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Synthesis and catalytic activity of a chiral periodic mesoporous organosilica (ChiMO)

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A chiral vanadyl salen complex having two peripheral trimethoxysilyl groups has been used to obtain a chiral periodic mesoporous organosilica having MCM-41 periodicity and the two Si–CH$_2$ groups anchored on the framework; this solid induces 30 % enantioselectivity in the cyanosilylation of benzaldehyde.

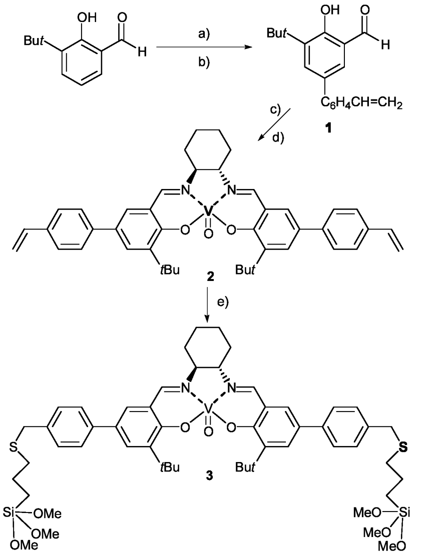
The synthesis of ordered mesoporous silicas[1] has opened a new field for the preparation of materials.[2] This has been recently expanded by the introduction of hybrid organic–inorganic materials comprising two siloxane units bridged by an organic component and containing ordered mesopores.[3–6] These solids are coined as periodic mesoporous organosilicas (PMOs).

Polysilsesquioxanes with ordered pore structure and controlled porosity can be obtained by using surfactants as structure directing agents. This procedure allows to introduce a large variety of functional groups within the walls generating functional frameworks. PMOs could complement and add extra functionality to the one achieved previously by grafting organic functions on the walls of the structured inorganic mesoporous materials by a post-synthesis treatment.

However it is known that it is not possible to achieve PMO materials with any desired functionality if they are synthesized only from bridged organosilica precursors. This is the case when very large organic groups are involved in the organosilica precursor since then it becomes difficult to achieve the proper assemblage with the surfactant. On the other hand the possibilities for preparing hybrid organic inorganic materials will increase if a surfactant assembled condensation of silica and the organic silane precursor is carried out. We will illustrate this here by carrying out the synthesis of, as far as we know, the first chiral mesostructured organosilica (ChiMO) in where the chiral organic component is a vanadyl salen complex.

The preparation of ChiMO required the synthesis of a chiral vanadyl salen complex having two terminal trimethoxysilyl groups attached to the ligand. This disilylated precursor **3** was obtained from a symmetric distyryl derivative of a chiral vanadyl salen complex **2** that was submitted to a C=C double bond addition reaction of 3-mercaptopropyltrimethoxysilane initiated by azoisobutyronitrile (AIBN) (Scheme 1). The distyryl vanadyl salen complex **2** that is the key intermediate in our synthetic scheme is analogous to the manganese complex previously reported in the literature.[7] This intermediate **2** and the disilylated precursor **3** were fully characterized by analytical and spectroscopic means with all the data being compatible with the proposed structure.

The precursor **3** was soluble in organic solvents such as halogenated hydrocarbons, acetone, acetonitrile and ethanol. The synthesis of the corresponding VOsalen@ChiMO was accomplished following the general procedure previously reported[8–9] introducing ethanol as co-solvent to increase the solubility of the precursor in aqueous solution. † The presence of O, N and V atoms achieves a suitable balance between hydrophilicity and hydrophobicity to permit the synthesis of a PMO material in spite of the large molecular size of the complexes. In the precedents reported on the literature so far much simpler organic components have been used.



