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Periodic mesoporous organosilica incorporating a catalytically active vanadyl Schiff base complex in the framework

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Abstract

A vanadyl Schiff base complex having two terminal trimethoxysilyl groups peripheral to the ligand has been used to obtain a MCM-41-like mesoporous organosilicate that has been found to catalyze efficiently the cyanosilylation of carbonyl groups. Evidence for the successful preparation of the periodic mesoporous organosilica is based on powder XRD (high periodicity), isothermal Ar adsorption (900 m^2/g), monomodal pore-size distribution (42 Å), diffuse reflectance UV–visible spectroscopy (characteristic absorption band of vanadyl salen complex), and ^{29}Si NMR (presence of T^3 silicon atoms, $CH_2–Si(OSi\equiv)_3$). In addition, we have been able to prepare a chiral vanadyl salen complex that is able to catalyze the carbonyl addition with 30% ee.

Keywords: Asymmetric catalysis; Heterogeneous catalysis; Periodic mesoporous organosilica; Vanadyl salen complexes; Cyanohydrins; Chiral MCM-41

1. Introduction

A general strategy for converting a homogeneous process into a heterogeneous one is to support the soluble catalyst onto large surface area inorganic carriers [1–5]. This methodology when applied to liquid-phase reactions may suffer, however, from the common problem of leaching of the active sites from the solid surface into the solution. In order to avoid or minimize the leaching, a refinement of the strategy based on solid supports consists in the covalent anchoring of the active sites on the inorganic oxides [6,7]. In this regard, MCM-41 and related mesoporous silicas have been widely used as supports [8] since they combine a very large surface area, typically above 800 m^2/g, with a large pore size that ensures easy accessibility of the active sites to substrates and reactants as well as permitting the inclusion of bulky catalysts in the internal voids. In related precedents to this work, transition metal complexes, in particular those derived from Schiff bases have been covalently attached to the surface of MCM-41. Two different possibilities have been developed in which the complex has been anchored either through the metal [9–12] or through the ligand [13–16]. In both cases the transition metal complex catalyst is hanging in the channels and the linker permits a wide distribution of conformations in which variable distances separate the complex and the silica walls.

More recently, a new family of periodic mesoporous organosilicas (PMOs) in which the organic compound is forming part of the silica framework rather than occupying the channel space has been reported [17–25]. The crucial issue for the preparation of PMOs is the synthesis of a convenient organic precursor that must contain two terminal alkoxy silane groups.

Among various applications of PMOs, one possibility would be the preparation of solid catalysts and specifically a metal Schiff base complex embedded into the PMO framework. Herein we have realized this opportunity by preparing a PMO containing a vanadyl Schiff base complex and demonstrating its catalytical activity toward the cyanosilylation of aldehydes, including some degree of enantioselectivity for the asymmetric version of this addition to C=O. After the experimental work was complete, we became aware of a recent publication in which an amorphous organosilica containing achiral pentadentade Co(II) salen was reported [22].

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2. Experimental

Diffuse reflectance UV–vis spectra of opaque powders were recorded in a Varian cary 5G UV–vis–NIR spectrophotometer adapted with a praying mantis attachment and using $BaSO_4$ as reference. The reflectance data were converted to the Kubelka–Munk function $F(R)$ that correlates with the absorbance of the complex [26]. IR spectra of the intermediates and precursors were recorded on KBr disks at room temperature on a Nicolet 710 FT spectrophotometer. Elemental combustion analyses were carried out using a Fisons EA 1108-CHNS-O analyzer. Vanadium analyses of the solids were carried out by quantitative atomic absorption spectroscopy after dissolving a given amount of the solid with concentrated hydrofluoric acid (40%) and nitric acid. The resulting liquor was diluted with water and a small quantity of acetonitrile was added before measurement to ensure the complete solubility of vanadium complexes. Powder diffraction data were collected on a Philips X'Pert diffractometer with Bragg–Brentano geometry provided with a secondary graphite monochromator. MS spectra were obtained using a VG-AutoSpec. Capillary gas chromatography was carried out in a HP5890 using a TRB-5 (30 m × 0.25 mm) column and operating with an injector temperature of 280 °C and a detector temperature of 300 °C (FID) or for chiral GC chromatography in a Fisons 8035 using a Chiraldex γ-TA (30 m × 0.25 mm) column and operating with an injector temperature of 230 °C and a detector temperature of 230 °C (FID). Ar and N_2 adsorption were carried out in a Micromeritics ASAP 2000 recorded at 87 and 77 K, respectively. ^1H and ^{13}C NMR spectra were recorded in a Brucker AV-300 using $CDCl_3$ as solvent and TMS as internal standard. ^{29}Si MAS NMR spectra were recorded on a Bruker 400 spectrometer with samples packed in zirconia rotors spinning at 5.5 kHz. Optical rotation data were obtained in a Jasco P-1030 polarimeter using the Na yellow line at 589 nm. Suspensions of 7.3 and 5.5 mg of VO(salen)$\propto$ChiMO before and after extraction, respectively, in 10 ml of 1,2-dichloroethane were placed in a 1 dm cell.

