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### Pore size matters! Helical heterogeneous catalysts in olefin oxidation

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#### Highlights

- Chiral MCM porous materials were synthesized (curved channels).
- Mo(II) complexes were immobilized in the chiral materials.
- The functionalized materials oxidized selectively several chiral substrates.
- The functionalized materials were reused for several runs keeping a high activity.

#### Abstract

Helical mesoporous materials of the MCM-41 type with different pore sizes were prepared, choosing as templates myristyl (C<sub>14</sub>) or cetyl (C<sub>16</sub>) trimethyl ammonium salts, and functionalized with Mo(II) active sites based on MoI<sub>2</sub>(CO)<sub>3</sub> (**1**) and MoBr( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> (**2**) fragments, respectively, using a pyridine-2-carbaldehyde ligand as anchor. The new materials were tested as the catalytic precursors in the epoxidation of *cis*-cyclooctene, styrene, *R*-(+)-limonene, *trans*-hex-2-en-1-ol, *cis*-3-hex-1-ol, and geraniol using *tert*butylhydroperoxide (tbhp) as oxidant. All catalysts were moderately to highly selective towards the epoxide products. The materials with larger pores (C<sub>16</sub> template) displayed a better catalytic activity, leading in general to higher conversions and selectivities, as well as faster kinetics. For instance, geraniol is epoxidized (more than 90 %) with conversions above 90 %. The major achievement of these catalysts, however, is the excellent product selectivity control, which is boosted when the allyl

complex **1** is used, reaching 100 % of the *2S,3R* species in the epoxidation of *trans*-hex-2-en-1-ol. The catalysts were also found to be stable through recycling experiments and truly heterogeneous with little or no leaching.

#### Keywords

Mesoporous materials; helical materials; molybdenum; oxidation catalysis; asymmetric catalysis

#### 1. Introduction

Organometallic complexes can efficiently and selectively catalyze many reactions and are widely applied in industrial processes. One of their drawbacks is the difficulty of separating the products from the reaction solution as well as recovering and recycling the catalyst. Heterogeneous catalysis, on the other hand, offers as the main advantage the easy recovery of the catalyst from the reaction products, making it the preferred approach in most industrial applications. As a drawback, selectivity is usually lower than that of many homogeneous systems. Although in recent times this gap has narrowed, designing more active and selective heterogeneous catalysts is still a priority and a challenge. Therefore, the possibility of incorporating active complexes in materials to yield heterogeneous catalysts has opened new routes for catalysis in recent years. <sup>1-3</sup> In terms of porous inorganic supports, the family of MCM materials, in particular MCM-41, developed by Mobil in 1992, features a wide range of advantages, from the ordered structure of hexagonal channels with diameters between 2 and 50 nm and high surface area, to the mechanical stability, and the chemical nature of its walls with reactive SiOH groups.<sup>5,6</sup> Recently, the search for heterogeneous catalysts with improved enantioselectivity became an active area of research.

Most effective ligands reported in homogeneous asymmetric catalytic reactions share one prominent common feature – a chiral environment in a rigid and bulky structure. This is vital to create an asymmetric microenvironment around the catalytically active site. By the same token, solid surfaces with confinement effects have been used with success to promote heterogeneous asymmetric catalysis, thus preserving or improving the high product enantioselectivity of their homogeneous analogues.<sup>7–14</sup> Suginome and coworkers reported asymmetric reactions where the stereocontrol was induced by chiral helical backbone polymers.<sup>15–18</sup> Therefore, the preparation of nanostructured materials with helical morphology opened a new field of research due to their potential applications in chiral selective separation, as well as recognition and enantioselective catalysis.<sup>19–23</sup> Nonetheless, the lack of active sites is a drawback not only in mesoporous materials, but also in the helical silica-based materials. In order to by-pass such limitations, different

approaches to introduce more active sites have been developed, ranging from co-condensation or post-synthesis procedures, to matrix doping.<sup>24,25</sup>

Although traditional oxidation catalysts were based on high oxidation state metals, such as Mo(VI), it is known that Mo(II) complexes can act as oxidants after being oxidized in situ by *tert*-butyl hydroperoxide (tbhp) to Mo(VI) species. These are catalytically active in olefin epoxidation in the presence of tbhp as oxygen source. Moreover, compared to the widely studied Mo(VI) complexes, the Mo(II) catalyst precursors offer usually easier handling and stability.<sup>4</sup> Following ongoing research assessing the performance of helical mesoporous materials in asymmetric catalysis,<sup>27</sup> the aim of the present work consists in developing more efficient and selective systems based on single-site active species.<sup>26</sup> We shall address the role of the pore size effect induced by confined space and how it can be tuned by immobilization of a variety of different active site species. Derivatives of  $[MoI_2(CO)_3(NCCH_3)_2]^{28}$  and  $[MoBr(\eta^3-C_3H_5)(CO)_2(NCCH_3)_2]^{29}$  with  $\alpha$ -diimine ligands have proven to be good catalysts in the epoxidation of olefins both in homogeneous and heterogeneous conditions and were thus chosen for this work.

