

# Efficiency of Polyoxometalate-Based Mesoporous Hybrids as Covalently Anchored Catalysts

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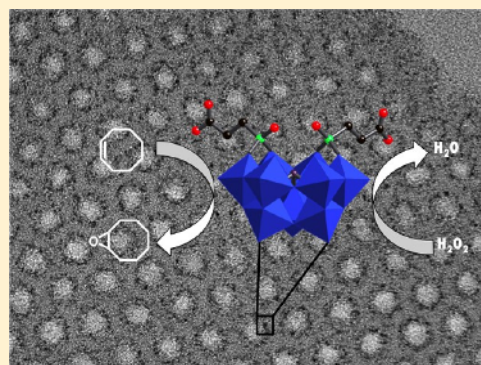
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## Supporting Information

**ABSTRACT:** Polyoxometalate (POM) hybrids have been covalently immobilized through the formation of amide bonds on several types of mesoporous silica. This work allows the comparison of three POM-based mesoporous systems, obtained with three different silica supports in which either the organic functions of the support (amine vs carboxylic acid) and/or the structure of the support itself (SBA-15 vs mesocellular foams (MCF)) were varied. The resulting POM-based mesoporous systems have been studied in particular by high resolution transmission electronic microscopy (HR-TEM) in order to characterize the nanostructuration of the POMs inside the pores/cells of the different materials. We thus have shown that the best distribution and loading in POMs have been reached with SBA-15 functionalized with aminopropyl groups. In this case, the formation of amide bonds in the materials has led to the nonaggregation of the POMs inside the channels of the SBA-15. The catalytic activity of the anchored systems has been evaluated through the epoxidation of cyclooctene and cyclohexene with H<sub>2</sub>O<sub>2</sub> in acetonitrile. The reactivity of the different grafted POMs hybrids has been compared to that in solution (homogeneous conditions). Parallels can be drawn between the distribution of the POMs and the activity of the supported systems. Furthermore, recycling tests together with catalyst filtration experiments during the reaction allowed us to preclude the hypothesis of a significant leaching of the supported catalyst.



## 1. INTRODUCTION

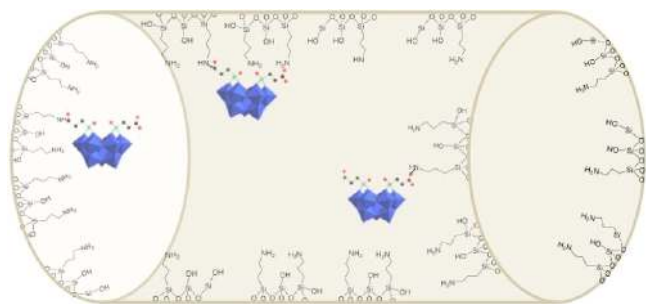
Regarding their unique properties in terms of thermal stability, resistance toward oxidative conditions, and/or hydrolysis (provided that pH conditions are controlled), polyoxometalates (POMs) have been thoroughly considered as intrinsic oxidation catalysts either in homogeneous or heterogeneous conditions.<sup>1–4</sup> In the latter case, POMs are generally dispersed on oxide supports in order to circumvent their very low surface area in the solid state. In most examples, POMs are not strongly chemically bonded to the support. Studies generally involve either a simple physisorption or an electrostatic interaction with a positively charged support, acting like counterions.<sup>3,5–10</sup> This strategy has also been recently applied to surface-modified graphene.<sup>11</sup> POMs may also be immobilized successfully into materials through various other strategies<sup>12</sup> such as their encapsulation into metal–organic frameworks (MOFs),<sup>13,14</sup> their intercalation into layered double hydroxides,<sup>15</sup> or their

one-pot embedding into a silica matrix via co-condensation sol–gel methods<sup>16</sup> (including the covalent grafting of vacant POMs into the walls of hybrid supports).<sup>17,18</sup>

We recently focused on the elaboration of new mesoporous materials functionalized with nucleophilic (vacant) POMs for applications in the field of anchored homogeneous catalysis.<sup>19</sup> In this preliminary work, we demonstrated, for the first time, that functionalization of both the vacant polyoxometalate species and the mesoporous silica support by complementary organic functions provides an efficient strategy for their covalent linkage. The principle was illustrated using an organophosphonate derivative of trivalent POMs bearing carboxylic acid functionalities on one hand and an NH<sub>2</sub>-functionalized mesoporous SBA-15 support on the other hand

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63 (Figure 1). It is noteworthy that, following this report, such a  
64 strategy has been applied to the grafting of organosilyl



**Figure 1.** Covalent grafting of phosphonate derivatives of vacant POMs onto the walls of NH<sub>2</sub>-functionalized SBA-15 silica. Counterions associated with the POMs are not represented for sake of clarity.

65 derivatives of Dawson-type POMs onto macroporous polymer  
66 matrices, via azide alkyne Huisgen cycloaddition.<sup>20</sup>

67 It is well-known that the efficiency of supported molecular  
68 catalysts is related not only to their accessibility but also to their  
69 dispersion and accessibility on the support. One of the keys for  
70 obtaining efficient materials are anchoring platforms with high  
71 specific surface and porosity, such as the SBA-15 silica used in  
72 our previous study.<sup>19</sup> However, an increasing number of  
73 inorganic supports are now available in the literature for  
74 catalysis purposes, with morphology and/or composition and/  
75 or surface modification that can now be easily modulated.<sup>21,22</sup>  
76 The effects of the modification of the support on the dispersion  
77 of the catalyst are thus questions we obviously need to address.  
78 Controlled immobilization of organometallic complexes in  
79 mesoporous silica has been reported.<sup>23</sup>