2.1. Compounds and materials

The solvents used in the reactions were of analytical quality or dried by standard methods. All chemicals were used as commercially available. Flash column chromatography was performed using SiO_2 60 (0.040–0.063 mm, Scharlau). Compounds **1** [27] and **2** [27], ligands **3** [28], and complexes **4** [29] were prepared according to the procedures reported in the literature.

2.2. Synthesis of compound **5a**

To a solution of **4a** (0.362 g, 0.64 mmol) in degassed $CHCl_3$ (10 ml) under N_2, AIBN (0.1 g) and 3-mercaptopropyltrimethoxysilane (1.57 g, 8 mmol) were added. The solution was heated under reflux for 20 h. The solvent was removed and pentane was added (10 ml). A green solid starts to precipitate affording **5a** (0.374 mg, 61%). IR (KBr): ν (cm^{-1}) = 3019, 2938, 2836, 1621, 1548, 1515, 1440, 1398, 1309, 1270, 1191, 1081, 981, 904, 817, 763, 595, 543, 520, 476 cm^{-1}; MS (FAB): 958; elemental analysis calcd (%) for $C_{46}H_{62}O_9N_2Si_2S_2V$ (958.32): C 57.65, H 6.53, N 2.92, S 5.86; found: C 57.56, H 6.70, N 3.03, S 6.10.

2.3. Synthesis of compound **5b**

Compound **5b** was prepared as described above for compound **5a**, substituting **4a** for **4b**, affording **5b** (0.44 mg, 63%) as a green solid. IR (KBr): ν (cm^{-1}) = 2938, 2838, 1615, 1541, 1426, 1399, 1347, 1313, 1258, 1173, 1084, 986, 816, 788, 570 cm^{-1}; MS (FAB): 1092; elemental analysis calcd (%) for $C_{56}H_{80}O_9N_2Si_2S_2V$ (1096,6): C 57.65, H 6.53, N 2.92, S 5.86; found: C 61.09, H 7.47, N 2.55, S 5.88.

2.4. Synthesis of the VOsalen$\propto$PMO: general procedure

Compounds **5a** and **5b** were used in combination with tetraethoxyorthosilicate (TEOS) in the synthesis of VOsalen $\propto$ PMO 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 compounds **5a** and **5b** were used as source of Si. Several TEOS:**5** molar ratios were tested, and highly structured materials can be obtained below 95:5. After mixing the reactants the resulting 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 ethanolic HCl for 0.5 g of solid).