#### 2. Results and Discussion

#### 2.1. Synthesis and characterization of materials

The helical mesostructured silica materials were prepared according to literature, using an entropydriven procedure with an achiral cationic surfactant template,  $[CH_3(CH_2)_{14}N(CH_3)_3Br]$  or  $[CH_3(CH_2)_{16}N(CH_3)_3Br]$ , and ammonia as co-surfactant (**Sil4, Sil6**, respectively).<sup>30</sup> The cosurfactant induces the formation of mesoporous channels with a helical shape, leading to a macroscopic chirality to these materials.<sup>30</sup> They also have a hexagonal structure with silanol groups at the surface that can be functionalized as the MCM materials.<sup>27</sup> The immobilization of the molybdenum complexes in the materials was made by a method reported in the literature, which consists in the grafting of the ligand followed by reaction with the metal precursor. The C<sub>5</sub>H<sub>4</sub>NCH=N(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> was the  $\alpha$ -diimine ligand chosen to immobilize the Mo(II) complexes in these materials, since its asymmetry might contribute to improve the enantioselectivity of the final catalysts. In order to bind the ligand to the material, it must be functionalized with Si(OEt)<sub>3</sub> groups, affording (C<sub>3</sub>H<sub>4</sub>NCH=N(CH<sub>2</sub>)<sub>3</sub>Si(OEt)<sub>3</sub> (**pyca**). The two modified helical materials **Si14-pyca** and **Si16-pyca** are obtained by reaction of **pyca** with the SiOH groups of **Si14, Si16**, and then coordinate to molybdenum (Scheme 1).

Grafting of the **pyca** ligand was straightforward by reaction with a suspension of **Si14** or **Si16** in toluene. The Mo complexes were then introduced by suspending the **Si14-pyca** and **Si16-pyca** materials in dichloromethane and then adding the precursor complexes, [MoI<sub>2</sub>(CO)<sub>3</sub>(NCCH<sub>3</sub>)<sub>2</sub>] (1)

and  $[MoBr(\eta^3-C_3H_5)(CO)_2(NCCH_3)_2]$  (2), to afford the Si14-pyca-1, Si16-pyca-1, Si14-pyca-2, and Si16-pyca-2 materials.



Scheme 1. Derivatization of Si14 and Si16 materials

CHN analyses of these materials showed 7.74 %C, 1.45 %H, and 1.85 %N, for **Si14-pyca-1**, 9.41 %C, 1.75 %H, and 1.92 %N, for **Si14-pyca-2**, 9.26 %C, 1.66 %H, and 2.03 %N for **Si16-pyca-1**, and 10.11 %C, 1.82 %H, and 2.09 %N for **Si16-pyca-2**. Based on the N content, these results also indicated that the loading of the **pyca** complex inside the pores is 0.66 mmol g<sup>-1</sup>, 0.69 mmol g<sup>-1</sup>, 0.73 mmol g<sup>-1</sup> and 0.75 mmol g<sup>-1</sup>, respectively. In addition, the Mo contents were determined to be 4.5%, 4.1%, 5.0% and 6.4%, corresponding to 0.45 mmol g<sup>-1</sup>, 0.43 mmol g<sup>-1</sup>, 0.53 mmol g<sup>-1</sup> and 0.68 mmol g<sup>-1</sup> respectively, and showing that all the Mo cores are coordinated to the surface grafted ligands.

All materials were additionally characterized by DRIFT, powder XRD, SEM and TEM, and <sup>29</sup>Si and <sup>13</sup>C CP MAS-DD NMR. Sorption/desorption N<sub>2</sub> isotherms were also carried out for textural parameters estimation. All spectroscopic/textural characterization features discussed in the following lines were found to be in agreement with related hybrid matrix mesoporous materials.<sup>26-30</sup> The helical channel matrices of the as-prepared **Si14** and **Si16** materials were confirmed by SEM and TEM measurements, Figure 1. The SEM images (not shown) for **Si14** and **Si16** materials consist of rod-like particles. The length of the rods ranges from hundreds of nanometers to 2 µm, whereas the rod diameter varies from 75 to 120 nm. TEM images confirm the helical channel

morphology and illustrate the existence of periodic lattice fringes (Figure 1) along the rods, indicating the presence of helical channels within the rods.<sup>22,30</sup> The periodicity of the lattice fringes indicates that there is a regular environment of the channels, along which reactants and products may diffuse without many constraints. The local structure was also confirmed by powder X-ray diffraction measurements, which agree with the published data and also make possible to confirm that the materials **Si14-pyca** and **Si16-pyca** and **Si14-pyca-1**, **Si16-pyca-1**, **Si14-pyca-2**, and **Si16-pyca-2** are mesostructured.



Fig. 1. TEM (a, b, and c) and SEM (d) images of the Si14-pyca-2 materials.

All the resulting materials were of good quality according to the X-ray diffraction (XRD) powder patterns (Figure 2), which confirmed the hexagonal structure of the materials, by showing 4 reflections indexed to a hexagonal cell as (100), (110), (200) and (210) in the 2-10° 20 range.



Fig. 2. Powder XRD of Si14-based parent and functionalized materials.

The  $d_{100}$  value of reflection (100) for **Si14** and **Si16** is estimated to be 36.4 Å and 40.7 Å, respectively, corresponding to lattice constants of a = 42.0 Å and a = 47.0 Å (a =  $2d_{100}/\sqrt{3}$ ). Materials **Si14-pyca**, **Si16-pyca**, and **Si14-pyca-1**, **Si16-pyca-1**, **Si14-pyca-2**, and **Si16-pyca-2**, obtained after stepwise functionalization with **pyca** and **1** or **2**, still show three reflections although with a slight deviation of the maxima toward higher  $2\theta$  values as compared to **Si14** and **Si16**. For **Si14-pyca**, the  $d_{100}$  value is 37.9 Å with a corresponding lattice constant a = 43.8 Å; for **Si14-pyca-1** and **Si14-pyca-2** the values are, respectively,  $d_{100} = 37.6$  Å and a = 43.4 Å, and  $d_{100} = 37.8$  Å and a = 43.6 Å. Similar observations were made for the set of materials **Si16-pyca, Si16-pyca-1**, and **Si16-pyca-2**. Besides this, data from all the materials are collected in Table 1, summarizing the evolution of their relevant textural properties until the immobilization of complexes **1** and **2**. The observed peak intensity reduction is common to all materials; it is even more significant in the materials with the Mo cores. This is not due to a crystallinity loss, but rather to an X-ray scattering contrast reduction between the silica walls and the pore-filling material. This has been observed for other types of materials and is well described in the literature.<sup>31,32</sup>

Nitrogen sorption/desorption studies at 77 K were performed and have revealed that **Si14** and **Si16** samples exhibit a reversible type IV isotherm (Figure 2), typical of mesoporous solids (pore width between 2 nm and 50 nm, according to IUPAC).<sup>33</sup> The calculated textural parameters ( $S_{BET}$  and  $V_P$ ) of these materials (Table 1) agree with the literature data.<sup>34,35</sup> The capillary

condensation/evaporation step in pristine materials appears in the 0.34–0.44 relative pressures range, while the sharpness of this step reflects a uniform pore size distribution.

