

# Synthesis of Chiral Periodic Mesoporous Silicas Incorporating Tartrate Derivatives in the Framework and Their Use in Asymmetric Sulfoxidation

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The synthesis of chiral periodic mesoporous organosilicas (ChiMO) of MCM-41 type using a bis-silylated tartramide derived from L-(+)-dimethyl tartrate (Sharpless and Kagan ligand) has been studied. The ChiMO materials were characterized by powder XRD, TEM, and nitrogen adsorption–desorption measurements, verifying their successful preparation. The evidence of the covalent bonding between the organic chiral precursor and the inorganic silica framework structure was confirmed by  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR solid state measurements. The synthesized chiral PMO was found to catalyze the asymmetric oxidation of thioanisole with good sulfoxide yield and moderate enantioselectivity. Reutilization of the “solid” chiral ligand led to similar optical yields to that obtained with the fresh ChiMO, revealing the true heterogeneous nature of the immobilized tartrate derivative.

## Introduction

The expectations in different scientific fields created by the appearance of organic–inorganic compounds in well-defined supramolecular structures are enormous. Thus, the combined properties of organic and inorganic groups in a single material have allowed researchers to prepare novel catalytic systems, to tailor materials for separation operations and optical and electronic devices, among many others from a huge variety of applications.<sup>1–4</sup> Different pathways have been described for the synthesis of these hybrid materials,<sup>5,6</sup> but the most widespread synthetic methodologies are the postsynthesis treatments and direct synthesis or co-condensation procedures. Using postsynthetic grafting routes, a great variety of organic groups have been incorporated onto the surface of mesoporous inorganic silica,<sup>7,8</sup> although usually the incorporation efficiency of the organic functionality to the final material is rather low. The simultaneous co-condensation (one-pot synthesis) of organoalkoxysilanes and the corresponding tetraalkoxysilanes silica precursors have

improved the incorporation of different organic moieties. More recently, since their discovery in 1999 by three different research groups,<sup>9–12</sup> the synthesis of periodic mesoporous organosilicas (PMO's) has received much attention. In this case, the bridge-bounded organic compounds are incorporated directly in the three-dimensional silica framework by the use of bis-silylated organosilica precursors like  $(\text{RO})_3\text{Si}-\text{R}'-\text{Si}(\text{OR})_3$ . The hydrolysis and condensation of such species in the presence of the micellar structure-directing agents produce the ordered periodic hybrid material which, after removal of the surfactant, exhibits a mesoscopic porous structure formed by an ordered array of pores with uniform size and shape, as well as walls of inorganic oxide organically functionalized by alkyl groups ( $\text{R}'$ ). In this way, the organic functionalization degree that can be reached in the final material is clearly superior to other synthetic methodologies. Thus, the so-obtained materials combine the very narrow pore size distribution, opened porous structure, and thermal stability of the inorganic parent structure with a huge number of different organic compounds incorporated into the material. The hybrid mixture of organic and inorganic components can lead to materials with a lot of potential applications, such as adsorption, chromatography, nanoelectronics, and mainly catalysis.

A particular case of application in catalysis is asymmetric synthesis, which is of critical importance in the production of adequate pharmaceuticals and agrochemicals.<sup>13</sup> This specific field is characterized by the use of chiral organic

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moieties to transfer optical activity to the final products. Recently, the heterogeneous asymmetric catalysis has focused the efforts of intensive research because of the easy separation and recovery of the catalyst from the reaction medium.<sup>14</sup> Most of the heterogeneous asymmetric catalysts have been synthesized through grafting or anchoring of homogeneous catalysts onto the solid support surface.<sup>13</sup> An interesting approach, related especially with mesostructured hybrid materials, is the direct anchoring of the chiral building blocks into the mesoporous structure by the use of bis-silylated chiral organic bridge precursors. For this case, few but interesting examples have been reported. Corma and co-workers<sup>15,16</sup> described for first time the synthesis of a chiral PMO named ChiMO (chiral mesostructured organosilica), prepared from mixtures of bis-silylated vanadyl–salen complexes and tetraethoxysilane (TEOS). The resulting material integrates the chiral organic bridges into the MCM-41 structure, showing a high ordering degree and displaying good catalytic activity in the cyanosilylation of benzaldehyde through cyanohydrins, though asymmetric induction was low compared to that achieved with its homogeneous counterpart.<sup>17</sup> García et al. reported another example of ChiMO material functionalized with chiral diurea ligands,<sup>18</sup> which showed enantioselective behavior as chiral auxiliary in the photo di- $\pi$ -methane rearrangement of dibenzobarrelene. Later, Li et al. reported the synthesis of a new ChiMO<sup>19</sup> in which a chiral diaminocyclohexane was incorporated into the framework of mesoporous silica, showing a quite high reaction rate and moderate enantioselectivity in the asymmetric transfer hydrogenation of ketones. Another example recently reported by Polartz and co-workers deals with the synthesis of a chiral PMO prepared from the prochiral bis(trialkoxysilyl)ethylene<sup>20</sup> and modified by asymmetric hydroboration in the presence of Rh-BINAP, although no application for this material has been described. In addition, attempts to obtain well-structured chiral PMO materials with higher organic loadings have not been completely successful. Two recent works related with the preparation of PMO's from 100% chiral bis-silylated functionalities have been found. Both of them evidence the lack of mesoscopic ordering in the final materials, since the X-ray diffraction patterns present a low quality. Moreover, the chiral organosilicas exhibit a type I isotherm, indicating the existence of mainly micropores.<sup>21,22</sup>