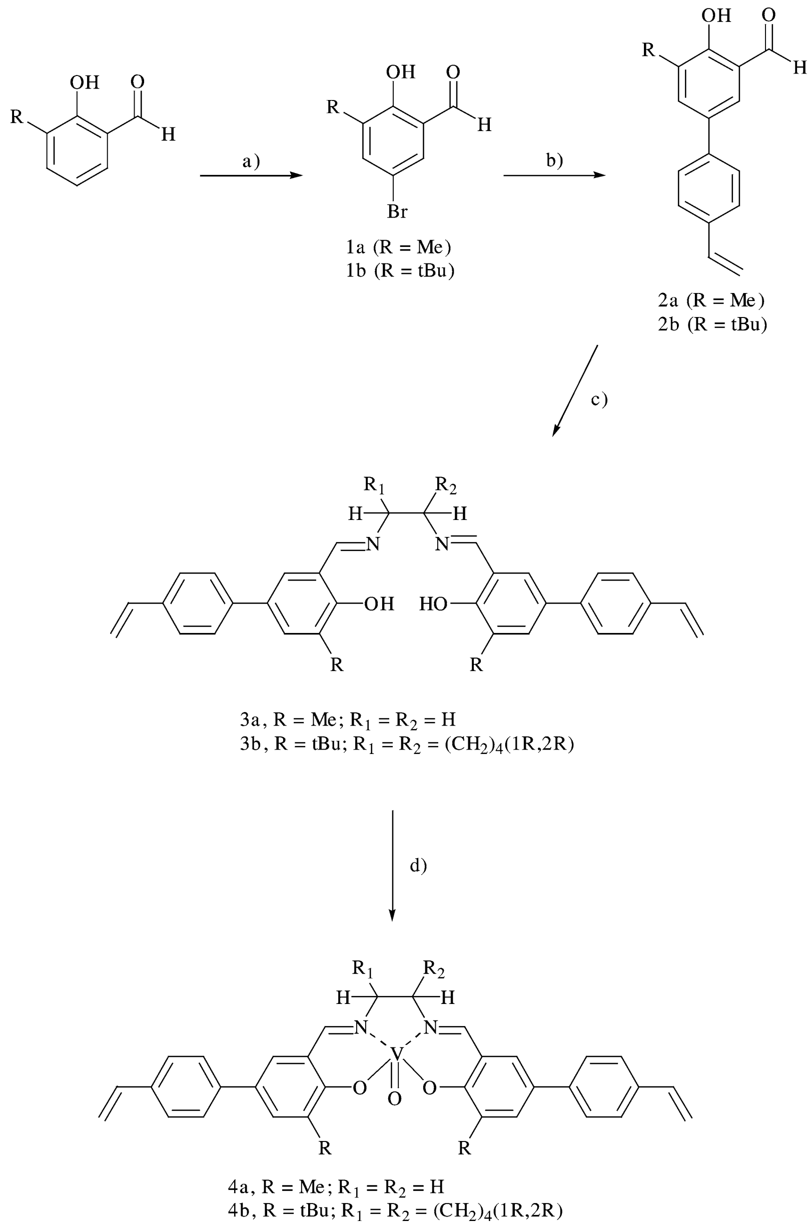
2.5. Cyanosilylation reaction of aldehydes with TMSCN

TMSCN (2.46 mmol, 0.328 ml) was added to a solution of aldehyde (0.82 mmol), nitrobenzene (0.82 mmol), and **VOsalen$\propto$PMO** (0.25 mol%) in dry $CHCl_3$ (1 ml). The solution was stirred under N_2 atmosphere at room temperature or 0 °C. The course of the reaction was followed with capillary gas chromatography. For the consecutive use of the catalyst, the reaction crude is filtered and the solid washed with fresh solvent, dried, and used in a next run. The leaching was determined by performing the reactions at the corresponding temperature under the reaction conditions described above until the conversion was about 30%. At this conversion, half the volume was filtered and the resulting clear solution allowed to react. The percentage of leaching was estimated by comparing the time-conversion plot of the two twin reactions with and without solid.

3. Results and discussion

In order to characterize the identity and purity of the vanadyl Schiff base complex as much as possible, we have developed a methodology in which the precursor of the PMO synthesis already consists in the catalytically active complex. This enables a complete characterization of the complex by conventional spectroscopic techniques in solution just before the last synthetic step. The sequence for the preparation of the vanadyl salen precursor is depicted in Scheme 1.

The synthetic route to graft the complex is based on the radical coupling between 3-mercaptopropyl trimethoxysilane and the *p*-styryl derivative of two different vanadyl salen complexes whose structures contain biphenyl units. The ligands in turn were prepared performing the Suzuki coupling between *p*-vinylphenylboronic acid and 4-bromosalicylaldehyde derivatives (step b in Scheme 1) [27], followed by the diimine formation using ethylenediamine or (1*R*, 2*R*)-(−)-1,2-diaminocyclohexane (step c in Scheme 1) [28]. The spectroscopic properties of the diiminecyclohexane-derived ligand **3b** coincide with those previously reported [27] and for ligand **3a** the data are compatible with the proposed structure (see Experimental). One alternative approach in which vanadyl complexation was the last step after the introduction of the trimethoxysilane groups on the ligand led to extensive hydrolysis and the formation of untreatable mixtures. Therefore, complexation of the



Scheme 1. Preparation of VOsalen intermediates. Conditions: (a) Br_2, CH_2Cl_2, 0 °C, 1 h; (b) 4-vinylphenylboronic acid, $[Pd(PPh_3)_4]$, 2 M Na_2CO_3, THF, 70 °C, 3 h; (c) diamine, EtOH, Δ, 1 h; (d) VOacac, MeOH, Rt, overnight.

vanadyl and salen ligand before attaching the trimethoxysilane groups as indicated in Scheme 1 was the preferred option. The reaction intermediates were fully characterized by chemical analysis, FAB-MS, IR, and NMR spectra. The disilylated vanadyl complexes **5** were also characterized analytical and spectroscopically. Although the ^{1}H NMR spectra of precursor **5** shows broad peaks probably due to some degree of oligomerization through the trimethoxysilane groups and/or to the presence of paramagnetic transition metal nuclei, the resolution was sufficient to confirm its structure.