80 In the present work, we propose an extended study of the  
81 grafting of hybrids POMs on various organically modified  
82 supports. Three mesoporous supports have been examined, in  
83 which either the organic functions displayed (aminopropyl vs  
84 carboxypropyl) or the type of material itself, SBA-15 vs MCF  
85 (siliceous MesoCellular Foam), was varied. We thus analyzed  
86 both effects on the dispersion of the POMs in the different  
87 materials, in particular by high resolution transmission  
88 electronic microscopy (HR-TEM). In addition, the dispersion  
89 has then been tentatively correlated with the catalytic efficiency  
90 of the supported POMs in the cyclooctene and cyclohexene  
91 epoxidation by H<sub>2</sub>O<sub>2</sub>, used here as convenient model  
92 reactions.<sup>24</sup>

## 2. EXPERIMENTAL SECTION

93 **2.1. Materials and Reagents.** Solvents and other reagents were  
94 obtained from commercial sources and used as received, except for  
95 triethylamine and acetonitrile, which were distilled. The complexes  
96 (<sup>n</sup>Bu<sub>4</sub>N)<sub>3</sub>NaH[As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>]<sub>19</sub>, TBA<sub>3</sub>NaH-  
97 (POM-CO<sub>2</sub>H), and (<sup>n</sup>Bu<sub>4</sub>N)<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}<sub>2</sub>]<sub>25,26</sub>  
98 TBA<sub>4</sub>H(POM-NH<sub>2</sub>), were prepared as previously described.

99 Solids were characterized by attenuated total reflection infrared  
100 spectroscopy, using Tensor R27 FTIR equipped with a ZnSe crystal  
101 with resolution better than 1 cm<sup>-1</sup>. Raman spectra were recorded on  
102 solid samples on a Kaiser Optica Systems HLSR spectrometer  
103 equipped with a near-IR laser diode working at 785 nm. The <sup>1</sup>H  
104 (300.13 MHz), <sup>13</sup>C (75.6 MHz), and {<sup>1</sup>H} <sup>31</sup>P NMR (121.5 MHz)  
105 solution spectra were recorded in 5 mm o.d. tubes on a Bruker Avance  
106 300 spectrometer equipped with a QNP probehead. <sup>13</sup>C CP MAS  
107 NMR spectra were recorded at 125.77 MHz on a Bruker AVANCE III  
108 500 spectrometer (11.7 T) with a 4 mm Bruker probe and at a  
109 spinning frequency of 10 kHz (recycle delay = 5 s, contact time = 10

ms). <sup>31</sup>P MAS NMR spectra were recorded at 283.31 MHz on a 110  
Bruker AVANCE III 700 spectrometer (16.4 T) equipped with 2.5  
111 mm Bruker probe and at a spinning frequency of 30 kHz. Chemical  
112 shifts were referenced to tetramethylsilane (TMS) for <sup>13</sup>C and to 85%  
113 aqueous H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. Thermogravimetric analyses (TGA) were  
114 performed under air with a TA-Instrument SDT Q600 between 20 and  
115 900 °C (air flow: 100.0 mL min<sup>-1</sup>, 10 °C min<sup>-1</sup>). Elemental analyses  
116 were performed by the Institut des Sciences Analytiques du CNRS  
117 (Villeurbanne, France). N<sub>2</sub> sorption analyses of the pretreated  
118 materials (100 °C) were obtained at -196 °C using an ASAP-2020  
119 Micromeritics apparatus. Small-angle XRD measurements were carried  
120 out on a Bruker D8 Advance XRD diffractometer. X-ray fluorescence  
121 analyses were conducted with an energy dispersive spectrometer  
122 (XEPOS with Turboquant powder software). HR-TEM analyses were  
123 realized on a microscope operating at 200 kV with a resolution of 0.18  
124 nm (JEOL JEM 2011 UHR) equipped with an EDX system (PGT  
125 IMIX-PC). Samples were dispersed in resin and cut with an  
126 ultramicrotome. The lamellas of 50 nm thickness were then deposited  
127 on Cu grid covered with an amorphous carbon film.

**2.2. Preparation of the Functionalized Supports.** **2.2.1. SBA-15 Silica with 3-Aminopropyl Groups (SBA-NH<sub>2</sub>).**<sup>19</sup> SBA-NH<sub>2</sub> was  
129 obtained in a two-step procedure, after functionalization of a  
130 preformed SBA-15 with 3-aminopropyltriethoxysilane, as follows.  
131

SBA-15 silica (1.0 g) previously dried at 350 °C for 12 h was  
132 dispersed in 50 mL of anhydrous toluene using an ultrasound bath for  
133 5 min and magnetic stirring. Then, 3-(aminopropyl)triethoxysilane  
134 (APTES) (1 mL, 4 mmol) was added, and after 1 h, the resulting  
135 mixture heated up to 110 °C. Reflux was maintained for 24 h, after  
136 which the suspension was filtered. The recovered solid was washed  
137 with toluene, acetonitrile, and ethanol (15 mL of each), and then air-  
138 dried. The resulting H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>SiO<sub>1.5</sub>/8SiO<sub>2</sub> solid was extracted with  
139 dichloromethane using a Soxhlet for 24 more hours.  
140

**2.2.2. SBA-15 Silica with Carboxypropyl Functions (SBA-CO<sub>2</sub>H).**<sup>27</sup>  
141 SBA-CO<sub>2</sub>H support was prepared following a one-pot procedure  
142 synthesis: Pluronic 123 (4.0 g) was dissolved in 150 mL of an aqueous  
143 solution of HCl (pH ~ 1.5). The resulting clear solution was then  
144 added to a mixture of (4-butyronitrile)triethoxysilane (BNTES) (1.04  
145 g, 4.5 mmol) and tetraethylorthosilicate (TEOS) (8.40 g, 40.4 mmol).  
146 The mixture was vigorously stirred for 3 h at room temperature until a  
147 transparent solution appeared. The solution was transferred to a hot  
148 bath at 60 °C, and NaF (76 mg, 1.8 mmol) was immediately added. In  
149 the present case, NaF was acting as catalyst for polycondensation  
150 process. A white precipitate was formed after a few minutes. After  
151 aging under regular stirring for 3 days at 60 °C, the resulting powder  
152 was filtered off, and the surfactant was selectively removed by Soxhlet  
153 extraction with ethanol for 24 h. After the material was dried at 120 °C  
154 under vacuum (0.1 mm Hg), HOOC(CH<sub>2</sub>)<sub>3</sub>SiO<sub>1.5</sub>/9SiO<sub>2</sub> was  
155 obtained as a white powder.  
156