Few examples of silica-supported enantioselective catalyst have been reported for the heterogeneous asymmetric oxidation of prochiral sulfides. The first example ever in this field was reported by Choudary et al.<sup>23</sup> These authors supported the Kagan reagent in the interlaminar space of pillared montmorillonite clay in a similar way to that used for the heterogenization of the Sharpless asymmetric epoxidation catalyst.<sup>24</sup> The final material showed good catalytic activity and enantioselective induction on the final sulfoxides, although reutilization was not described. Later, Cross et al.<sup>25</sup> reported the immobilization of copper(II) chiral Schiff bases in the inner void fraction of zeolites, using an encapsulation procedure. Although the resultant materials displayed catalytic activity in the oxidation of thioanisole, the enantiomeric excess induced on the reaction products was negligible. Li et al. published the synthesis of a tartramide chiral ligand obtained through a procedure with five steps for subsequent grafting onto the silica surface of the pores of a mesostructured MCM-41 material.<sup>26</sup> The final hybrid organic–inorganic material was employed in the asymmetric epoxidation of allyl alcohol. More recently, Corma et al.<sup>27</sup> reported the immobilization of similar Cu(II) Schiff bases on MCM-41 using a tethering heterogenization method. The so-prepared materials displayed moderate asymmetric induction on the oxidized species. These two last results might indicate that the heterogenization of a chiral catalyst on a controlled, non-sterically hindered environment, like the ordered pores of a mesostructured material, could be beneficial for the heterogenization of a chiral catalyst, in accordance with data reported by Thomas et al.<sup>28</sup>

Thus, in order to take advantage of the promising results achieved with chiral PMOs in asymmetric reactions, here we report the heterogenization of the Kagan catalyst for asymmetric sulfoxidation in a shaped ChiMO. To the best of our knowledge, herein, we describe the first synthesis of a periodic mesoporous organosilica integrating a chiral modified tartrate (Sharpless and Kagan ligand) as organic bridge into the framework of MCM-41. The modified bis-silylated tartramide synthesis involves only two steps, in contrast with the grafting strategy of Li et al. mentioned above, and subsequently was coupled with TEOS in a cocondensation reaction under basic conditions. The maximum content of chiral precursor in the material not leading to a significant reduction in mesoscopic order of the resulting materials was 15% of the total silicon loading. The chiral precursor was previously synthesized by amidation of dimethyl tartrate with an aminoorganosilane by using *n*-

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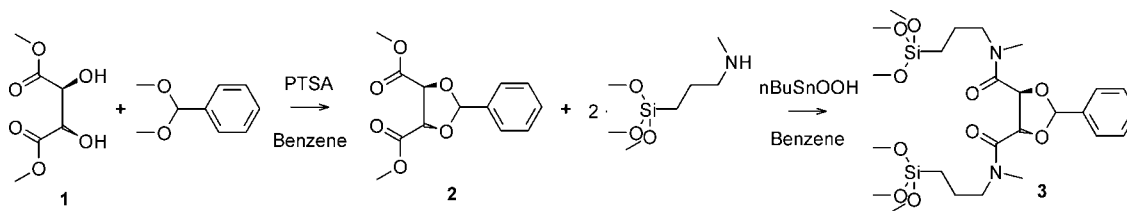
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## Scheme 1. Synthesis of Bis-Silylated Chiral Tartramide 3



butylstannonic acid as catalyst. The synthesized chiral PMO was found to be enantioselective in the asymmetric oxidation of sulfides.

### Experimental Section

**Synthesis of the Precursor.** All the synthesis steps were carried out in oven-dried glassware under nitrogen atmosphere. The solvents were dried using standard methods as follows: benzene was distilled from Na, methylene dichloride from  $P_2O_5$  and acetone from  $CaCl_2$ . (*N*-Methyl-3-aminopropyl)trimethoxysilane (Gelest), tetraethylorthosilicate (TEOS, Alfa), and cetyl trimethylammonium bromide (CTABr, Aldrich) were used as received. Scheme 1 shows the synthesis of bis(*N*-methyl-*N*-propyltrimethoxysilyl)tartramide, which was accomplished in two steps.

In the first step, L-(+)-dimethyl tartrate (**1**; 10.0 g, 55.6 mmol) was protected, accordingly to the method described by Seebach,<sup>29</sup> with benzaldehyde dimethyl acetal to give dimethyl (4*R*,5*R*) 2-phenyl-1,3-dioxolane-4,5-dicarboxylate (**2**). The product was purified by crystallization from benzene/petroleum ether (50% vol) to give white acicular crystals in a high yield (**2**; 13.1 g, 49 mmol, 98%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 3.84 (s, 6H,  $CO_2CH_3$ ), 4.92 (d, 2H,  $J$  = 4.0 Hz,  $-OCH-$ ), 6.15 (s, 1H,  $CH-Ph$ ), 7.47 ppm (5H,  $H_{Ph}$ ). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 52.9 ( $CO_2CH_3$ ), 76.7 ( $-OCH-$ ), 106.6 ( $CH-Ph$ ), 127.0, 128.2, and 129.9 ( $HC^{Ph}$ ), 135.0 ( $C^{Ph}$ ), 169.8 ( $CO_2CH_3$ ).

Protected dimethyl tartrate (**2**; 3.5 g, 13.1 mmol) was reacted with 2 equiv of (*N*-methyl-3-aminopropyl)trimethoxysilane (5.2 g, 26.9 mmol) in benzene under reflux conditions. The reaction was catalyzed by *n*-butylstannonic acid (0.1 equiv)<sup>30</sup> and a Dean–Stark apparatus was used for solvents lighter than water for the removal of methanol by azeotropic distillation. The reaction was monitored by TLC and continued until completion. The crude reaction was then concentrated in vacuo and the residue purified by flash chromatography using a polystyrene Amberlite-type resin as stationary phase and acetone/methylene dichloride 50% (vol) as mobile phase. The double silane-functionalized tartramide was obtained as a yellow oil and used without further purification (**3**; 7.3 g, 12.4 mmol, 94.6%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 0.78 (m, 4H,  $SiCH_2$ ), 1.87 (m, 4H,  $SiCH_2CH_2$ ), 2.29 (m, 4H,  $-NCH_2-$ ), 2.43 (m, 6H,  $NCH_3$ ), 3.51 (m, 18H,  $SiOCH_3$ ), 5.08 (d, 2H,  $J$  = 4.02 Hz,  $CHO$ ), 5.71 (s, 1H,  $CH-Ph$ ), 7.32 ppm (m, 5H,  $C^{Ph}H$ ). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 6.6 ( $-SiCH_2-$ ), 17.8 ( $-SiCH_2CH_2-$ ), 33.7 ( $NCH_3$ ), 50.7 ( $SiOCH_3$ ), 52.3 ( $-NCH_2-$ ), 105.8 ( $CHO$ ), 106.1 ( $CH-Ph$ ), 127.25, 128.5, and 129.9 ( $HC^{Ph}$ ), 136.3 ( $C^{Ph}$ ), 167.3 ( $-C(O)N-$ ).