Precursors **5a** and **5b** were soluble in organic solvents such as halogenated compounds, acetone, acetonitrile, and ethanol. The synthesis of the corresponding VOsalen∝PMO was accomplished following the general procedure previously reported [20,21] for PMOs (Scheme 2) introducing minor amounts of ethanol as cosolvent to increase the solubility of precursors **5a** and **b** in the aqueous phase until a clear solution is obtained. TEOS was used as Si source in addition to compounds **5a** and **b** and the TEOS/**5** molar ratio in the mother gel was 98:2 and 99:1 for VO(salen)∝PMO and VO(salen)∝ChiMO, respectively. The presence of O, N, and V heteroatoms seems to achieve a suitable balance between hydrophilicity and hydrophobility to permit the synthesis of a PMO material despite the large molecular size of the complexes as compared to much simpler precedents reported in the literature so far.

The resulting PMO solids were characterized by powder X-ray diffraction where the characteristic peaks indicating the hexagonal MCM-41-like ordering were observed. Figs. 1 and 2 shows the powder X-ray diffraction corresponding to as-synthesized VO(salen)∝PMO and VO(salen)∝ChiMO (ChiMO = Chiral PMO), respectively. The as-synthesized PMOs contain the channels completely filled with cetyltrimethylammonium bromide used as a structure-directing agent for the synthesis of the solids. For the salen complexes incorporated on the PMOs to be useful as catalysts, it is necessary to remove CTABr completely without damaging the complex or collapsing the pores of the PMOs. This was accomplished by exhaustive room temperature solid-liquid extraction of the as-synthesized PMOs using acidified ethanol as solvent. After extraction, powder X-ray diffraction showed that the periodic structure of the PMO was preserved (see Figs. 1 and 2).

Isothermal Ar and N_2 adsorption of the extracted VO (salen)∝PMO indicates that the solid has a specific surface area of 900 m^2/g and a pore diameter of about 42 Å. Comparison of the distance between two neighboring channels obtained by XRD with the pore-size data by isothermal gas adsorption gives the wall thickness value of 6 Å which is normal for MCM-41 silicates. A pictorial representation of the vanadyl complexes covalently grafted to the channels is shown in Scheme 2.

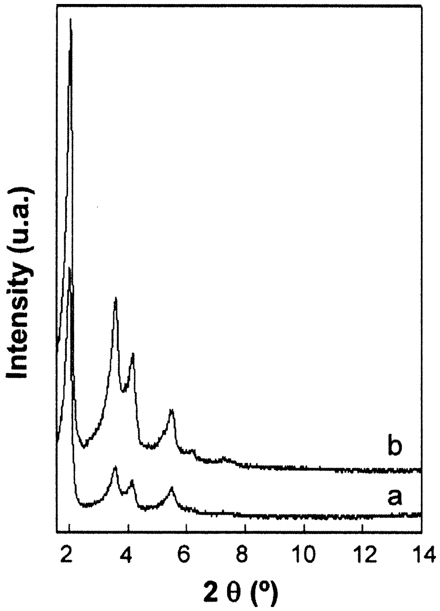


Fig. 1. X-ray diffraction of VO(salen)∝PMO before extraction of the template (a) and after extraction the template (b).