**2.2.3. MesoCellular Foam Silica with Aminopropyl Functions (MCF-NH<sub>2</sub>).** MCF-NH<sub>2</sub> was obtained in a two-step procedure, after  
157 functionalization of a preformed MCF<sup>28</sup> with 3-aminopropyltriethoxysilane, as follows.  
158

First, Pluronic 123 (8.0 g) was added to 240 mL of distilled water  
159 and 40 mL of concentrated chlorhydric acid (37%). The mixture was  
160 heated at 40 °C until complete dissolution of Pluronic 123.  
161 Trimethylbenzene (9.2 mL, 8 g) was introduced dropwise as a  
162 swelling agent. After 2 h, TEOS (18 mL, 80 mmol) was also added  
163 dropwise, and the resulting suspension was further heated at 40 °C for  
164 24 h. NH<sub>4</sub>F (98 mg) was introduced 15 min before hydrothermal  
165 treatment. The latter was performed at 100 °C in a FEP bottle for an  
166 additional 24 h. The suspension was filtered, and the obtained solid  
167 was washed with water, dried at 60 °C, and finally calcined (24 °C h<sup>-1</sup>)  
168 at 550 °C for 6 h.  
169

Second, 1.0 g of freshly dried MCF silica (350 °C, 12 h) was added  
170 to 50 mL of anhydrous toluene. The resulting suspension was stirred  
171 at room temperature, and APTES (1.0 mL, 4 mmol) was introduced.  
172 After 2 h, the reaction mixture was heated until toluene reflux (110  
173 °C) and maintained at this temperature for 24 h. Then, the suspension  
174 was filtered. The recovered solid was washed successively with 15 mL  
175 of toluene, 15 mL of acetone, and then 15 mL of ethanol, and air-dried  
176

Table 1. Textural Data of the Supports before and after POM Coupling

	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	pore vol ( $\text{cm}^3 \text{g}^{-1}$ )	pore diameter or window for MCF (nm) desorption	pore diameter or cell for MCF (nm) adsorption
SBA-NH <sub>2</sub>	398	0.7	6.2	8.0
SBA-CO <sub>2</sub> H	536	1.0	7.0	9.2
MCF-NH <sub>2</sub>	327	1.5	7.1	17.4
POM-CO <sub>2</sub> H@SBA-NH <sub>2</sub>	185	0.33	4.7	7.0
POM-NH <sub>2</sub> @SBA-CO <sub>2</sub> H	477	1.0	6.2	9.2
POM-CO <sub>2</sub> H@MCF NH <sub>2</sub>	245	1.0	6.2	17.3

180 for 24 h. Finally, the solid was extracted using a Soxhlet during 24 h  
181 with dichloromethane as the solvent.

182 **2.3. Covalent Binding of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) with SBA-**  
183 **NH<sub>2</sub><sup>19</sup> and MCF-NH<sub>2</sub>.** Samples of (<sup>n</sup>Bu<sub>4</sub>N)<sub>3</sub>NaH-[As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)-  
184 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>] (0.66 g, 0.2 mmol) and SBA-NH<sub>2</sub> silica (0.60 g, 4  
185 mmol g<sup>-1</sup> (nominal) of -NH<sub>2</sub> groups) (or MCF-NH<sub>2</sub>, 0.60 g, 4 mmol  
186 g<sup>-1</sup> (nominal) of -NH<sub>2</sub> groups) were introduced in 100 mL Schlenk  
187 tubes and kept under vacuum overnight. The POM-CO<sub>2</sub>H complex  
188 was dissolved under argon in 20 mL of freshly distilled acetonitrile.  
189 Triethylamine (164 μL, 0.12 g, 1.2 mmol) was then added and the  
190 resulting mixture cooled in an ice bath. After 30 min, isobutyl-  
191 chloroformate (156 μL, 0.16 g, 1.2 mmol) was introduced, and the  
192 resulting solution was stirred for 30 min (solution 1). In parallel, SBA-  
193 NH<sub>2</sub> or MCF-NH<sub>2</sub> silica was dispersed in distilled acetonitrile (5 mL)  
194 in the other Schlenk tube under argon. Solution 1 was then transferred  
195 to the dispersion of the support via cannula. The resulting suspension  
196 was stirred overnight at room temperature under argon, and then  
197 filtered. The recovered solid, i.e., POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> or POM-  
198 CO<sub>2</sub>H@MCF-NH<sub>2</sub>, was finally extracted using a Soxhlet over 2 days  
199 with acetonitrile as the solvent. Chem Anal.: POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>:  
200 W(%) 19.12; Si(%) 23.08. POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>: W(%) 14.55;  
201 Si(%) 26.20.

202 **2.4. Covalent Binding of TBA<sub>4</sub>H(POM-NH<sub>2</sub>) with SBA-CO<sub>2</sub>H.**  
203 Samples of (<sup>n</sup>Bu<sub>4</sub>N)<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>}] (0.26 g, 0.078  
204 mmol) and SBA-CO<sub>2</sub>H (0.5 g, 1.5 mmol g<sup>-1</sup> of -CO<sub>2</sub>H groups) were  
205 each introduced in a 100 mL Schlenk tube and kept under vacuum  
206 overnight. The SBA-CO<sub>2</sub>H support was then placed under argon with  
207 10 mL of freshly distilled acetonitrile, and then *N*-hydroxysuccinimide  
208 (NHS; 1.8 mmol; 0.207 g) and 1-(3-(dimethylamino)propyl)-*N'*-  
209 ethylcarbodiimide hydrochloride (EDC; 0.9 mmol; 0.172 g) were  
210 successively introduced. The resulting suspension was stirred for 3 h at  
211 room temperature. In parallel, the TBA<sub>4</sub>H(POM-NH<sub>2</sub>) complex was  
212 placed under argon and dissolved in 10 mL of freshly distilled  
213 acetonitrile. This solution was then transferred to the dispersion of the  
214 support using a cannula. The resulting suspension was stirred  
215 overnight at room temperature under argon, and then filtered. The  
216 solid recovered, i.e., POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H, was extracted using a  
217 Soxhlet over 2 days with acetonitrile as the solvent. Chem Anal.: W  
218 (%) 5.83; Si (%) 31.05.