**Synthesis of Chiral Periodic Mesoporous Organosilica.** The preparation of MCM-41 type chiral PMO materials was studied by means of the method described by Lin and co-workers.<sup>31</sup> In a regular synthesis, CTABr (2.53 g, 7 mmol), diethylamine (5.1 g,

70 mmol), and  $H_2O$  (100 g, 5.6 mol) were magnetically stirred in a beaker until complete dissolution. To the transparent resultant solution, TEOS and the tartramide precursor were added separately by dropping. Different materials were prepared in the molar range tartramide to TEOS from 0.05 to 0.13. The resultant gel was then stirred at room temperature for 4 h and afterward transferred to an autoclave to be aged. The aging step of the gel was carried out under static conditions at 100 °C and autogenous pressure for 48 h. The resultant materials were then recovered by filtration and air-dried. As-made materials were treated with an ethanolic solution of hydrochloric acid (0.5 N; 1.5 g of as-made material per 400 mL of acid solution) for the simultaneous removal of the surfactant and the cleavage of the benzylidene acetal protecting group.

**Synthesis of Chiral-Organic Grafted MCM-41.** For comparison, a postsynthetic functionalization of a silica-based MCM-41 with the chiral bis-silylated tartramide was carried out. Thus, MCM-41 was prepared following the method described by Lin et al.<sup>31</sup> Upon calcination for the template removal in air atmosphere at 550 °C for 5 h, the solid is outgassed at 150 °C under vacuum overnight. Then, the chiral precursor was grafted onto the silica surface following the next procedure: 1 g of the previously synthesized MCM-41 and 150 mL of toluene were placed in a flask equipped with a mechanical stirrer and a reflux condenser. The mixture was stirred during 60 min to achieve a homogeneous dispersion, and afterwards, 0.2 g of *p*-toluenesulfonic acid and 2.5 mmol of bis-silylated tartramide were added. The mixture was then heated under reflux and stirring for 24 h. The resultant suspension was filtered off and purified by means of repetitive washing in methanol, dichloromethane, and ether. Finally, prior to the analysis, the solid product was dried at 100 °C for 12 h.

**Characterization Techniques.** The so-prepared materials were characterized by means of different analytical techniques. Thus, nitrogen adsorption–desorption isotherms were collected at 77 K using a Micromeritics TriStar 3000 unit. The samples were previously outgassed in  $N_2$  flow at 125 °C during 8 h before analysis. Surface specific areas were calculated using the BET method. Pore size distributions were determined by the BJH method using the KJS correction and assuming cylindrical pore geometry. The total pore volume was assumed as the one recorded at  $P/P_0 = 0.985$ . X-ray powder diffraction patterns were collected on a Philips X'pert diffractometer fitted with an accessory for low-angle measurements. XRD analyses were recorded using the  $Cu\ K\alpha$  line in the  $2\theta$  range from 0.5 to 10° with a step size of 0.02°. FTIR analyses were collected, using the KBr buffer technique, on a Mattson Infinity series apparatus in the wavelength range from 4000 to 400  $cm^{-1}$  with a step size of 2  $cm^{-1}$  and collecting 64 scans for each analysis. NMR spectra for liquid samples were recorded on a Varian Mercury 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm), in reference to the residual proton signals from the deuterated solvents. Solid-state <sup>13</sup>C and <sup>29</sup>Si MAS NMR experiments were performed on a Varian Infinity 400 MHz spectrometer fitted with a 9.4 T magnetic field. These nuclei resonate at 100.53 and 79.41 MHz, respectively. An H/X 7.5 mm MAS probe and  $ZrO_2$  rotors spinning at 6 kHz were used. For CP experiments, the cross-polarization time was determined to guar-

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**Table 1. Physicochemical Properties for Chiral PMO Materials**

sample	TEOS/Chiral precursor <sup>a</sup>	N <sub>2</sub> adsorption analysis			X-ray diffraction			<sup>29</sup> Si NMR	
		S <sub>g</sub> <sup>b</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	D <sub>p</sub> <sup>c</sup> (Å)	V <sub>p</sub> <sup>d</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	d <sub>100</sub> <sup>e</sup> (Å)	a <sub>0</sub> <sup>f</sup> (Å)	Wt <sup>g</sup> (Å)	T/(T + Q) <sup>h</sup>	η <sup>i</sup> (%)
MCM-41	100:0	971	26	0.938	33	39	13	0	
MCM-41 Gr <sup>j</sup>	85:15	922	24	0.812	31	36	12	3	10
PMO-10	90:10	821	21	0.829	39	45	24	8.5	42.5
PMO-15	85:15	742	19	0.675	41	47	28	11.5	38.3
PMO-20	80:20	559	16	0.645	44	51	35	10.8	27.0