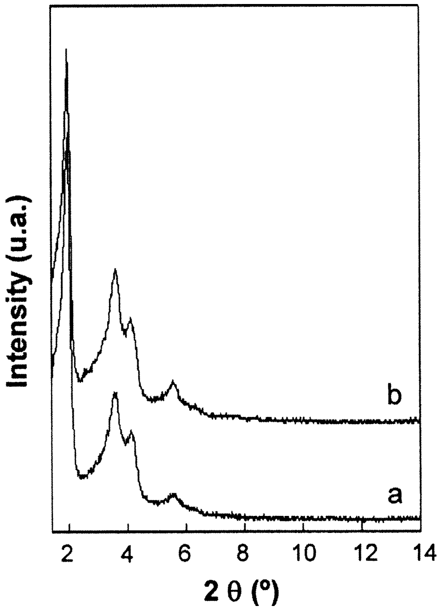
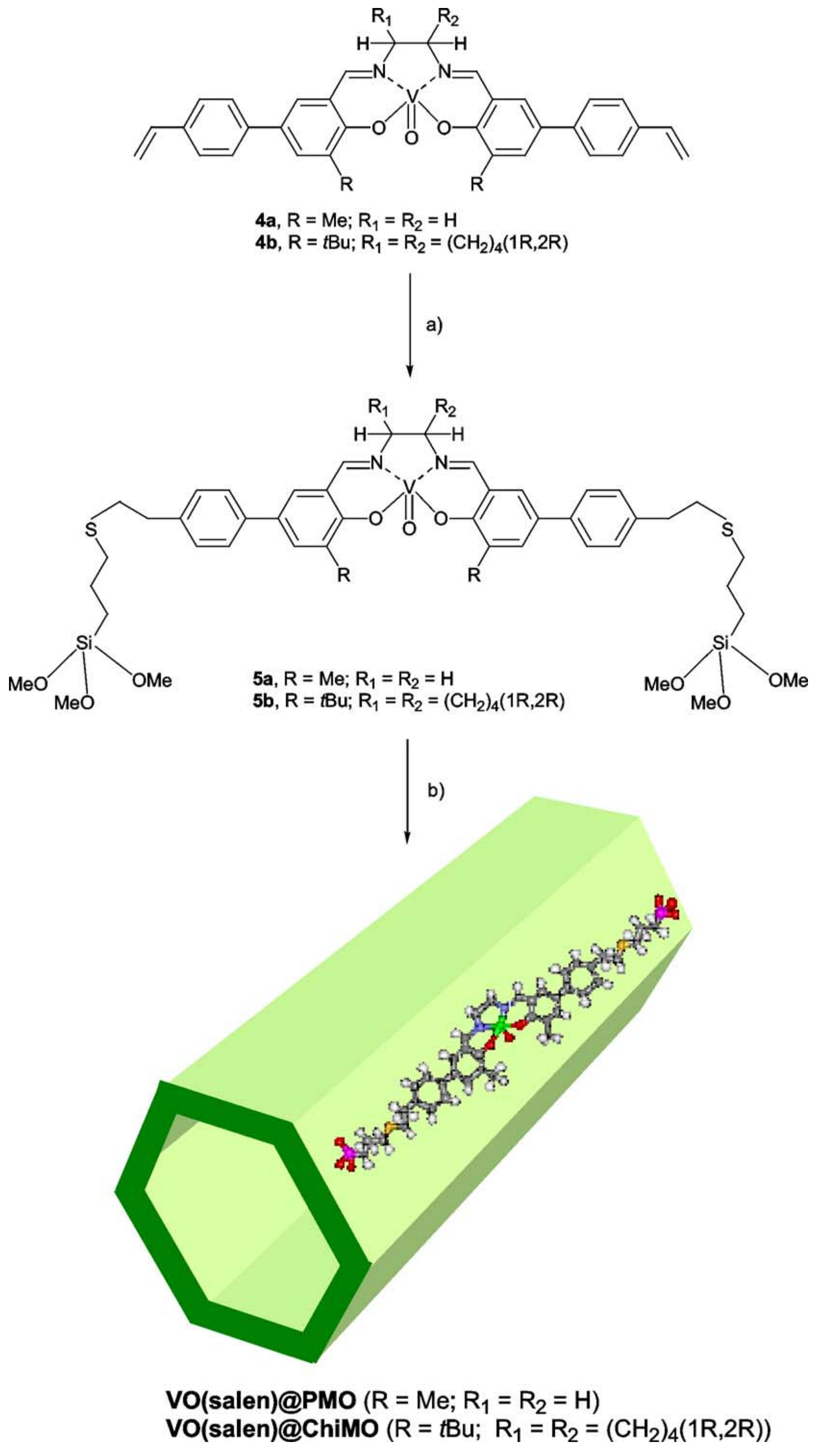


Fig. 2. X-ray diffraction of VO(salen)∝ChiMO before extraction of the template (a) and after extraction the template (b).

The vanadium content of the solids was analyzed by treating the PMOs with a hydrofluoric/nitric acid mixture and determining the vanadium in the resulting liquor. The vanadium content is indicated in Table 1. From these data it can be concluded that although the specific vanadium content before and after extraction is similar, the extraction to remove the template has reduced considerably the amount of vanadium. In fact, as in the as-synthesized PMOs the CTABr template contributes approximately 40% to the total weight of the solid. Removal of the template causing a reduction in the weight of a given amount of solid should produce an "apparent" increase in the vanadium content per gram. However, Table 1 shows that instead of an increase, the specific vanadium content is similar before and after extraction. This indicates that a part of the vanadium has been lost during the



Scheme 2. Preparation of VO(salen)∝PMO and VO(salen)∝ChiMO. Conditions: (a) 3-mercaptopropyltrimethoxysilane, AIBN, $CHCl_3$ (degassed), 70 °C, 20 h; (b) TEOS, NH_3, CTAB, H_2O, EtOH, 90 °C, 4 days.