Scheme 1 a) Br$_2$, CH$_2$Cl$_2$, 0 °C, 1 h; b) 4-vinylphenylboronic acid, [Pd(PPh$_3$)$_4$], 2 M Na$_2$CO$_3$, THF, 70 °C, 3 h; c) (1*R*,2*R*)-diaminocyclohexane, EtOH, reflux, 1 h; d) VOacac, MeOH, r.t., overnight; e) 3-mercaptopropyltrimethoxysilane, AIBN, CHCl$_3$ (degassed), 70 °C, 20 h;

The resulting PMO solid was characterized by powder X-ray diffraction where the typical pattern of hexagonal MCM-41-like ordering was observed. Figure 1 shows the powder X-ray diffraction corresponding to as-synthesized VOsalen@ChiMO. The synthesized ChiMO contains the channels completely filled with cetyltrimethylammonium bromide (CTABr) used as structure directing agent for the synthesis of the solids. This was removed by exhaustive solid liquid extraction at 40 °C of the as-

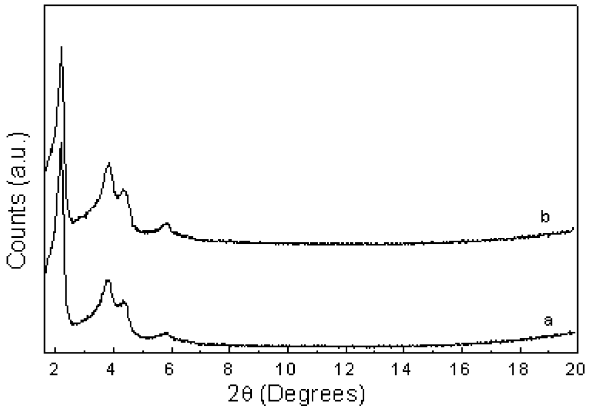


Fig. 1 X-ray diffraction of VOsalen@ChiMO before (a) and after extracting the CTAB (b).

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synthesized PMO using acidified ethanol solution as solvent. After extraction, powder X-ray diffraction showed that the periodic structure of the ChiMO was preserved (see Figure 1). The presence of the salen complex in the ChiMO has been proved by diffuse-reflectance UV–Visible spectra.

From the Ar adsorption isotherm and following the Hovarth–Kavazoe equation it is found that the pore diameter of the mesoporous ChiMO after template removal is 4.5 nm with a BET surface area of 900 m^2 g^{-1} (Figure 2).

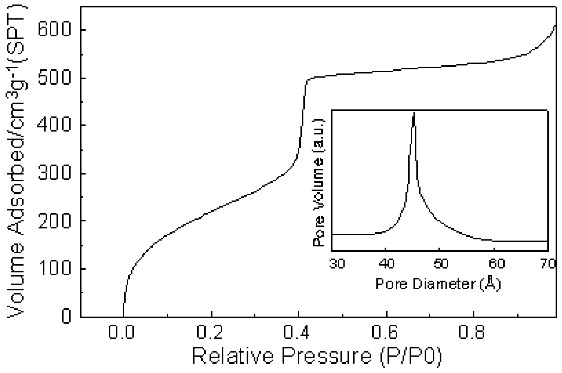

Fig. 2 Isothermal gas adsorption of VOsalen@ChiMO. The insert shows the Hovarth–Kavazoe plot of the data.

The covalent linkage of the salen complex to the silicate framework is demonstrated from the ^{29}Si MAS NMR spectra presented in Figure 3. As can be seen there, the spectrum contains three bands appearing at ~ −110, ~ −100 and ~ −90 ppm that can be associated to Si(4Si), Si(3Si1OH), and Si(2Si2OH) or Si(3Si1C). Cross polarization of ^{1}H to ^{29}Si strongly enhances the signal at ~ −100ppm corresponding to Si(3Si1OH), but affects proportionally much less the ^{29}Si MAS NMR signal appearing at ~ −90 ppm, indicating that this peak also corresponds to groups Si(3Si1C), that will result from the inclusion of the salen in the silica wall of the mesoporous material.