<sup>a</sup> Proportion of chiral tartramide precursor incorporated into the gel during the synthesis step on a molar basis. <sup>b</sup> Specific surface area calculated by the BET method. <sup>c</sup> Pore size diameter calculated by the BJH method. <sup>d</sup> Total pore volume registered at  $P/P_0 = 0.985$ . <sup>e</sup> Interplanar spacing. <sup>f</sup> Cell unit parameter calculated assuming hexagonal ordering. <sup>g</sup> Wall thickness calculated as  $Wt = a_0 - D_p$ . <sup>h</sup> Proportion of organosilicon atoms incorporated into the final material. <sup>i</sup> Incorporation efficiency of the chiral functionality onto the final material. <sup>j</sup> MCM-41 material functionalized with chiral bis-silylated tartramide through the grafting method.

ante the total proton polarization, verifying the Hartmann–Hann condition. In addition, to allow an accurate quantification of silanol groups, <sup>29</sup>Si NMR spectra using a one pulse sequence were also obtained. For <sup>13</sup>C acquisition,  $\pi/2$  pulse, number of scans, repetition delay, and contact time were 4.25  $\mu$ s, 2000 scans, 3 s, and 1 ms, respectively. The <sup>29</sup>Si experiments were performed for 3000 scans,  $\pi/2$  pulse of 3.5  $\mu$ s, and 15 s of repetition time. The <sup>29</sup>Si CP experiment contact period was 10 ms since cross-polarization depends upon heteronuclear dipolar interaction, and the greater the distance the larger the cross-polarization time. <sup>13</sup>C and <sup>29</sup>Si chemical shifts were externally referenced to adamantane and tetramethylsilane, respectively.

**Catalytic Tests.** Reaction tests for the asymmetric oxidation of sulfides were carried out under nitrogen atmosphere using standard Schlenk techniques. The PMO used as solid chiral ligand was previously outgassed and dried in a Kugelrohr apparatus at 130 °C under vacuum (1 Torr) overnight before being employed in the catalytic tests. The conditioned material was then transferred at room temperature into a jacketed glassware reactor connected to a chiller unit for the external control of the reaction temperature. Inert conditions were ensured by passing a continuous nitrogen stream through the reactor which was maintained during the overall the reaction procedure. Freshly distilled dichloromethane (50 mL) was then transferred into the reactor via syringe and the mixture magnetically stirred. Titanium isopropoxide (0.056 mmol) and 2-propanol (0.224 mmol) were added drop by drop to the resultant suspension. The mixture was then aged for 2 h in order to promote the contact between the titanium species and the chiral ligand sites present in the PMO material. After the aging step, both cumyl hydroperoxide (CHP, 0.56 mmol) and methyl phenyl sulfide (0.56 mmol) were added separately by dropping onto the catalytic suspension. Sample aliquots were collected in order to assess the evolution of the reaction. The mixture was allowed to react for a total period of 24 h. The conversion of substrate as well as the enantiomeric excess (ee) transferred onto the sulfoxide were evaluated by means of chiral HPLC analysis on a Varian ProStar fitted with a chiral column (R,R-Whelk-01) operating under isocratic conditions (1.5 mL min<sup>-1</sup>) using a mobile phase of *n*-heptane/IPA = 92:8 (vol). Chromatograms were collected at 254 nm, the maximum in the UV absorbance spectra for both the substrate and the reaction product.

## Results and Discussion

The mesostructured organosilicas with chiral ligands incorporated into the framework were obtained following a direct cocondensation procedure through the surfactant-assembling pathway. In this strategy, (*N*-methyl-3-aminopropyl)trimethoxysilane was reacted with chiral protected dimethyl tartrate, following the procedure shown in Scheme 1, to give bis-silylated tartramide chiral ligands. Subsequently, the asymmetric organosilicon precursor was used

in combination with TEOS to prepare chirally modified MCM-41-type materials, using cetyltrimethylammonium bromide (CTABr) as structure-directing agent. A series of solids were prepared in which the ratio of chiral moiety related to TEOS was varied in the ranges 10:90, 15:85, 20:80, and 25:75. Table 1 summarizes the physicochemical properties of the solid samples so obtained. Also, pure silica MCM-41 type material and chiral bis-silylated tartramide grafted on MCM-41 (MCM-41 Gr) were included as reference samples. With regard to the latter, a reduction in the porosity (BET surface area, pore diameter, and pore volume) is shown in comparison to pure silica MCM-41.

Isothermal N<sub>2</sub> adsorption measurements of the extracted chiral PMO have allowed determining the BET surface area, pore size distribution, and total pore volume for the prepared materials. All these parameters decrease insofar as the content of chiral organosilicon precursor increases in the synthesis gel.

Figure 1 shows the adsorption–desorption isotherms as well as the pore size distribution for the prepared samples. PMO-10 and -15 materials show nitrogen adsorption–desorption curves lying in the group of type IV isotherms, according to the IUPAC classification, typical for mesoporous solids. The steep region detected in the adsorption branch around  $P/P_0 = 0.32$ , corresponding to the capillary condensation of nitrogen in uniform pores, evidences the formation of well-structured solid materials, mainly in the case of the pure silica MCM-41 sample. This conclusion is supported by the narrow pore size distribution detected for these materials. On the other hand, the ordering degree seems to be influenced by the content of the organic functionality. Although the width of the pore size distribution seems not to be greatly modified, the area below the pore size distribution, which is the total pore volume, decreases when increasing the organic ligand loading. Besides, as above-mentioned, the mean pore size is displaced to lower values because of the same reasons already exposed. These measurements suggest the formation of well-structured solid materials for samples with molar ratios of chiral precursor/TEOS lower than 15:85, while higher loadings of the chiral functionality lead to structurally distorted materials.