219 **2.5. Preparation of the POM-CO<sub>2</sub>H-Supported on SBA-NH<sub>2</sub>**  
220 **Sample by Incipient Wetness Impregnation.** A sample of SBA-  
221 NH<sub>2</sub> (0.5 g) with a pore volume of 0.7 mL g<sup>-1</sup> was put in contact with  
222 0.19 g of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) in 0.35 mL of CH<sub>3</sub>CN. After  
223 complete absorption of the liquid phase by the SBA-NH<sub>2</sub> support, the  
224 sample was dried under vacuum. It is noteworthy that the amount of  
225 POMs introduced was equal to the amount of POMs found in the final  
226 POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> material obtained after covalent grafting (W:  
227 19.2%, corresponding to 28.9% of anions [As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)-  
228 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>]<sup>5-</sup> (POM-CO<sub>2</sub>H)).

229 **2.6. Catalytic Studies.** In homogeneous conditions, experiments  
230 of cyclooctene (or cyclohexene) epoxidation were performed in a 50  
231 mL round-bottom flask equipped with a condenser and magnetic  
232 stirrer at room temperature or at 50 °C. The catalysts, TBA<sub>3</sub>NaH-  
233 (POM-CO<sub>2</sub>H) or TBA<sub>4</sub>H(POM-NH<sub>2</sub>) (80 mg, 24 μmol/1 equiv), 20  
234 mL of acetonitrile, 0.78 mL of cyclooctene or 0.60 mL of cyclohexene  
235 (6 mmol/250 equiv), 0.9 mL of decane (as an internal standard), and  
236 0.6 mL of H<sub>2</sub>O<sub>2</sub> (30%/6 mmol/250 equiv) were introduced  
237 successively in the flask. The resulting solutions were analyzed by

gas chromatography on a Delsi Nermag DN 200 GC apparatus 238  
equipped with a flame ionization detector and a Macherey-Nagel 239  
Optima-5 capillary column (length 30 m, internal diameter 0.32 mm, 240  
thickness 1 μm). 241

In heterogeneous conditions, experiments of cyclooctene/cyclo- 242  
hexene epoxidation were performed in three 5 mL flasks (for analysis 243  
at 3, 6, and 24 h) under stirring at room temperature. The solid 244  
catalysts POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> (40 mg), POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H 245  
(114 g), or POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub> (55 mg), corresponding to 1.2 × 246  
10<sup>-3</sup> mmol/1 equiv of POM-NH<sub>2</sub> or POM-CO<sub>2</sub>H, 1 mL of 247  
acetonitrile, 39 μL of cyclooctene (250 equiv) or 30 μL of cyclohexene 248  
(250 equiv), 45 μL of decane, and 30 μL of H<sub>2</sub>O<sub>2</sub> (30%, 250 equiv) 249  
were introduced successively in each flask. The supernatant of the 250  
resulting suspensions was analyzed by gas chromatography as 251  
described above. Blank reactions have been also performed with the 252  
different supports SBA-NH<sub>2</sub>, SBA-CO<sub>2</sub>H and MCF-NH<sub>2</sub>, before the 253  
POMs-grafting steps. No catalytic activity was found for these 254  
materials in the absence of the POMs. For the recycling experiment, 255  
the catalyst has been filtered on a glass frit (por 4), rinsed with a few 256  
milliliters of CH<sub>3</sub>CN, dried at air, and reused without any further 257  
treatments. 258

### 3. RESULTS AND DISCUSSION

In this work, three different POM-grafted materials were 259  
prepared in order to compare the nanostructuration of the 260  
active phase at the surface of the pores. These materials were 261  
obtained through the covalent binding of POM hybrids with 262  
three different functionalized mesoporous silica supports. In the 263  
continuity of our previous works, the strategy we used 264  
consisted of the coupling of complementary functions, one at 265  
the oxide-support and the second one on the termination of the 266  
organic groups introduced in the POM framework. In this 267  
respect, two different effects were studied: (1) the grafting 268  
reaction of POM hybrids on a given type of support (in the 269  
present case SBA-15 displaying anchoring aminopropyl or 270  
carboxypropyl functions); (2) the type of mesoporosity of the 271  
silica hosts, SBA-15 versus MCF, both functionalized with the 272  
same organic (aminopropyl) functions. 273

**3.1. Characterization of SBA-NH<sub>2</sub>, SBA-CO<sub>2</sub>H, and**  
**MCF-NH<sub>2</sub> Materials.** **3.1.1. Thermogravimetric Analyses.** 274  
The thermogram of SBA-NH<sub>2</sub> (see Supporting Information 275  
Figure S1) performed under air from room temperature up to 276  
900 °C shows two weight losses. The first one (3%), under 100 277  
°C, can be attributed to the loss of water molecules weakly 278  
adsorbed on the silica surface. The second one (17%, 100–800 279  
°C) can be assigned to the loss of aminopropyl functions. This 280  
analysis demonstrated that SBA-NH<sub>2</sub> is functionalized with 3 281  
mmol of NH<sub>2</sub> g<sup>-1</sup> (ca. 75% incorporation yield). 282  
283

Similarly, the thermogravimetric analysis of MCF-NH<sub>2</sub> 284  
exhibits two weight losses, respectively, of 2% and 15%. The 285  
second weight loss (100–800 °C) can still be attributed to 286  
aminopropyl functions. The MCF-NH<sub>2</sub> support was found to 287  
be functionalized by 2.3 mmol of NH<sub>2</sub> g<sup>-1</sup> (ca. 60% 288  
incorporation yield). In comparison, the TGA-DTA analysis 289

290 of SBA-CO<sub>2</sub>H shows that it was functionalized with 1.7 mmol  
291 of -CO<sub>2</sub>H g<sup>-1</sup> (ca. 100% incorporation yield).