The intensity of the NMR signal was strongly expanded in order to see if partially condensed species of the type Si(2Si,1OH,1C) and Si(1Si,2OH,1C) appearing at ~ −40 and ~ −60 ppm respectively were also formed. From this study it can be concluded that a very small number of Si(2Si,1OH,1C) may exist. Therefore it can be concluded that the majority of the precursor is covalently grafted through both Si atoms to the inorganic framework.

From the chemical vanadium analysis of the final material, it is estimated that 2.5% of the Si present should correspond to the silane groups of the salen complex. This value corresponds quite well with the 2.4% calculated from ^{29}Si NMR by assuming that the signal at ~ −90 ppm corresponds to the silane groups.

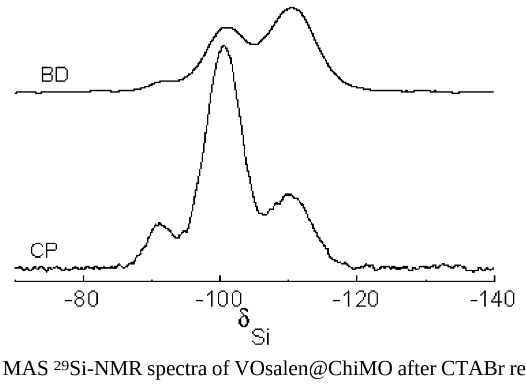

Fig. 3 MAS ^{29}Si-NMR spectra of VOsalen@ChiMO after CTABr removal. BD: block decay; CP: ^{1}H to ^{29}Si cross polarization.

If we accept at this point that a ChiMO has been obtained that includes the salen complex in its structure, the material should be chiral. To check this, we have determined directly the optical activity of the solid by measuring the deviation angle of plane polarised light using a conventional polarimeter of a suspension of as-synthesized and extracted VOsalen@ChiMO. Direct measurement of optical activity is possible since the suspension of the VOsalen@ChiMO in 1,2-dichloroethane is sufficiently transparent and lasts sufficiently long before settling down to allow this measurement. The value of specific optical activity measured was −2.54 ° g^{-1} for the extracted VOsalen@ChiMO. Control experiments with achiral MCM-41 do not give measurable optical activity. The above observation constitutes a direct evidence of the chirality of VOsalen@ChiMO.

The resultant material (0.25 mmol% (0.25 mmol% with respect to benzaldehyde)) shows a high TON (320) for the room temperature cyanosilylation with TMSCN (3 eq.) of benzaldehyde with an enantiomeric excess (ee) of 30%. The material as catalyst is extremely stable and no leaching was observed. In contrast, a MCM-41 in which *tert*-butyl VOsalen was adsorbed leached a significant amount of the complex to the solution. On the other hand, the activity of VOsalen@ChiMO compares well to a MCM-41 in which a VOsalen complex having a 10-undecenyloxy substituent was covalently grafted to the walls (V content 0.04 mmol × g^{-1}) through a 3-mercaptopropyl group giving a TON after 72 h reaction time of 287 and an ee value of 63%. We are now studying what causes the lower than expected ee observed for VOsalen@ChiMO.

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Notes and references

† Compound **3** was used in combination with TEOS in the synthesis of VOsalen@ChiMO and cetyltrimethylammonium bromide (CTABr) as the structure-directing agent. The molar proportions of the components in the precursor gel were: 1.0 Si :0.12 CTABr :8.0 NH_3 (20 %) :114 H_2O :10 EtOH. TEOS and compound **3** were used as the source of Si in various proportions from 85:15 and 95:5. After mixing the reactants, the resulting clear gel was transferred to a polyethylene container and heated at 90 °C for 4 days. The solid obtained was washed with water and dried in air at 60 °C. The structure-directing agent was removed by extracting the solid with dilute ethanolic HCl acid solution at 40 °C for 2 h (20 ml of 0.5 M ethanolic HCl for 0.5 g of solid). The vanadium content after extraction was 0.014 mmol g^{-1} and the specific optical rotation was measured using a conventional JASCO polarimeter and the yellow Na line in a 1 dm cell.

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