The periodic structure of the template-free chiral PMO was determined by powder X-ray diffraction (Figure 2). The characteristic reflection peak at  $2\theta = 2^\circ$ , corresponding to the  $d_{100}$  basal plane of MCM-41, confirms the formation of a mesoporous structure for those solids in which the ratio of TEOS/chiral precursor was 85:15 and 90:10, PMO-15 and

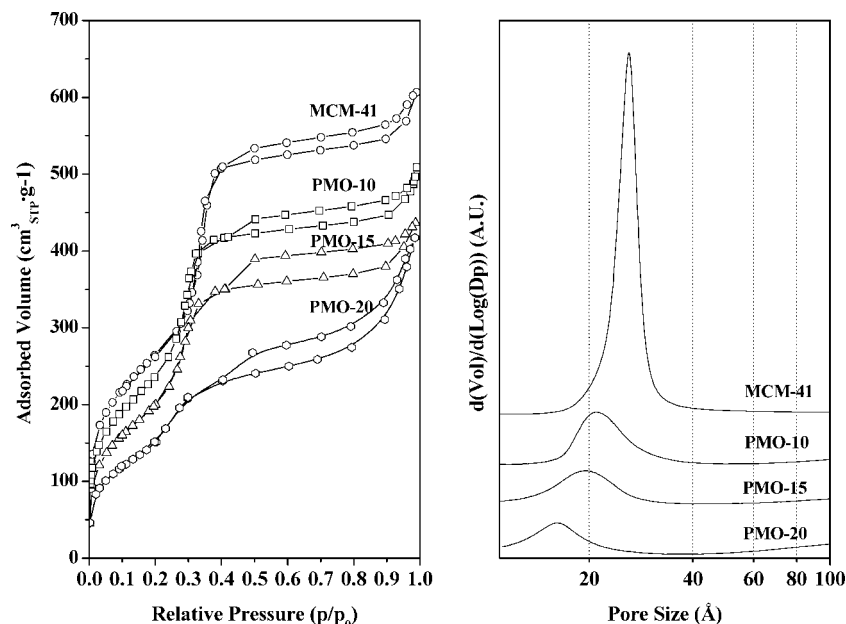


Figure 1. N<sub>2</sub> Adsorption–desorption isotherms and pore size distribution for PMO materials with different chiral ligand loadings.

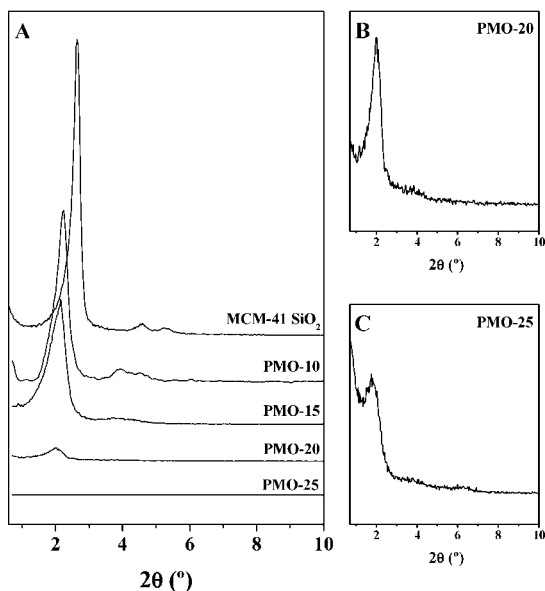


Figure 2. (A) XRD patterns recorded for Chiral PMO samples with MCM-41 topology and magnification of (B) PMO-20 and (C) PMO-25 diffraction patterns.

-10, respectively. These materials preserve the periodic structure even after the template CTABr removal by washing with acidified ethanol. Regarding the locations of the XRD reflections, both the interplanar spacing and cell unit dimension calculated from XRD analyses increase when higher loadings of organic precursor are used. These results, together with the reduction observed for the pore size diameter, means an increase of the wall thickness in the PMO materials, which is in accordance with results previously described for other PMO materials.<sup>4</sup> This result is further evidence for the incorporation of the chiral organic ligand to the mesoporous structure of final PMO materials. On the other hand and according to the nitrogen adsorption results, XRD patterns of the solids with a ratio of TEOS/chiral precursor of 80:20 and 75:25 show materials without the expected mesostruc-

ture, mainly in the latter, as can be observed in Figure 2 (graphs B and C). Therefore, the lack of structure is detected, most likely due to the large amount of bis-silylated chiral precursor used, which generates variations in the sol during the synthesis. Thus, from the results obtained it follows that a TEOS/chiral precursor ratio of 85:15 is the optimum to obtain a material mesoscopically well ordered and with significant amounts of chiral organic inductor in the solid framework. Table 1 also shows the X-ray diffraction parameters for pure silica MCM-41 and MCM-41 Gr, revealing that the latter retains the mesostructured ordering of the former starting silica phase.

Figure 3 depicts TEM images obtained for sample PMO-15 as definitive evidence of the structure ordering achieved on these chiral modified mesostructured materials. This sample shows the typical honeycomb structure from MCM-41 type mesostructured materials.

Regarding the incorporation of the chiral ligands to the framework of the PMO materials, FTIR spectra were obtained for the accurate characterization of the chirally functionalized PMO materials. Figure 4 depicts the FTIR analyses recorded for the starting compounds used in the synthesis of the bis-silylated chiral tartramide derivative as well as the materials prepared following the procedure previously described. Figure 4c shows that the transamidation of **2** with (*N*-methyl-3-aminopropyl)trimethoxysilane leads to a displacement of the carbonyl stretching band from 1740 cm<sup>-1</sup> to 1645 cm<sup>-1</sup>. This modification, the most meaningful in the FTIR spectrum recorded for **3**, is caused by the transformation of the ester functionality into an amide group. The absence of the signal at 1740 cm<sup>-1</sup> indicates a complete transformation of the tartrate starting material during the transamidation reaction. Besides, the previously mentioned characteristic signals from bis-silylated tartramide are present in the final PMO materials, as shown in the Figure 4d. Thus, although the signal corresponding to the stretching vibration of the carbonyl group at the amide functionality is