292 **3.1.2. Structural Study of SBA-NH<sub>2</sub>, SBA-CO<sub>2</sub>H, and MCF-**  
293 **NH<sub>2</sub> Materials.** The X-ray powder diffraction patterns at 2θ  
294 (0.5–3°) of the SBA-NH<sub>2</sub> and SBA-CO<sub>2</sub>H materials (see  
295 Supporting Information, Figure S2a,b) exhibited three peaks,  
296 the first one being far more intense than the other two. These  
297 signals were, respectively, assigned to the (100), (110), and  
298 (200) reflections of the expected hexagonal *P6m* structure. It is  
299 noteworthy that the intensities of the peaks related to the (110)  
300 and (200) reflections are smaller for SBA-CO<sub>2</sub>H.

301 Transmission electron microscopy (TEM) confirmed the  
302 structure of SBA-NH<sub>2</sub> and SBA-CO<sub>2</sub>H. The micrographs  
303 obtained by HR-TEM on both supports (see Supporting  
304 Information Figure S3) displayed the same organized tubular  
305 networks. Their textural data (see Table 1) were also  
306 comparable, although a larger specific surface was determined  
307 in the case of SBA-CO<sub>2</sub>H. The micrographs of MCF-NH<sub>2</sub>  
308 confirmed the cellular foam structure of this support and the  
309 existence of cells with smaller apertures (windows) (Figure 2).

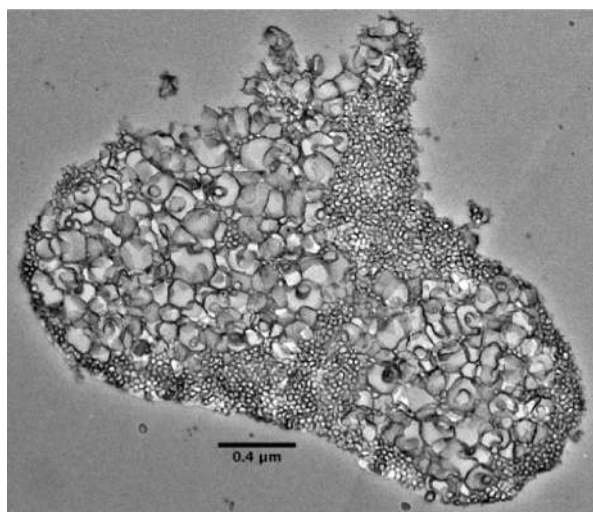


Figure 2. HR-TEM micrograph of MCF-NH<sub>2</sub> materials.

310 **3.1.3. Nitrogen Physisorption.** The nitrogen physisorption  
311 isotherms and the pore-size distribution of the two SBA  
312 supports are shown in Figure S4 (see Supporting Information).  
313 The adsorption/desorption isotherms are of type IV with a  
314 hysteresis loop. The pore sizes were calculated from the  
315 desorption branches of the isotherms using the Barret–Joyner–  
316 Hallenda (BJH) formula (Table 1). This method is used for the  
317 determination of the pore-size distribution of materials with  
318 pores larger than 4 nm, and it is appropriate for our silica  
319 supports (SBA-NH<sub>2</sub> and SBA-CO<sub>2</sub>H). Values calculated from  
320 the adsorption branches were also determined in the case of  
321 MCF-NH<sub>2</sub> (Table 1).

322 **3.2. Characterization Studies of the POM-Grafted**  
323 **Materials.** Two different POMs, with organic functions  
324 complementary to those of the supports, were used: the  
325 previously reported (<sup>n</sup>Bu<sub>4</sub>N)<sub>3</sub>NaH[As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)-  
326 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>] complex, TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H),  
327 which contains two carboxylic acid functions, and the bis-  
328 anilino derivative TBA<sub>4</sub>H(POM-NH<sub>2</sub>), (<sup>n</sup>Bu<sub>4</sub>N)<sub>4</sub>H-  
329 [PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] (see Figure 3).<sup>29</sup>  
330 As previously reported,<sup>19</sup> the TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H)  
331 complex was easily grafted onto the NH<sub>2</sub>-functionalized

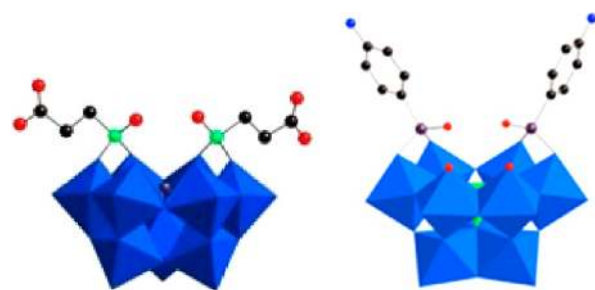


Figure 3. Structural representation of POM-CO<sub>2</sub>H (left) and POM-NH<sub>2</sub> (right) anions. WO<sub>6</sub> and PO<sub>4</sub> polyhedra are shown in blue and green, respectively. The As, P, N, O, and C atoms are shown, respectively, in prune, green, blue, red, and black.

332 supports through the formation of amide bonds. For this  
333 purpose, isobutylchloroformiate (<sup>t</sup>BuOC(O)Cl) was used as a  
334 coupling agent, in the presence of triethylamine. This  
335 procedure was repeated in the present work with SBA-NH<sub>2</sub>  
336 (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>), and adapted also to MCF-NH<sub>2</sub>  
337 (POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>), which was not described until  
338 now. Both POM-functionalized amino supports were charac-  
339 terized by <sup>13</sup>C NMR (Supporting Information, Figure S5), <sup>31</sup>P  
340 CP-MAS NMR (Supporting Information, Figure S6), and  
341 Raman (Supporting Information, Figure S7) and IR spectro-  
342 copies, in order to confirm the integrity of the POMs after  
343 grafting and the formation of amide bonds (with <sup>13</sup>C CP-MAS  
344 NMR and IR). From this study, it was found that the spectra  
345 displayed similar patterns for both materials, in accordance with  
346 those previously reported.<sup>19</sup> Additionally, the powder X-ray  
347 diffraction patterns of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> (Supporting  
348 Information Figure S2c) displayed the diffraction peaks  
349 characteristic of the hexagonal structuration of the mesopores,  
350 indicating that the modified material kept the SBA-15 structure.