The material functionalized with the **pyca** ligand presents much lower N<sub>2</sub> uptake in the isotherm, accounting for the decreases in both  $S_{BET}$  (33% and 31%) and  $V_P$  (49% and 42%), as seen in Table 1. These findings indicate that the ligand was immobilized on the internal silica surface (Figure 3,

Table 1). For the **Si14-pyca-1**, **Si16-pyca-1**, **Si14-pyca-2**, and **Si16-pyca-2** materials, the  $S_{BET}$  and  $V_P$  decrease relative to **Si14-pyca** or **Si16-pyca** is 71%, 48%, 77% and 55%, respectively. This result is in agreement with the  $p/p\theta$  coordinate decrease in the isotherm inflection points after post-synthesis treatments.<sup>36</sup> Furthermore, the maximum of the PSD curve (Figure 3) determined by the BJH method,  $d_{BJH}$ , for **Si14** materials changes from 32.8 Å to 27.5 Å (Table 1); on the other hand for materials **Si16** the changes are between 35.4 Å and 28.5 Å, all values have shifted to lower values after each step and the PSD curves also lose their characteristic shapes. These observations indicate a decrease in the materials pore diameter as well as a loss of the pore size uniformity. Textural parameters for all materials (Table 1) were also found to match values reported in the literature for related systems.<sup>26,37,38</sup>

#### Table 1

Textural parameters of host and composite materials from powder XRD and  $N_2$  isotherms at 77 K, for all prepared materials.

Materials	$d_{100}({ m \AA})$	A (Å)	$S_{BET}$ / m <sup>2</sup> .g <sup>-1</sup>	$\Delta S_{BET}$ <sup>a</sup> / %	$V_p / \text{cm}^3.\text{g}^{-1}$	$\Delta V_p$ <sup>b</sup> / %	d <sub>BJH</sub> / (Å)
Si14	36.4	42.0	1008	-	0.79	-	32.8
Si14-pyca	37.9	43.8	678	-33	0.40	-49	28.6
Si14-pyca-1	37.6	43.6	292	-71	0.20	-75	28.5
Si14-pyca-2	37.8	43.4	520	-48	0.28	-65	27.5
Si16	40.7	47.0	1161	-	1.04	-	35.4
Si16-pyca	42.2	48.7	803	-31	0.60	-42	31.2
Si16-pyca-1	42.7	49.3	270	-77	0.21	-80	28.5
Si16-pyca-2	41.4	47.8	527	-55	0.36	-65	28.5



**Fig. 3.** Nitrogen adsorption studies of **Si14** parent and corresponding functionalized materials at 77K: isotherms (right) and pore size distribution curves (left).

Diffuse reflectance infrared spectroscopy (DRIFT) was also used to characterize the materials (Figure 4 for the **Si14** and Figure S1 for the **Si16** derivatives). The DRIFT spectra of the parent materials **Si14** and **Si16** are typical of a silicate with a broad band in the 3600-3000 cm<sup>-1</sup> range due to hydrogen bonding silanol groups. Other important features comprise the band at ca. 1634 cm<sup>-1</sup> due to OH bending modes, and an intense broad band at 1240-950 cm<sup>-1</sup> assigned to asymmetric stretching vibration modes of the mesoporous framework (vSi-O-Si).<sup>39</sup> After grafting the **pyca** ligand, affording the materials **Si14-pyca** and **Si16-pyca**, the DRIFT spectra show an overall similar profile dominated by the absorptions of the host mesoporous materials. Additionally, new bands were detected evidencing the ligand presence within the pores. The 1637 cm<sup>-1</sup> band can be assigned to the vC=N mode in addition to the OH bending mode of the matrix. Grafting of the pyca ligand was also monitored by probing its vC=N mode, observed in the pyridine moiety of the free **pyca** ligand 1634 cm<sup>-1</sup>. After grafting, this mode is blue shifted to 1637 cm<sup>-1</sup>, which is consistent with the expected transformation resulting in the formation of silvl esters, as documented in the literature.<sup>40</sup> Upon binding the molybdenum complexes  $[MoI_2(CO)_3(CH_3CN)_2]$  (1) and  $[MoBr(\eta^3 -$ C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (2), affording materials Si14-pyca-1, Si14-pyca-2, Si16-pyca-1, and Si16**pyca-2**, respectively, new bands characteristic of the vC=O stretching modes are observed in the DRIFT spectra. Three bands at 2040, 1975 and 1940 cm<sup>-1</sup> and 2042, 1980 and 1944 cm<sup>-1</sup> are displayed in the materials containing 1, Si14-pyca-1 and Si16-pyca-1, while only two, at 1950 and 1863 cm<sup>-1</sup> and 1952 and 1871 cm<sup>-1</sup> can be seen in the spectra of Si14-pyca-2 and Si16-pyca-2 bearing complex 2.

The shift of these bands relative to those of the precursor complexes **1** and **2** reflect the metal– ligand binding. Additionally, the absence of the bands due to the vC=N vibrational modes from the acetonitrile (CH<sub>3</sub>CN) ligands shows that they have been replaced by the immobilized ligand.