solid-liquid extraction process. Probably the part of the complex not covalently bound to the solid was removed during the extraction process. Also visually, the green color of the as-synthesized materials faded after extraction. The diffuse-reflectance UV–visible spectra of the two VOsalen∝PMOs can also serve to record spectroscopically this visual effect before and after extraction (Figs. 3 and 4). However, despite this decrease in the specific vanadium content, it is worth remarking that the extracted PMOs still contain catalytically significant amounts of vanadium metal as indicated by the chemical analysis as well as intact vanadyl salen complexes as confirmed by spectroscopy. Thus in the UV–vis spectroscopy these vanadyl salen complexes exhibit the most characteristic visible absorption band at about 380 nm that is

Table 1
Analytical and optical activity data of the vanadium-containing PMOs

Catalyst	V content (mmol/g)	Optical rotation (°/g)
VO(salen)∝PMO before extraction	0.017	–
VO(salen)∝PMO after extraction	0.015	–
VO(salen)∝ChiMO before extraction	0.016	−3.28
VO(salen)∝ChiMO after extraction	0.014	−2.54

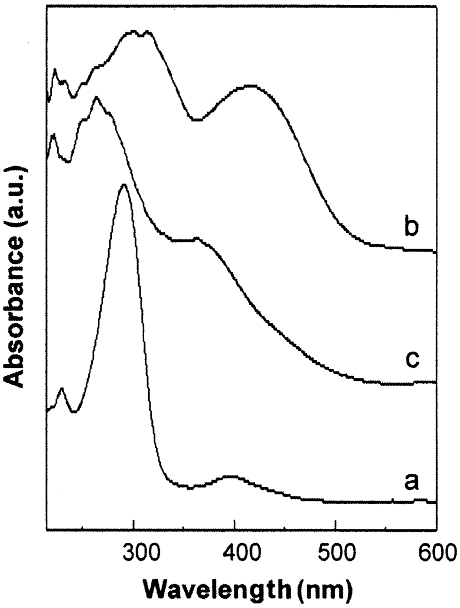


Fig. 3. UV–vis absorption spectra of compound **5a** (a) and diffuse reflectance of VO(salen)∝PMO before extraction of the template (b) and after extraction the template (c).

also present in the precursors **5ab**. Moreover, a remarkable hypsochromic shift of this absorption band is observed on the removal of the template, indicating that the complex is sensitive to the polarity changes of the pores as consequence of the CTA^+ removal.

In addition, IR spectrum of the extracted VO(salen)∝PMO shows the characteristic vibrations common for metal salen complexes at 1615 cm^{-1} (imine stretching vibration) and at 1535 cm^{-1} (metallosalen vibration). ^{29}Si MAS-NMR spectroscopy is also compatible with the covalent grafting of VO(salen) into the silica walls (Fig. 5). It is known that in solution the silicon peaks for T^0 [$–CH_2–\mathbf{Si}(OR)_3$], T^1 [$–CH_2–\mathbf{Si}(OR)_2(OSi\equiv)$], T^2 [$–CH_2–\mathbf{Si}(OR)(OSi\equiv)_2$], and T^3 [$–CH_2–\mathbf{Si}(OSi\equiv)_3$] appear around −40, −50, −70, and −90 ppm, respectively. The last T^3 type of Si would have a chemical shift close to the Q^2 and Q^3 signals of the silica framework. As the inset of Fig. 5 shows, an expansion of the ^{29}Si MAS-NMR does not reveal the presence of T^0, T^1, or T^2 silicon atoms despite the loading of VO(salen). Furthermore, the ^{29}Si NMR spectrum recorded by cross-polarizing ^{29}Si from ^1H (spectrum CP in Fig. 5) reveals an increase in the intensity of the Si peaks compared to Q^4 Si lacking H in its coordination sphere compatible with the presence of T^3 atoms. Thus, ^{29}Si MAS-NMR is the firmest evidence that the Si atoms of precursor **5** are covalently attached to the silicate framework.