351 The second POM TBA<sub>4</sub>H(POM-NH<sub>2</sub>) contains two aniline  
352 functions.<sup>26</sup> The coupling procedure between these anilines and  
353 the carboxylic functions of the SBA-CO<sub>2</sub>H was adapted from  
354 previous work done by some of us dealing with gold surfaces  
355 functionalized with carboxylic acid moieties (see section 2.4).<sup>30</sup>  
356 X-ray fluorescence (XRF) and chemical elemental analysis  
357 determined POM contents of the three materials at once. The  
358 obtained results are given in Table 2. It is worth noting that

Table 2. W/Si Molar Ratio and POM Content for POM-Grafted Materials

	W/Si molar ratio		POMs content (mmol g <sup>-1</sup> )
	XRF	elem anal.	
POM-CO <sub>2</sub> H @SBA-NH <sub>2</sub>	0.087	0.120	0.1
POM-NH <sub>2</sub> @SBA-CO <sub>2</sub> H	0.020	0.028	0.035
POM-CO <sub>2</sub> H @MCF NH <sub>2</sub>	0.047	0.084	0.085

359 both techniques gave similar trends for the W/Si ratio, with the  
360 higher content in POMs being observed in the case of the  
361 -NH<sub>2</sub> functionalized supports. The POM contents (given in  
362 mmol per g of materials, based on the chemical elemental  
363 analysis results) are in the range 3.5 × 10<sup>-2</sup> to 1 × 10<sup>-1</sup> mmol  
364 g<sup>-1</sup> of functionalized supports. This corresponds to the  
365 following POM loadings: (1) 9.2 wt % based on the anions  
366 [PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]<sup>5-</sup> (POM-NH<sub>2</sub>) for POM-  
367 NH<sub>2</sub>@SBA-CO<sub>2</sub>H, (2) 22.0 and 28.9 wt % based on the  
368 anions [As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>]<sup>5-</sup> (POM-

369 CO<sub>2</sub>H), respectively, for POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub> and POM-  
370 CO<sub>2</sub>H@SBA-NH<sub>2</sub>.

371 POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H was also characterized by <sup>31</sup>P and  
372 <sup>13</sup>C CP-MAS NMR (see Supporting Information, Figure S8),  
373 and IR and Raman spectroscopies. Unfortunately, the  
374 significantly weaker content of POMs in POM-NH<sub>2</sub>@SBA-  
375 CO<sub>2</sub>H (W/Si molar ratio = 0.028 (0.02 by XRF), see Table 2)  
376 did not allow us to characterize the formation of amide bonds  
377 by all spectroscopies mentioned above.

378 Furthermore, textural data of this material were compared to  
379 those of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> and POM-CO<sub>2</sub>H@MCF-  
380 NH<sub>2</sub>. As expected, the greater the amount of POMs introduced  
381 (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>), the greater the S<sub>BET</sub> is decreased.  
382 We thus observed a significant diminution of the pore volume  
383 after grafting POM-CO<sub>2</sub>H anions onto SBA-NH<sub>2</sub> materials,  
384 consistently with our previous results. Such low values of S<sub>BET</sub>  
385 are generally observed for other POMs/SBA-15 systems  
386 obtained by classical POMs deposition, at high POMs  
387 loading.<sup>31</sup> On the other hand, the pore volume remained  
388 approximately constant in the case of POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H.  
389 It is worth noting that pore volumes and diameter variations  
390 may be hardly compared in the three materials since MCF  
391 structure is obviously different due to the presence of windows  
392 and cells.

393 **3.3. High Resolution Transmission Electron Microscopy (HR TEM) of the POM-Grafted Supports.** All three  
394 POM-grafted supports (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>, POM-  
395 NH<sub>2</sub>@SBA-CO<sub>2</sub>H, and POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>) were char-  
396 acterized by high resolution TEM, after microtome cutting. The  
397 comparison between the supports before (see Figure 2 and  
398 Supporting Information Figure S3) and after POM grafting  
399 (Figures 4–6) was undoubtedly instructive. First of all, it can be  
400 observed at low magnification that the grafting of POMs did  
401 not alter the intrinsic structure of the supports, even in the  
402 presence of triethylamine.

404 By classical HR-TEM, the presence of POMs at the surface  
405 of the silica grains was not observed, even at high magnification.  
406 In contrast, microtome cuttings turned out to be a powerful

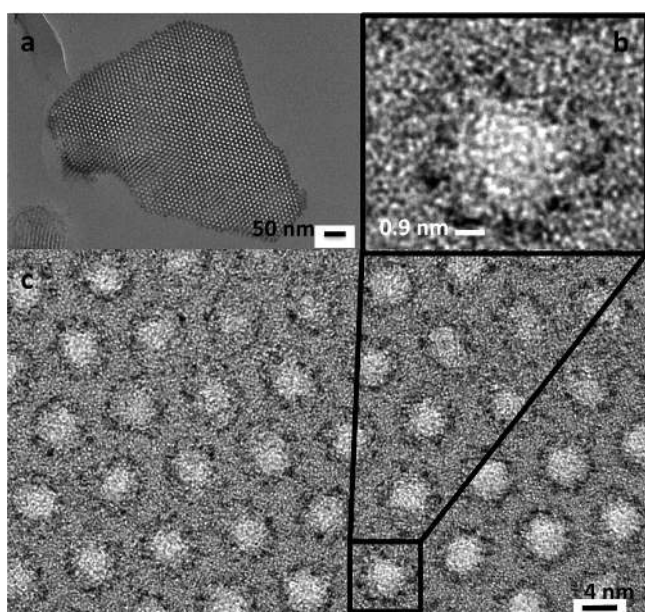


Figure 4. HR TEM micrographs (microtome cutting) of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> at different magnifications.