Fig. 4. Infrared Spectra of the Si14 parent and corresponding functionalized materials.

<sup>13</sup>C and <sup>29</sup>Si solid state NMR spectroscopy studies were also performed on the materials and the resonances observed were assigned according to the literature.<sup>28</sup> <sup>13</sup>C CP MAS-DD NMR spectra for **Si14-pyca, Si14-pyca-1** and **Si14-pyca-2** are presented in Figure 5 and in Figure S2 (Supporting Information) for **Si16-pyca, Si16-pyca-1**, and **Si16-pyca-2**.



Fig. 5. <sup>13</sup>C CP MAS-DD NMR spectra of Si14-pyca, Si14-pyca-1 and Si14-pyca-2 materials.

In the <sup>13</sup>C spectra (Figure 5) three strong signals are observed in the 0 - 100 ppm range corresponding to the aliphatic carbons closer to the SiOR group in the ligands. The signal at the

lower  $\delta$  is attributed to the carbon linked to Si, at 9.5 ppm for **Si14-pyca**, at 9.1 ppm for **Si14-pyca-1**, and at 10.1 ppm for **Si14-pyca-2**. Several signals observed between 100 ppm to 200 ppm are assigned to the pyridyl and imine carbons of the **pyca** ligand. In general the same signals are observed in the <sup>13</sup>C solid state NMR spectra of the materials after their reaction with the Mo core of the precursor complexes.

Figure 6 shows the <sup>29</sup>Si CP MAS-DD NMR spectra for pristine **Si14** and the derivatized **Si14-pyca**, **Si14-pyca-1**, and **Si14-pyca-2** materials (the corresponding spectra for the **Si16** derivatives can be found in Figure S3 in Supporting Information). The parent **Si14** material displays two broad convoluted resonances in the <sup>29</sup>Si CP MAS-DD NMR spectrum at -101.1 and -111.3 ppm, assigned to  $Q^3$  and  $Q^4$  species of the silica framework, respectively  $[Q^n = -Si(OSi)_n(OH)_{4n}]$ . A weak shoulder is also observed at -92.1 ppm due to the  $Q^2$  species. The  $Q^3$  sites are associated with single silanols Si-OH (including hydrogen-bonded silanols), whereas the  $Q^2$  sites correspond to geminal silanols  $[Si(OH)_2]$ . The <sup>29</sup>Si CP MAS-DD spectrum of **Si14-pyca** also displays three broad signals at -92.5, 101.5, and 102.1 ppm, assigned to  $Q^2$ ,  $Q^3$  and  $Q^4$  organosilicon species, respectively. New signals corresponding to the  $T^1$ ,  $T^2$  and  $T^3$  species of the  $Si(OR)_3$  groups of **pyca** ligand were also observed at -49, -54.8 and -66.3 ppm, respectively.

The <sup>29</sup>Si CP MAS-DD spectra in Figure 6 show that reaction of **Si14-pyca** with the (organo)metallic complex  $[MoI_2(CO)_3(CH_3CN)_2]$  (1) did not significantly change the environment of Si, as expected, indicating that the metal fragment reacted with the immobilized ligand and did not interact with the wall surface.



Fig. 6. <sup>29</sup>Si CP MAS-DD NMR spectra of Si14 parent and functionalized materials.

All the information gathered from the different characterization techniques allows us to conclude that the functionalization of the surface of the helically shaped pores materials with the **pyca** ligand and their subsequent coordination with metal fragments was performed successfully.

### 2.2. Catalytic Studies

The catalytic activity of the **Si14-pyca-1**, **Si14-pyca-2**, **Si16-pyca-1**, and **Si12-pyca-2** materials was benchmarked in olefin epoxidation using *tert*-butylhydroperoxide (tbhp) as oxygen source. Special attention was dedicated to stereoselectivity of products to test the specific helical features of the matrix. We have therefore studied the catalytic epoxidation of *cis*-cyclooctene, styrene, *cis*-hex-3-en-1-ol, *trans*-hex-2-en-1-ol, geraniol, and R-(+)-limonene (Table 2). Blank runs (without catalyst and in the presence of oxidizing agent) gave virtually no conversion of starting material. All materials catalyzed selectively the oxidation of *cis*-cyclooctene to the corresponding epoxide, without formation of any by-products (Table 2, entries 1 to 4). The conversions are high, ranging from 79 to 89 % in **Si14-pyca-2**, **Si16-pyca-1**, and **Si16-pyca-2**, and much lower for the **Si14-pyca-1** material (31 %). Although the Mo loading in **Si14-pyca-1** material is 4.10 %, it is the lowest in all the materials and may have a direct influence in cyclooctene epoxide yield. The kinetic profiles are very fast for the materials reaching high conversions, but much slower for **Si14-pyca-1** (Figure 7-bottom). The complexes **1** <sup>28</sup> and **2**<sup>29</sup> exhibited conversions of 63 and 99 %, respectively, which increased to 80 and 100 % when they were immobilized in MCM-41 (**MCM-1** and **MCM-2**).



**Fig. 7.** Kinetic profiles for *cis*-cyclooctene oxide yield (bottom) and R-(+)-limonene conversion (top).

All materials present low conversions for the epoxidation of *cis*-hex-3-en-1-ol (entries 9-12) and styrene (entries 5-8), **Si14-pyca-2** reaching 75%, but all the others remaining below 56 %. For styrene (sty), the major product detected is not the epoxide but benzaldehyde, formed by oxidative cleavage of the former. Styrene conversion was 61 and 100 % in the presence of **1** and **MCM-1**. <sup>28</sup> Complex **2** and **MCM-2** showed modest conversions of 29 and 49 %, but higher selectivities toward the epoxide (82 and 58 %, respectively). Complex **2** and **MCM-2** converted 100 and 99 % of both *cis*-hex-3-en-1-ol and geraniol to the corresponding epoxides (100% for the first and with lower selectivity for geraniol), but at higher temperatures. <sup>29</sup> For the epoxidation of geraniol (ger), the large pore materials **Si16-pyca-1** and **Si16-pyca-1** display very high conversions and selectivity, yielding geraniol-2,3-epoxide as the major product (Table 2, entries 18 and 20) with selectivity of 94% and 91%, respectively. The by-product is geranial, obtained in the presence of the other two catalysts with yields of 36% (**Si14-pyca-1**) and 60% (**Si14-pyca-2**).