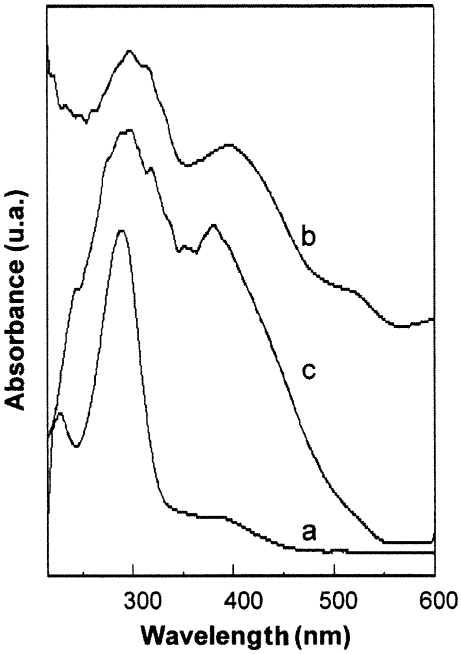


Fig. 4. UV–vis absorption spectra of compound **5b** (a) and diffuse reflectance of VO(salen)∝ChiMO before extraction of the template (b) and after extraction the template (c).

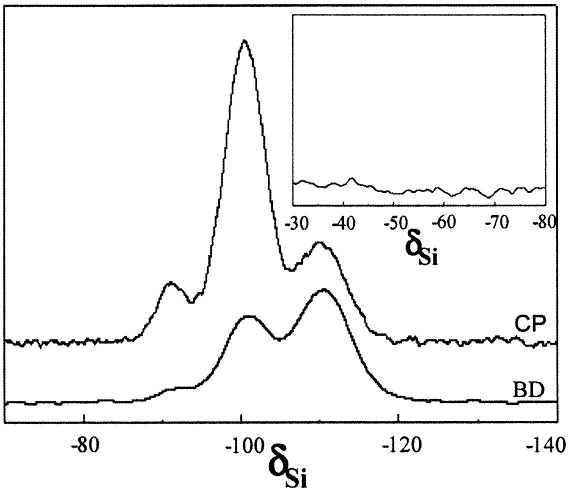
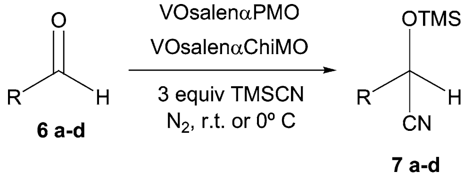


Fig. 5. MAS ^{29}Si NMR spectra of VOsalen∝ChiMO after CTABr removal. BD, block decay; CP, ^1H to ^{29}Si cross-polarization. The inset shows an expansion of the higher field part of the BD spectrum.

The catalytic activity of VO(salen)∝PMO after extraction was tested for the room-temperature cyanosilylation of aldehydes in chloroform using trimethylsilyl cyanide as reagent (Scheme 3). This cyanosilylation has been previously reported to be promoted by vanadyl salen complexes in homogeneous solution [30,31]. In our case, using a series of aldehydes we have observed a high activity of VO(salen)∝PMO as heterogeneous catalyst for this reaction. The results are listed in Table 2 from which it can be seen that high conversion with essentially complete selectivity to the silylated



6	R
a	C_6H_5
b	p-F-C_6H_4
c	p-(CH_3O)-C_6H_4
d	n-C_5H_{11}

Scheme 3. Cyanosilylation of aldehydes mediated by VO(salen)∝PMO.

Table 2
Results of the cyanosilylation of aldehydes using VO(salen)∝PMO as heterogenous catalyst[a]

Aldehyde (**6**)	Run[b]	Conversion (%)
a	1	82
a	2	79
a	3	83
a	4	71
b	–	86
c	–	81
d	–	79

[a] Reactions were carried out at room temperature under N_2 atmosphere for 48 h: aldehyde (0.82 mmol), TMSCN (3 eq), **VO(salen)∝PMO** (0.25 mol%), nitrobenzene (0.82 mmol), and $CHCl_3$ (1 ml). No leaching detected. Selectivity toward **7** > 98%. Mass balance > 95%.

[b] With the same catalyst.

cyanohydrins was achieved using vanadium to substrates molar ratio as low as 2.5×10^{-3}. A control experiment in which a mesoporous MCM-41 silicate prepared as the VO(salen)∝PMO but lacking the precursor **5a** in the mother gel, upon removal of the template by extraction, gave under the same reaction conditions a conversion of benzaldehyde to the cyanohydrin about 8%.

When working on solid catalysts, the possibility that some catalytically active species is desorbed from the solid and leached out to the solution must be properly addressed. In fact, as noted before when commenting the CTABr template removal by solid-liquid extraction, we have already observed a significant decrease of the vanadium content of the solids. To establish the absence of vanadium bleeding that could be responsible for some degree of catalytic activity, we have performed the cyanosilylation of benzaldehyde under the normal reaction conditions indicated in Table 2, but we have stopped the reaction at 30% of conversion. At this time, the solid was filtered out and the solution was allowed to react for the normal reaction time. Analysis of the reaction mixture clearly demonstrated that the reaction completely stopped when the solid was filtered out and no further conversion was observed after the filtration. This clearly indicates that it is the presence of the solid that promotes the reaction and apparently not the vanadium species that could have migrated to the solution.

