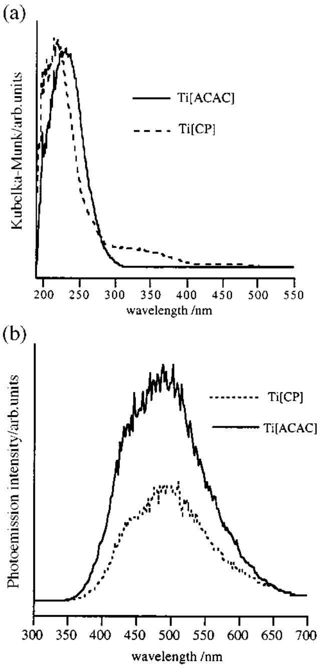


Fig. 1 (a) UV–VIS diffuse reflectance spectra recorded using a Perkin Elmer spectrometer equipped with an integrating sphere attachment. The absorbance output from the instrument was converted using the Kubelka-Munk algorithm. (b) Photoluminescence spectra recorded at 77 K (λ_{ex} = 250 nm) using a SPEX FLUOROLOG-2 1680 spectrometer. For all UV–VIS spectroscopy measurements samples were ground to fine powders and inserted into quartz cells purpose-made for *in situ* thermal treatments. Samples were pre-oxidised and spectroscopy measurements were conducted under strict exclusion of air.

The major difference between the photoemission spectra for Ti[CP] and Ti[ACAC], both reoxidised and degased in the same way, was that the Ti[ACAC] emission bands were 2–3 times more intense than the Ti[CP] bands. Adsorption of oxygen onto the Ti-doped samples only partially quenched the photoemission signals, though somewhat more for the Ti[CP] sample than for the Ti[ACAC] sample. This suggested that more of the Ti(IV) sites in the Ti[ACAC] sample were inaccessible (*e.g.* situated within the silica framework) to the oxygen than in Ti[CP].[17] These results agree substantially with what could be predicted from the partitioning behaviour of the titanium precursor in the original synthesis gels.

Our results have shown that a one-pot TLCT synthesis procedure can be used to introduce catalytically active sites into mesoporous silica. The accessibility of the Ti(IV) sites to external gaseous probe molecules (oxygen in the case of our photoluminescence studies) has been found to depend on the hydrophobic or hydrophilic nature of the titanium precursor used in the synthesis gel. We propose that this method for producing metal-incorporated mesoporous materials may be generalised to many other species of catalytic interest.

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Notes and references

† The reaction solution consisted of 0.1 mM phenol red, 0.05 M KBr, 5 mM H_2O_2 and 0.05 M Hepes buffer (pH ≈ 6.5); 0.16 g of finely ground Ti[CP] catalyst was added to this. The samples were continuously shaken throughout the tests using an electrical flask shaker (moderate speed), and at regular intervals decanted samples were taken for spectroscopic analysis.

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