We extended the tests to substrates, such as *trans*-hex-2-en-1-ol, *cis*-hex-3-en-1-ol, and *R*-(+)-limonene, with more functional groups, to evaluate more extensively both chemo- and

stereoselectivity. As shown in Table 2, epoxidation of *trans*-hex-2-en-1-ol led to the formation of hexan-1-ol-2,3-epoxide as major product in all catalytic systems tested. For *R*-(+)-limonene, however, the results were different (Table 3, entries 9 to 12). Two major products, the endocyclic 6,7-epoxide and the diepoxide (2,3 and 6,7), were obtained for all catalysts in ratios close to 40/60 %, the **Si14** based materials favoring the first, with low/medium conversion, and the **Si16** ones affording more diepoxide and displaying a high conversion (above 93 %). The kinetic profiles are similar for all catalysts (Figure 7, top) during the first minutes. There is an induction period, but the more active **Si16** materials display a higher rise than the others and reach higher conversions, as discussed.

When assessing the catalytic performance of heterogeneous systems, it is important to evaluate catalyst stability in terms of both active center leaching and recycling. To test active site leaching, the oxidation of *trans*-2-hexen-1-ol was chosen. The catalyst was removed by filtration after 2 h reaction of a normal run, and the reaction was followed until the end of the 24 h period. The conversion of *trans*-2-hexen-1-ol was 22% after 2 h, and did not change during the remaining time, although it reached 58 % when the catalyst was not removed (entry 16). This shows clearly that the reaction stops when the heterogeneous catalyst was filtered off the reaction slurry and that there is little or no leaching to the homogeneous phase. It is possible to conclude that the catalysts are truly heterogeneous in nature.

The recycling experiments were conducted using **Si16-pyca-1**, **Si14-pyca-2**, and **Si16-pyca-2** as catalyst, and *trans*-hex-2-en-1-ol as substrates during five successive runs (Table 2, entries 14 and 16). The catalyst was filtered, washed with dichloromethane, and dried prior to each recycling experiment. For **Si16-pyca-1**, the conversion and selectivity toward the epoxide are maintained (or slightly increased to ~97 %) during four runs both decreasing in the fifth by 22 %. The results change a bit more when the catalyst contains the allyl complex (**Si14-pyca-2**, and **Si16-pyca-2**), but remain close to the initial values of the first run both in conversion and in selectivity.

**Table 2.** Catalytic olefin epoxidation of *cis*-cyclooctene, styrene, *cis*-hex-3-en-1-ol, *trans*-hex-2-en-1-ol, geraniol, and *R*-(+)-limonene using **Si14/16-pyca-1/2** catalysts.

Entry	<b>Epoxide</b> <sup><i>a</i></sup>	Catalyst	Conv. % <sup>b</sup>	Select. % <sup>c</sup>
1		Si14-pyca-1	31	100
2		Si16-pyca-1	83	100
3		Si14-pyca-2	79	100
4		Si16-pyca-2	89	100
5		Si14-pyca-1	56	17
6		Si16-pyca-1	75	11
7		Si14-pyca-2	18	37
8		Si16-pyca-2	29	28
9		Si14-pyca-1	21	100
10	OH	Si16-pyca-1	50	100
11	↓ Û	Si14-pyca-2	53	100
12	O OH	Si16-pyca-2	33	100
13	ОН	Si14-pyca-1	65	73
14		Si16-pyca-1	97/97/98/97/75 <sup>d</sup>	89/88/93/86/79 <sup>d</sup>
15	Un	Si14-pyca-2	76/65/63/51/51 <sup>d</sup>	84/91/98/75/69 <sup>d</sup>
16		Si16-pyca-2	58/57/54/59/56 <sup>d</sup>	69/75/83/85/82 <sup>d</sup>
17	Q_	Si14-pyca-1	35	57/36 <sup>e</sup>
18	ОН ОН	Si16-pyca-1	94	94
19		Si14-pyca-2	34	29/60 <sup>e</sup>
20		Si16-pyca-2	91	91
21		Si14-pyca-1	57	$51/38^{\mathrm{f}}$
22		Si16-pyca-1	98	$40/58^{\mathrm{f}}$
23		Si14-pyca-2	73	$60/35^{f}$
24		Si16-pyca-2	93	$44/54^{\mathrm{f}}$

<sup>*a*</sup> All reactions were carried in dichloromethane in the presence of 2 eq. of oxidant (tbhp) and 175 mg of heterogeneous at 328 K; <sup>*b*</sup> Calculated after 24 h; <sup>*c*</sup> Calculated as 'Yield of epoxide''/'Conversion''x100% calculated after 24 h; <sup>*d*</sup> 1/2/3/4/5 run; <sup>*e*</sup> Selectivity for geranial; <sup>*f*</sup> Selectivity for diepoxide.

Mixtures of two major products (endocyclic epoxide and diepoxide) were obtained in the oxidation of R-(+)-limonene with all the catalysts, and for geraniol (2,3-epoxide and geranial) with the small

pore materials **Si14-pyca-1** and **Si14-pyca-2**. Only for the large pore materials was the geraniol oxidation selective toward the epoxide (>90 %) with high conversion. Oxidation of styrene always led to benzaldehyde as major product after 24 h, though at shorter reaction times (8 h) epoxide is generally the major product.