In agreement with the previous experiment about the leaching, the solid catalyst maintains the initial activity of the fresh catalyst upon consecutive reusing. As indicated in Table 2, the VO(salen)∝PMO after being used in one reaction was simply filtered, washed with fresh solvent, and reused for a consecutive run. The VO(salen)∝PMO catalyst was used in this way in four consecutive runs with only a minor decrease in the conversion during the final run (see Table 2). Maintenance of the initial catalytic activity upon reusing would have been impossible with significant leaching and catalyst deactivation. The VO(salen)∝PMO catalyst was also efficient for promoting the cyanosilylation addition of other aldehydes with high conversions and excellent selectivities (see Table 2).

In solution, chiral vanadyl salen complexes have been shown to be highly enantioselective catalysts for the asymmetric cyanosilylation of aldehydes [30,31]. Herein, to demonstrate the generality of our methodology to develop solid catalysts with a PMO structure, we also proceeded to obtain a PMO containing a chiral vanadyl salen complex, namely VO(salen)∝ChiMO. To have some evidence that chirality of the complex has been preserved during the synthesis of VO(salen)∝ChiMO solid, we have determined the optical activity of the solids by directly measuring the deviation angle of plane-polarized light in suspensions of as-synthesized and extracted VO(salen)∝ChiMO using a conventional polarimeter. Direct measurement of optical activity is possible since the suspension of the VO(salen)∝ChiMO in 1,2-dichloroethane is sufficiently transparent and lasts sufficiently to allow this measurement. The results of the specific optical activity determination for the chiral VO(salen)∝ChiMO are also included in Table 1. These data are also consistent with the vanadium analysis that indicates that removal of the CTABr template also produces a decrease in the optical activity of extracted VO(salen)∝ChiMO. However, it is important to note that the optical activity measurement conclusively establishes the chiral nature of the VO(salen)∝ChiMO solid. We have tested the activity and enantioselectivity of this VO(salen)∝ChiMO for the cyanosilylation of benzaldehyde at low temperatures (0 °C). Although good conversion and selectivity were obtained, the asymmetric induction of the solid was comparable to that reported for chiral VO(salen) complexes anchored on MCM-41 [32], but significantly much lower than that reported for analogous complexes in solution [30,31]. The residual activity of the silicate walls to effect the non-enantioselective formation of cyanohydrin (less than 10% in the blank control) may explain in part this lower enantioselectivity of the VO(salen)∝ChiMO. The results of cyanosilylation of benzaldehyde are shown in Table 3.

In an attempt to increase the enantiomeric excess (ee), the VO(salen)∝ChiMO solid was submitted to silylation of free silanol groups using ethoxytrimethylsilane as silylating

Table 3
Results of the cyanosilylation of aldehydes using VO(salen)$\propto$ChiMO as heterogenous asymmetric catalyst[a]

Aldehyde (**6**)	Surface silylation	Conversion (%)	ee (%)
a	No	80	30
a	Yes	76	28

[a] Reactions were carried out at 0 °C under N_2 atmosphere for 72 h: **6a** (0.82 mmol), TMSCN (3 eq), **VO(salen)$\propto$ChiMO** (0.25 mol%), nitrobenzene (0.82 mmol), and $CHCl_3$ (1 ml). No leaching detected. Selectivity towards **7** $>$ 98%. Mass balance $>$ 95%.

reagent. In earlier reported works in which MCM-41 has been used as support for enantioselective catalysts, it has been observed that free silanol groups decrease the asymmetric induction of solid catalyst [32]. However, as seen in Table 3, silylation of VO(salen)$\propto$ChiMO did not produce any positive effect on the enantioselectivity of the catalyst. On the contrary, enantioselectivity was found to decrease slightly. This failure to improve the asymmetric induction by silylation seems to point out that the OH groups are not responsible for the decrease of the ee values.

4. Conclusions

In conclusion, we have demonstrated that the methodology previously reported for the preparation of periodic mesoporous organosilicas can also be employed to develop solid catalysts containing metal salen complexes forming part of the silicate walls. The resulting PMOs exhibit good activity and high selectivity. Significantly, we have also been able to demonstrate the chirality in some PMO (ChiMO) solids containing chiral complexes by direct measurement of their optical activity. In addition, ChiMO was found to be capable of acting as enantioselective heterogeneous catalyst.

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