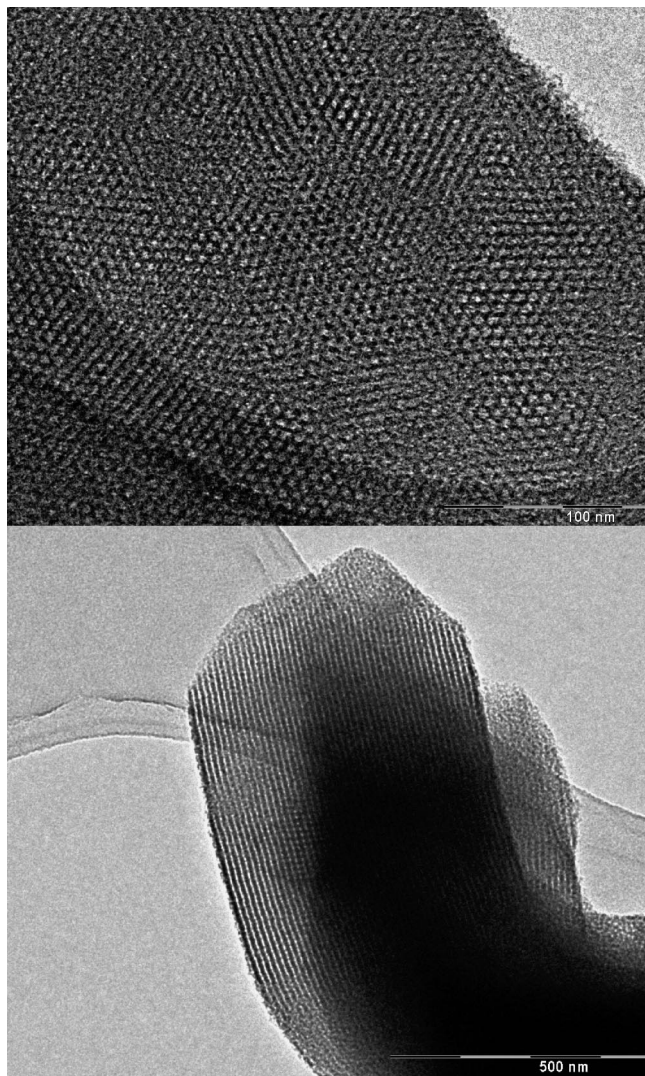


Figure 3. TEM images recorded for sample PMO-15.

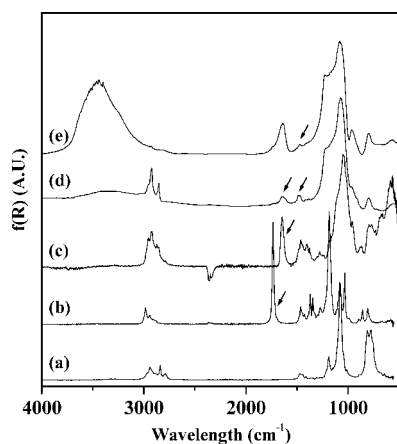


Figure 4. FTIR spectra collected for (a) (*N*-methyl-3-aminopropyl)trimethoxysilane; (b) (*4R,5R*) 2-phenyl-1,3-dioxolane-4,5-dicarboxylate, **2**; (c) bis-silylated tartramide ligand **3**; (d) as-made sample PMO-15; and (e) sample PMO-15 after surfactant extraction.

partially hidden by the physisorbed water binding signal at  $1640\text{ cm}^{-1}$ , the signal located at  $1440\text{ cm}^{-1}$ , which is attributed to the vibration of the double bond  $\text{C}=\text{C}$  at the protecting benzilidene acetal group, is clearly visible in the spectra recorded for the as-made PMO material. On the

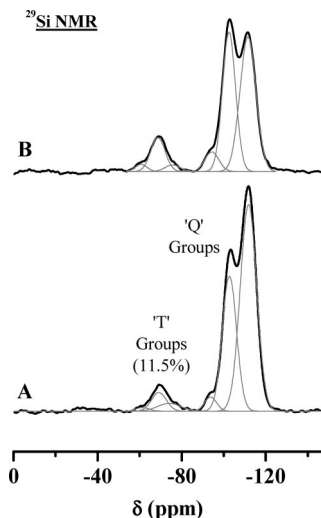
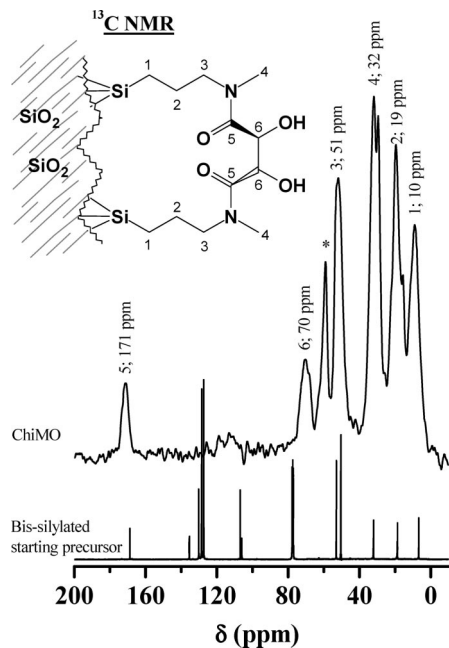


Figure 5.  $^{29}\text{Si}$  solid state NMR spectra (A, single pulse; B, cross-polarization) recorded for sample PMO-15.

contrary, the great decrease achieved in the intensity of this signal in the spectrum recorded for the extracted PMO, depicted in Figure 4e, might be reasonably ascribed to the cleavage of the protecting group during the surfactant removal step because of the acidic conditions.<sup>32</sup> Anyway, the signal corresponding to the presence of the benzilidene acetal, though reduced, is present, indicating that some fraction of the immobilized chiral tartramide species is still protected.