The evaluation of the enantioselectivity induced by the chiral nature of the heterogeneous catalysts was the aim of a set of tests. The oxidation of *cis*-hex-3-en-1-ol, *trans*-hex-2-en-1-ol and R-(+)-limonene was performed in conditions allowing the determination of the enantiomeric ratios. The results (Table 3) show that the epoxide from *cis*-hex-3-en-1-ol is not obtained with high optical selectivity. The two diastereomers 3R, 4S and 3S, 4R are formed in almost 50:50 amounts, except in the presence of **Si14-pyca-2**, containing the allylic bromide complex **2**, where the latter is slightly preferred (66 %). Both *cis* and *trans* diastereomers of R-(+)-limonene 6,7-epoxides are also obtained independently of the catalyst, in a 1:2 ratio, with a preference for the *trans* with three of them and 1:1 with **Si14-pyca-1**. This result differs from what was obtained in the oxidation of S-(-)-limonene by complex **2** and **MCM-2** (100 % conversions), where the main product was the diepoxide in 96 and 88 %. Although the % of the *cis* and *trans* epoxides was too small, they were in 2:1 and 1:1 amounts.

The situation is completely different when it comes to epoxidation of the *trans*-hex-2-en-1-ol substrate. The diastereomeric ratio is much higher in general, with a preference for the 2*S*, 3*R* diastereomer relative to the 2*R*, 3*R*, but both **Si14-pyca-2** and **Si16-pyca-2** lead to 100 % of the 2*S*, 3*R*. These two catalysts contain the complex [MoBr( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(pyca)] (2) immobilized in the two different materials (Table 3).

**Table 3**Product selectivity

Catalyst			
	OH	ОЧ	
	$(3R,4S)^{a,b}$	$(3S, 4R)^{a,b}$	
Si14-pyca-1	49	52	
Si16-pyca-1	45	55	
Si14-pyca-2	34	66	
Si16-pyca-2	45	54	
	O OH	Л ОН	
	$(2S,3R)^{a,c}$	$(2R, 3R)^{a,c}$	
Si14-pyca-1	69	31	
Si16-pyca-1	90	10	
Si14-pyca-2	100	0	
Si16-pyca-2	100	0	
	Jun Co		
	<i>cis</i> -limox <sup>b</sup>	<i>trans</i> -limox <sup>b</sup>	
Si14-pyca-1	56	44	
Si16-pyca-1	27	73	
Si14-pyca-2	34	66	
Si16-pyca-2	37	63	

<sup>a</sup> Determined by chiral GC; <sup>b</sup> Values refers to enantiomeric ratio;

<sup>c</sup> Values refers to diastereomeric ratio.

These heterogeneous catalyst show reduced performance compared to other previous reported ones, also based on helical mesoporous materials with Mo(II) complexes, but with a 2,2'-bipyridine derived ligand.<sup>27</sup> On the other hand, both complexes **1** and **2** bearing the pyca ligand and immobilized in MCM-41 (**MCM-1** and **MCM-2**) have proved to be active catalysts and they display some chiral discrimination.<sup>28,29</sup> It binds to the material wall by its long arm, while the ligand in other materials had a bidentate and bifunctionalized ligand that might be bound to the surface more rigidly. These topological differences may control the activity of the catalysts and explain the different behavior. Pore diameter does not significantly influence the selectivity, although it affects the kinetics, as discussed above. For a given catalyst the large pore system consistently performs

better than the narrow pore one, independently of the substrate (Figure 8). The allylic complexes **2** are in general more selective than complexes **1**, despite the nature of the material.



**Fig. 8.** Substrate (*cis*-cyclooctene, *cis*-hex-3-en-1-ol, *trans*-hex-2-en-1-ol, and *R*-(+)-limonene) conversion kinetics vs pore size profile. Please notice the different ranges in the vertical scales.

#### 3. Experimental Section

#### 3.1. General

All reagents were obtained from Aldrich and used as received. Commercial grade solvents dried and deoxygenated by standard procedures (Et<sub>2</sub>O, tetrahydrofuran and toluene over Na / benzophenone and CH<sub>2</sub>Cl<sub>2</sub> over CaH<sub>2</sub>), distilled under nitrogen, and kept over 4 Å molecular sieves. The **pyca** ligand<sup>28</sup> was prepared according to literature methods. The helical mesostructured silica materials synthesis followed a reported procedure with achiral cationic surfactant templates, using ammonia as co-surfactant and [CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>N(CH<sub>3</sub>)<sub>3</sub>Br] to prepare **Si14** materials, or [CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>N(CH<sub>3</sub>)<sub>3</sub>Br] to prepare **Si16**.<sup>30</sup>

FTIR spectra were obtained as Diffuse Reflectance (DRIFT) measurements on a Nicolet 6700 in the 400-4000 cm<sup>-1</sup> using 2 cm<sup>-1</sup> resolution. Powder XRD measurements were taken on a Philip

Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using a monochromatized Cu-Kα radiation as incident beam, using 40 kV and 30 mA.

Solid state NMR measurements were performed at room temperature on a Tecmag/Bruker 300 wide bore spectrometer operating at 59.60 and 75.47 MHz for the observation of <sup>29</sup>Si and <sup>13</sup>C resonances, respectively. The standard magic angle spinning (MAS) cross-polarization – dipolar decoupling RF pulse sequence (CP-DD) was carried out at ca. 4 kHz spinning rate. For the acquisition of <sup>29</sup>Si spectra, were selected 5 ms contact time, 6 s recycling delay and a number of scans always higher than 3000; the Hartmann-Hahn condition was optimized using tetrakis-trimethylsilyl-silane and tetramethylsilane (tms) was the external reference to set the chemical shift scale ( $\delta = 0$ ). <sup>13</sup>C spectra were recorded with 2 ms contact time, 4s recycling delay and a number of scans higher than 900. The Hartmann-Hahn condition was optimized using glycine, also the external reference to set the chemical shift scale (<sup>13</sup>CO at 176.1 ppm).