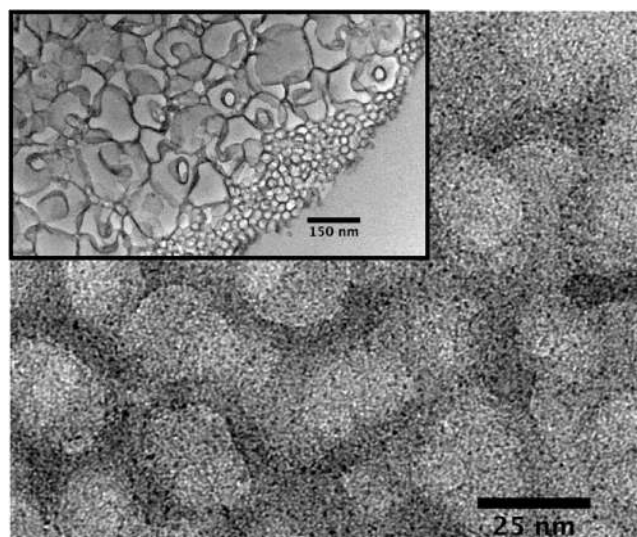


Figure 5. HR TEM micrographs (microtome cuttings) of POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub> at different magnifications.

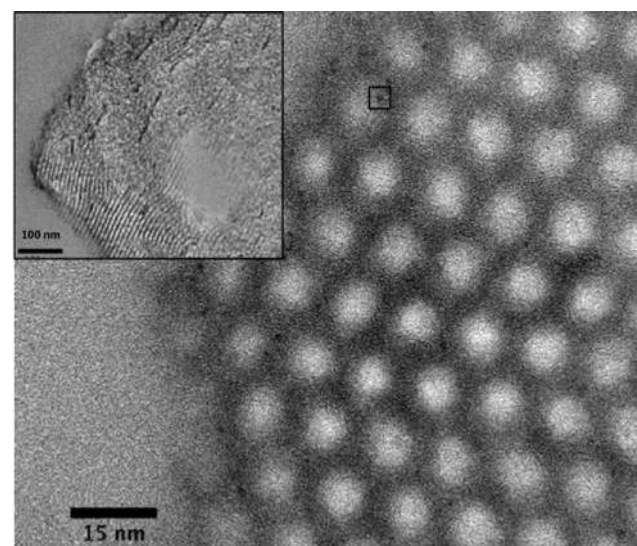


Figure 6. HR TEM micrographs (microtome cutting) of POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H at different magnifications.

407 tool, since it was possible to clearly identify the presence and,  
408 above all, the exact location of the POMs inside the pores or  
409 cells of the materials. In the case of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>  
410 (Figure 4), we clearly observed the regular distribution of  
411 POMs at the periphery of the channels. POMs appeared thus  
412 arranged in a monolayer in the pores, covering almost the  
413 whole inner surface. The efficiency of the microtome cutting,  
414 combined with the image contrast provided by heavy W atoms  
415 in the silica matrix, led us to consider that POMs did not form  
416 aggregates in these materials (average size of “dark” dots about  
417 0.9 nm, Figure 4b). The covalent grafting of POMs onto the  
418 walls through the formation of amide functions led then to  
419 isolated anions and, thus, facilitated in a very efficient way the  
420 nanostructure of the catalysts on the support.

421 Examination of the elemental composition of a single grain of  
422 material by X-ray energy-dispersive spectroscopy (XEDS, see  
423 Supporting Information Figure S9 for more details) indicated  
424 that the ratio W/Si = 0.16 is on the same order of magnitude as  
425 that obtained by chemical analysis (W/Si = 0.12, Table 2).

426 Moreover, XEDS also confirmed that the W atoms present in  
427 the solid were concentrated in the pores, with a measured W/Si  
428 ratio equal to 0.29 after deconvolution of the XEDS spectrum  
429 recorded on an area focused on one pore.

430 HR-TEM micrographs of POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub> (Figure  
431 5) also revealed the presence of POMs at the periphery of the  
432 cells. However, their distribution appeared less regular than in  
433 POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> materials. This is obviously linked to  
434 the structure of the MCF silica, in which cells having walls with  
435 different intrinsic properties replaced cylindrical pores. Never-  
436 theless, the size of the dots (attributed to the POMs) observed  
437 in all micrographs was mostly found to be around 1 nm. POMs  
438 still appeared as individual cluster anions, as observed in the  
439 case of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>. As demonstrated in the  
440 previous materials, XEDS also confirmed that W atoms are  
441 mainly concentrated in the cells (Supporting Information,  
442 Figure S10).

443 HR-TEM micrographs of POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H (Figure  
444 6) showed far fewer “dark” dots attributed to POMs, as  
445 expected due to the weakest POMs contents. Furthermore,  
446 while the distribution of POMs in the -NH<sub>2</sub> functionalized  
447 supports appeared regularly in every pore of the silica, in  
448 particular for POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>, we observed that only a  
449 few channels are covered with POMs (insert in Figure 6). In  
450 addition, the size of the POMs containing dots was evaluated,  
451 and it was found to be larger than that in the previous materials  
452 (about 1.8 nm for the dot inside the black square in the top of  
453 Figure 6, and larger ones were observed on several other  
454 micrographs). This suggests that POM-NH<sub>2</sub> anions were not  
455 found in the form of isolated species but preferably of  
456 aggregates of a few clusters. This makes us question the  
457 covalent grafting of POM-NH<sub>2</sub> at the surface of the SBA-CO<sub>2</sub>H  
458 and, thus, the efficiency of the coupling procedure we used.  
459 XEDS was also performed on the materials, and we found that  
460 the W/Si ratio measured on a whole grain was identical (0.028)  
461 to the value found by chemical analysis. We also observed an  
462 increase of this value (up to 0.048) when the X-ray beam was  
463 concentrated on a single channel (Supporting Information,  
464 Figure S11). This increase led then to an unambiguous  
465 localization of the POMs in the SBA channels.