Another piece of evidence of the organic chiral precursor covalent incorporation to the inorganic silica framework is obtained by solid-state  $^{29}\text{Si}$  NMR. Figure 5 shows the  $^{29}\text{Si}$  NMR spectrum of the PMO MCM-15 material after CTABr surfactant removal. The spectrum displayed two regions of major intensity, centered at about  $-100$  to  $-110$  and about  $-70$  ppm. These two regions correspond to  $\text{Si}(\text{O}-\text{R})_4$  and  $\text{RSi}(\text{O}-\text{R})_3$  species, respectively, where R is the chiral organic group. The  $-100$  to  $-110$  ppm pattern is composed of at least three contributions, at about  $-92$ ,  $-100$ , and  $-110$  ppm, which correspond to  $(\equiv\text{SiO})_2\text{Si}(\text{OR}')_2$  ( $\text{Q}^2$ ),  $(\equiv\text{SiO})_3\text{Si}(\text{OR}')$  ( $\text{Q}^3$ ), and  $(\equiv\text{SiO})_4\text{Si}$  ( $\text{Q}^4$ ) species, respectively, where  $\text{R}' = \text{Et}$  or  $\text{H}$ . The lower-shielding pattern is formed by one peak at about  $-69$  ppm, dealing with species containing the chiral organic ligand groups,  $\text{RSi}(\text{OSi}\equiv)_n$  ( $\text{T}^n$ ). As the  $^{29}\text{Si}$  NMR spectrum was obtained by a direct one-pulse experiment, the quantification of the species associated with the respective intensities can be obtained from the deconvolution of the spectrum. Thus, the incorporation efficiency of the chiral organic moiety in the silica framework was calculated (Table 1). The increase in the amount of the bis-silylated tartramide derivative does not contribute to enhancing the incorporation of the chiral ligand into the framework of the final PMO material, suggesting a limit to incorporating higher amounts of the organosilicon precursor. Increasing the loading of organosilicon precursor induces a negative influence on the ordering of the final materials without enhancing the incorporation degree of the chiral

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**Figure 6.**  $^{13}\text{C}$  solid-state NMR spectra acquired and signals' assignment of sample PMO-15 and bis-silylated tartramide chiral precursor.

functionality. The results point to an optimum ratio of TEOS to chiral precursor to be used in order to achieve high incorporation degrees of the chiral ligand in well-structured materials. This optimal molar ratio is reached when the molar ratio of TEOS/bis-silylated tartramide corresponds to 85:15.

In  $^{29}\text{Si}$  CP-MAS NMR experiments, depicted in Figure 5,  $\text{Q}^3$ ,  $\text{Q}^2$ , and T species peak intensities are enhanced over the  $\text{Q}^4$  signal, since the latter lacks of H in coordination sphere. This increase in T species also allows us to isolate the different species that compose the signal around  $-70$  ppm. Thus, this lower-shielding pattern is composed of one major peak at about  $-69$  ppm, corresponding to  $\text{RSi}(\text{OSi}\equiv)_2\text{OR}'$  ( $\text{T}^2$ ) species, and two shoulders at  $-60$  ppm and  $-75$  ppm, due to species containing chiral ligand groups,  $\text{RSi}(\text{OSi}\equiv)(\text{OR}')_2$  ( $\text{T}^1$ ) and  $\text{RSi}(\text{OSi}\equiv)_3$  ( $\text{T}^3$ ), respectively, where  $\text{R}' = \text{H}$  or Et. This result indicates the presence of Si atoms covalently bonded to carbon atoms, mainly by  $\text{T}^2$  species, confirming the presence of organic functionalities supported into the final material.

Regarding the identification of these organic species incorporated into the framework of mesostructured materials, this can be inferred from the  $^{13}\text{C}$  CP-MAS NMR spectra. Figure 6 depicts the  $^{13}\text{C}$  CP-MAS NMR spectrum recorded from PMO-15. The spectrum displays different signals that have been assigned to the different functional groups of the silica-supported tartramide chiral species. The lower-shielding chemical shift at about 171 ppm corresponds to quaternary carbons at the carbonyl groups,  $\text{C}=\text{O}$ , from the synthesized amide. The presence of a single peak confirms the formation of the symmetrical tartramide and the role of butylstannonic catalyst leading to formation of the bis-silylated chiral tartramide. The signals centered at 32 and 51 ppm can be assigned to  $\text{NCH}_3$  and  $\text{NCH}_2$ , respectively, which indicates the presence of the nitrogen atom in the material. Also, the two sharp peaks centered at 10 and 19 ppm were assigned to  $\text{Si}-\text{CH}_2$  and  $\text{Si}-\text{CH}_2-\text{CH}_2$ , respec-

**Table 2.** Catalytic Results of Asymmetric Oxidation of Methyl Phenyl Sulfide by Chiral PMO<sup>a</sup>

run	catalyst	catalytic results at different reaction times <sup>b</sup>		
		1 h	3 h	24 h
1	blank	0 (—)	0 (—)	2 (0)
2	MCM-41 Gr	20 (6)	28 (4)	35 (2)
3	PMO-15	45 (32)	61 (29)	70 (31)
4	PMO-15 <sup>c</sup>	40 (27)	46 (27)	58 (26)

<sup>a</sup> Reactions performed at  $-20$  °C in  $\text{CH}_2\text{Cl}_2$  as solvent. <sup>b</sup> Sulfoxide yield and induced enantiomeric excess in parentheses. <sup>c</sup> Reutilization test.

tively. In addition, the chemical shift at 70 ppm, composed by the overlapping of two signals, comes from the two chiral carbon atoms bonded to hydroxyl groups,  $\text{CH}-\text{OH}$ . The relative importance of the residual ethoxy groups or protons bonded to ligand-bearing silicon and nonligand-bearing silicon moieties can be also inferred from the  $^{13}\text{C}$  NMR. The spectrum shows two peaks centered at 18 and 59 ppm that could be related to the presence of the residual ethoxy groups coming from nonhydrolyzed ethoxide functionalities. Therefore, all these data confirm the presence of the immobilized tartramide organic precursor in the inorganic material framework. Figure 6 also shows the  $^{13}\text{C}$  NMR spectrum of the bis-silylated tartramide chiral precursor. The spectrum exhibits significant signals at around 130 ppm, corresponding to aromatic signals, and two sharp peaks centered at 100 and 104 ppm, assigned to protected hydroxyl groups. On the contrary, the spectrum of PMO-15 sample shows almost complete absence of the 130 and 104 ppm signals, and on the other hand, the shift from 100 to 70 ppm indicates that the deprotection of the chiral precursor ligand has been achieved. Accordingly, both goals, the tartramide chiral precursor deprotection and the structure directing agent ( $\text{CTA}^+$  species) removal, have been reached in a single step, which is evidence of the simple and efficient developed protocol.