The N<sub>2</sub> sorption measurements were obtained in an automatic apparatus (ASAP 2010; Micromeritics). BET specific surface areas ( $S_{Bet}$ ,  $p/p_0$  from 0.03 to 0.13) and specific total pore volume,  $V_p$  were estimated from N<sub>2</sub> adsorption isotherms measured at 77 K. The pore size distributions (PSD) were calculated by the BJH method using the modified Kelvin equation with correction for the statistical film thickness on the pore walls <sup>41,42</sup>. The statistical film thickness was calculated using Harkins-Jura equation in the  $p/p_0$  range from 0.1 to 0.95. Microanalyses for CHN and Mo quantification were performed at CACTI, University of Vigo. CHN analyses were performed on a Fisons EA 1108; Mo quantification was performed on a Perkin Elmer Optima 4300DV using In as internal standard.

SEM images were obtained on a FEG-SEM (Field Emission Gun Scanning Electron Microscope) from JEOL, model JSM-7001F. TEM images were obtained on a Hitachi microscope, model H8100 with a LaB6 filament using an acceleration tension of 200 kV.

#### 3.2. Synthesis of Si14-pyca and Si16-pyca

A solution of the **pyca** ligand (0.70 g, 1.1 mmol) in 10 mL of toluene was added to a suspension of 1 g of the materials **Si14** or **Si16** in 10 mL of toluene. The mixture was heated at 373 K during 9 hours. The resulting solid was filtered, washed with 4x20 mL of dichloromethane and dried under vacuum.

#### Si14-pyca

Elemental analysis (%): found C 10.33, H 1.61, N 2.44.

DRIFT (KBr, v/cm<sup>-1</sup>): 3412 (s), 3266 (w), 2977 (m), 2928 (m), 1637 (s), 1618 (s), 1475 (m), 1444 (m), 1385 (m), 1236 (s), 1086 (s), 963 (s), 799 (m). <sup>13</sup>C CP/MAS (DD) NMR (δ ppm): 9.5 (C<sub>10</sub>), 16.6 (OCH<sub>2</sub>CH<sub>3</sub>), 23.7 (C<sub>9</sub>), 50.9 (C<sub>8</sub>), 58.0 (OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>). <sup>29</sup>Si CP MAS-DD NMR (δ ppm): -49.0 (T<sup>1</sup>), -54.8 (T<sup>2</sup>), -66.3 (T<sup>3</sup>), -92.5 (Q<sup>2</sup>), -101.5 (Q<sup>3</sup>), -112.1 (Q<sup>4</sup>).

### Si16-pyca

Elemental analysis (%): found C 11.85, H 1.73, N 2.72.

DRIFT (KBr, v/cm<sup>-1</sup>): 3480 (s), 3415 (s), 2981 (w), 2827 (w), 1637 (s), 1618 (s), 1572 (s), 1561 (s), 1413 (s), 1385 (s), 1236 (s), 1082 (s), 966 (w), 791 (m). <sup>13</sup>C CP MAS-DD NMR (δ ppm): 9.5 (C<sub>10</sub>), 16.6 (OCH<sub>2</sub>CH<sub>3</sub>), 23.7 (C<sub>9</sub>), 50.9 (C<sub>8</sub>), 58.6

(OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>).

<sup>29</sup>Si CP/MAS (DD) NMR (δ ppm): -57.5 (T<sup>2</sup>), -101.3 (Q<sup>3</sup>), -109.5 (Q<sup>4</sup>).

### 3.3. Synthesis of Si14-pyca-1 and Si16-pyca-1

A solution of  $[MoI_2(CO)_3(CH_3CN)_2]$  (0.335 g, 0.65 mmol) in 5 mL of dichloromethane was added to a suspension of 0.9 g of **Si14-pyca** or **Si16-pyca** in 15 mL of dichloromethane. The mixture was stirred under inert atmosphere at room temperature overnight. The resulting solid was filtered, washed with 2x20 mL of dichloromethane and dried several hours under vacuum.

### Si14-pyca-1

Elemental analysis (%): found C 7.74, H 1.45, N 1.85, Mo 4.50. DRIFT (KBr, v/cm<sup>-1</sup>): 3409 (s), 3259 (w), 3235 (w), 2979 (w), 2931 (w), 2040 (s), 1975 (s), 1940 (s), 1637 (s), 1618 (s), 1448 (w), 1408 (w), 1385 (m), 1235 (s), 1088 (s), 958 (m), 802 (m), 473 (s). <sup>13</sup>C CP MAS-DD NMR (δ ppm): 9.1 (C<sub>10</sub>), 16.9 (OCH<sub>2</sub>CH<sub>3</sub>), 20.8 (C<sub>9</sub>), 42.5 (C<sub>8</sub>), 58.6 (OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>). <sup>29</sup>Si CP MAS-DD NMR (δ ppm): -48.3 (T<sup>1</sup>), -56.5 (T<sup>2</sup>), -92.9 (Q<sup>2</sup>), -101.1 (Q<sup>3</sup>), -109.7 (Q<sup>4</sup>).

### Si16-pyca-1

Elemental analysis (%): found C 9.26, H 1.66, N 2.03, Mo 5.00. DRIFT (KBr, ν/cm<sup>-1</sup>): 3415 (s), 2980 (w), 2931 (w), 2853 (w), 2042 (s), 1980 (s), 1944 (s), 1618 (s), 1466 (w), 1447 (m), 1385 (m), 1237 (s), 1087 (s), 962 (m), 802 (s), 459 (s). <sup>13</sup>C CP MAS-DD NMR (δ ppm): 10.1 (C<sub>10</sub>), 17.2 (OCH<sub>2</sub>CH<sub>3</sub>), 30.2 (C<sub>9</sub>), 51.8 (C<sub>8</sub>), 59.6 (OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>).

<sup>29</sup>Si CP MAS-DD NMR (δ ppm):-48.3 (T<sup>1</sup>), -56.5 (T<sup>2</sup>), -92.9 (Q<sup>2</sup>), -101.1 (Q<sup>3</sup>), -109.7 (Q<sup>4</sup>).

### 3.4. Synthesis of Si14-pyca-2 and Si16-pyca-2

A solution of  $[MoBr(\eta^3-C_3H_5)(CO)_2(CH_3CN)_2]$  (1.0 mmol, 0.355 g) in 5 mL of dichloromethane was added to a suspension of 0.9 g of **Si14-pyca** or **Si16-pyca** in 15 mL of dichloromethane. The mixture was stirred in inert atmosphere at room temperature overnight. The resulting solid was filtered, washed with 2x20 mL of dichloromethane and dried under vacuum.

### Si14-pyca-2

Elemental analysis (%): found C 9.41, H 1.75, N 1.92, Mo 4.10. DRIFT (KBr, v/cm<sup>-1</sup>): 3415 (s), 3245 (w), 2980 (w), 2924 (w), 2853 (w), 1950 (s), 1863 (s), 1639 (s), 1618 (s), 1474 (m), 1447 (m), 1385 (m), 1235 (s), 1085 (s), 964 (m), 797 (s), 592 (w), 452 (s). <sup>13</sup>C CP MAS-DD NMR ( $\delta$  ppm): 9.1 (C<sub>10</sub>), 17.2 (OCH<sub>2</sub>CH<sub>3</sub>), 42.8 (C<sub>9</sub>), 54.1 (C<sub>8</sub>), 59.6 (OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>). <sup>29</sup>Si CP MAS-DD NMR ( $\delta$  ppm): -57.3 (T<sup>2</sup>), -101.5 (Q<sup>3</sup>), -109.7 (Q<sup>4</sup>).

### Si16-pyca-2

Elemental analysis (%): found C 10.11, H 1.82, N 2.09, Mo 6.40. DRIFT (KBr, v/cm<sup>-1</sup>): 3409 (s), 3260 (w), 2978 (w), 2927 (w), 1952 (s), 1871 (s), 1618 (s), 1468 (w), 1445 (w), 1385 (m), 1238 (s), 1090 (s), 967 (m), 806 (s), 452 (s). <sup>13</sup>C CP MAS-DD NMR (δ ppm): 8.8 (C<sub>10</sub>), 17.2 (OCH<sub>2</sub>CH<sub>3</sub>), 41.8 (C<sub>9</sub>), 52.8 (C<sub>8</sub>), 59.3 (OCH<sub>2</sub>CH<sub>3</sub>), 100-200 (C<sub>pyridine,imine</sub>). <sup>29</sup>Si CP MAS-DD NMR (δ ppm):-48.7 (T<sup>1</sup>), -56.1 (T<sup>2</sup>), -101.5 (Q<sup>3</sup>), -108.5 (Q<sup>4</sup>).

### 3.5. Catalytic studies

The materials were tested as catalysts in the epoxidation of olefins and allylic alcohols, such as, *cis*-cyclooctene, styrene, 1-octene, *trans*-hex-2-en-1-ol, *cis*-3-hex-1-ol, geraniol and R-(+)-limonene, using *t*-butylhydroperoxide (tbhp) as oxidant (Aldrich, 5.5 M in decane). The catalytic oxidation tests were carried out at 328 K under air in a vessel equipped with a magnetic stirrer and a condenser. In a typical experiment the vessel was loaded with olefin or alcohol (100%), internal standard (dibutyl ether, DBE), catalyst (175 mg), oxidant (200%) and 3 mL of dichloromethane as solvent. The final volume of the reaction was ca. 6 mL. Addition of the oxidant determined the initial time of the reaction. Conversion, product yields and stereochemistry were monitored by sampling periodically and analyzing them using a Shimadzu QP2100-Plus GC/MS system and a capillary column (Teknokroma TRB-5MS/TRB-1MS or Restek Rt- $\beta$ DEXsm) operating in the linear

velocity mode. Leaching and recycling experiments, in general, were carried out as described above for *trans*-hex-2-en-1-ol epoxidation using material **Si16-pyca-2** and **Si16-pyca-1** as catalyst; conversion and product yields were monitored as described above. For the leaching experiments after 2 h reaction, the catalyst was filtered off, and the reactions continued under the same conditions.

In the case of the recycling experiments, after each cycle (24 h), the catalyst was filtered, washed with dichloromethane, and dried prior to reuse in a new catalytic cycle.

#### 4. Conclusions

In this work we assessed the capacity of helical mesoporous materials, with different pore diameter, and containing two different kinds of immobilized Mo(II) complexes, to induce chirality in catalytic reactions. The materials with both pore diameters were studied in parallel to test symmetric and asymmetric substrates, to evaluate stereoselectivity enhancement.

The helical nature of the materials was confirmed by TEM experiments. As main conclusions, the performance of the materials synthesized in the presence of the longer  $C_{16}$  chain surfactants (larger pore) was better, leading in general to higher conversions and selectivities (Table 2). In addition, they also showed faster kinetics, probably owing to the easier diffusion fluxes of reactants and products inside the pores. On the other hand, the use of a metal complex containing an asymmetric ligand in the active site is found to enhance product stereoselectivity independently of the host material. The not very high activity of these catalysts was compensated by their robustness, as attested in the recycling experiments by the comparable conversions and selectivities along four/five runs, and their heterogeneous nature, probed in experiments in which leaching was not observed to any meaningful extent.

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