To investigate the catalytic properties of the obtained solid, the asymmetric oxidation of methyl phenyl sulfide was employed as reaction test, using the chiral PMO as "solid" asymmetric ligand for the induction of enantioselectivity onto the final product. Asymmetric sulfoxides are very useful auxiliaries in asymmetric synthesis as intermediates in multistep synthesis or as biologically active compounds.<sup>33</sup> The best homogeneous conditions were used for carrying out the reaction,<sup>34</sup> so a molar combination of  $\text{Ti}(\text{O}i\text{-Pr})_4/\text{chiral tartramide}/i\text{-PrOH}$  1:4:4 was chosen (Kagan catalyst). Cumyl hydroperoxide was used as oxidizing agent because of the better performance of this oxidant in asymmetric sulfoxidation.<sup>34</sup> The catalytic results, including the sulfoxide yield as well as the induced enantiomeric excess, corresponding to the chiral PMO are collected in Table 2. A blank reaction (run 1) was performed as reference in the presence of the ChiPMO but in absence of any titanium source. In this way, neither appreciable substrate conversion nor induced enantioselectivity was accomplished, even for such long reaction time as 24 h. With regard to the catalytic

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behavior of the chiral PMO material prepared, increasing sulfoxide yields are achieved for longer reaction times (run 3). On the other hand, the enantiomeric excess induced onto the final sulfoxides is kept constant during the overall reaction process around 30% ee, being one of the higher values achieved with heterogeneous chiral precursors. On the other hand, the chiral PMO has been successfully reused as solid chiral ligand in the sulfoxidation reaction (run 4). In this case, lower sulfoxide yields are achieved, whereas the induced enantioselectivity is maintained at a similar level to that obtained for the fresh catalyst. This result confirms the true heterogeneous behavior of the organic chiral tartramide moieties supported in the way of a chiral periodic mesoporous organosilica. In addition, and for comparative purposes, MCM-41 grafted with the bis-silylated tartramide (MCM-41 Gr) was used as catalyst in the same reaction (run 2). Bearing in mind the physicochemical properties, the more striking differences showed by this sample are related to the amount of chiral organic ligand incorporated onto the silica walls measured by the  $^{29}\text{Si}$  NMR solid state analysis (Table 1), revealing an important decrease compared with the PMO samples. Also, it is important to remark that the grafting procedure could lead to a nonhomogeneous distribution of the chiral organic groups and even clogging of some pores, in contrast with the homogeneous organic distribution in chiral PMO. Moreover, the grafting process has been carried out by reaction of bis-silylated tartramide with the free silanol groups of the pore surfaces, and consequently, residual nonreacted silanols remain at the surface.<sup>7</sup> The latter have been proved to be harmful in Kagan–Sharpless enantioselective oxidation, because they are able to react with titanium isopropoxide and TBHP, impeding the titanium–tartramide complex formation.<sup>35</sup> All these reasons could be related with the worse reaction results found with this sample, not only because of the sulfoxide yield (35%) but mainly the poor enantiomeric excess obtained (2%) at 24 h in the asymmetric sulfoxidation of thioanisole.

To confirm the heterogeneous nature of the reaction, a reaction test was carried out with the liquid obtained after the removal of the solid by filtration. The catalyst was taken off from the reaction mixture when the enantioselectivity

reached 21.5% (0.5 h), and then the filtrate was stirred at the same reaction temperature. After 24 h, the enantiomeric excess induced over the sulfoxidation product dropped down to 4.5%. This result indicates that the reaction continues through the titanium source that remains in the solution, which catalyzes the sulfoxidation of thioanisole without inducing enantiomeric excess. Accordingly, the tartramide remains attached to the PMO and no leaching is contributed to the reaction, corroborating that the asymmetric oxidation of methyl phenyl sulfide is enantioselectively catalyzed by the solid catalyst.

Finally, bearing in mind, on the one hand, the textural properties defined by the isothermal  $\text{N}_2$  adsorption measurements and X-ray diffraction analysis and, on the other hand, the previous good catalytic activity showed, it follows that the incorporation of the organic tartramide is mainly placed in the porous wall more than in the occluded internal silica framework, which would contribute negatively to the induced enantioselectivity over the final sulfoxide.

### Conclusions

In conclusion, we have synthesized a bis-silylated chiral tartramide precursor from L-(+)-dimethyl tartrate (Sharpless and Kagan ligand) for the preparation of chiral periodic mesoporous organosilicas, with the organic moiety in the inorganic silica framework. The mesoscopic order of the final materials depends on the amount of the organic functionality in the initial gel mixture, reaching an optimum value when the molar ratio TEOS/bis-silylated chiral precursor is 85:15. FTIR experiments show the complete transformation of the tartrate and its ester functionality into the chiral tartramide compound. Additionally, solid state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR experiments confirm the presence of the chiral organic precursor in the silica wall covalently bonded to silicon atom. The so obtained PMO's exhibit a good activity (70% sulfoxide yield) and moderately enantioselectivity (30% ee) in the asymmetric sulfoxidation of methyl phenyl sulfide, being reusable in repeated catalytic tests. In addition, the absence of tartramide leaching has been ascertained.

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