466 **3.4. HR-TEM Study of Noncovalently Bound Anions**  
467 **POM-CO<sub>2</sub>H in Mesoporous SBA-15.** For this study, in order  
468 to point out the added value of the covalent grafting procedure  
469 for the POM nanostructure, we prepared a different POM-  
470 CO<sub>2</sub>H-supported SBA-NH<sub>2</sub> sample, obtained by incipient  
471 wetness impregnation of SBA-NH<sub>2</sub> with a solution (CH<sub>3</sub>CN)  
472 of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H). In this experiment, the amount of  
473 POMs introduced was equal to that found in the final POM-  
474 CO<sub>2</sub>H@SBA-NH<sub>2</sub> materials obtained after covalent grafting  
475 (approximately 40% in mass), with the volume of solvent  
476 corresponding to the pore volume of the SBA-NH<sub>2</sub> used (0.7  
477 cm<sup>3</sup> g<sup>-1</sup>). Several examples of HR-TEM micrographs obtained  
478 after microtome cutting are presented in Figure 7. First of all,  
479 we found by XEDS that the distribution of POMs was very  
480 irregular in the different grains of SBA-15. POMs were not  
481 present in all domains. Furthermore, in the case of POM-  
482 containing grains, POMs were generally not observed as  
483 isolated clusters (like in POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> materials) but  
484 preferably as aggregates whose sizes were found in the 1.5–20  
485 nm range. These micrographs also showed that some channels  
486 were not “filled” at all by POMs (see Figure 7, top left and  
487 right), on the contrary to what was observed previously in  
488 POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H samples. This seems to confirm that

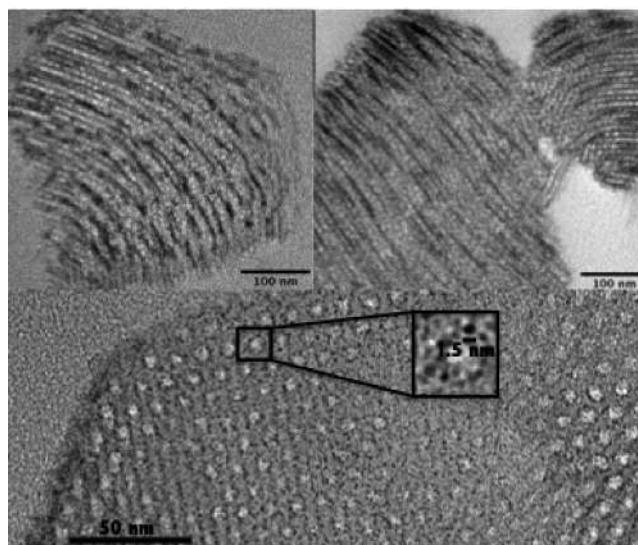


Figure 7. HR-TEM micrographs of SBA-NH<sub>2</sub> supports covered by TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) after wet impregnation.

489 the nature of the interactions between POM-NH<sub>2</sub> anions and  
490 SBA-COOH was probably not covalent.

491 **3.5. Comparative Study of the Catalytic Performance**  
492 **of Homogeneous vs Anchored Homogeneous Catalysts:**  
493 **The Case Studies of Cyclooctene/Cyclohexene Epox-**  
494 **idation with H<sub>2</sub>O<sub>2</sub>.** 3.5.1. *Epoxidation of Cyclooctene/*  
495 *Cyclohexene with H<sub>2</sub>O<sub>2</sub> in Homogeneous Conditions.*  
496 Examples of the reactivity of heteropolytungstates that contain  
497 no additional transition-metal ions,<sup>3,32</sup> including organo-  
498 phosphonyl derivatives of POMs<sup>33,34</sup> in alkenes epoxidation  
499 processes can be found in the literature. Among all these  
500 studies, only one using organophosphonyl derivatives of  
501 trivalent POMs platforms was described so far, by the group of  
502 Bonchio.<sup>33</sup> Furthermore, the experimental conditions used in  
503 the present study may hardly be compared to those of Bonchio  
504 et al., who worked at very high temperature with microwave  
505 assistance.

506 Prior to the study of the catalytic performances of  
507 TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) and TBA<sub>4</sub>H(POM-NH<sub>2</sub>) covalently  
508 supported onto mesoporous silica, we have checked the activity  
509 of the corresponding POMs under homogeneous conditions.  
510 The model reactions were, respectively, the epoxidation of  
511 cyclooctene and cyclohexene with aqueous H<sub>2</sub>O<sub>2</sub> carried out at  
512 room temperature (excepted for some experiments specifically  
513 driven at 50 °C) in acetonitrile with the following catalyst/  
514 alkene/H<sub>2</sub>O<sub>2</sub> ratio equal to 1:250:250. As expected, no reaction  
515 occurred in the absence of the catalysts, and we also checked  
516 that no H<sub>2</sub>O<sub>2</sub> consumption was detected in the absence of  
517 cyclooctene/cyclohexene.

518 *Cyclooctene Epoxidation.* With both complexes, the  
519 conversion of cyclooctene into epoxycyclooctane in acetonitrile  
520 and at room temperature was observed with very high yields  
521 (respectively, 96% and 97%, see Table 3, entries 1 and 2) after  
522 24 h. It is also noteworthy that, in all experiments described in  
523 this section, we did not detect products other than  
524 epoxycyclooctane, so it can be considered that the  
525 epoxycyclooctane selectivity was 100%. Differences between  
526 the two POMs were however shown for short time reaction  
527 since a longer induction period seemed to be necessary for  
528 TBA<sub>4</sub>H(POM-NH<sub>2</sub>) catalyst (conversion 2.6% after 3 h).

Table 3. Epoxidation Conversion of Cyclooctene with Homogeneous and Anchored Catalysts<sup>a</sup>

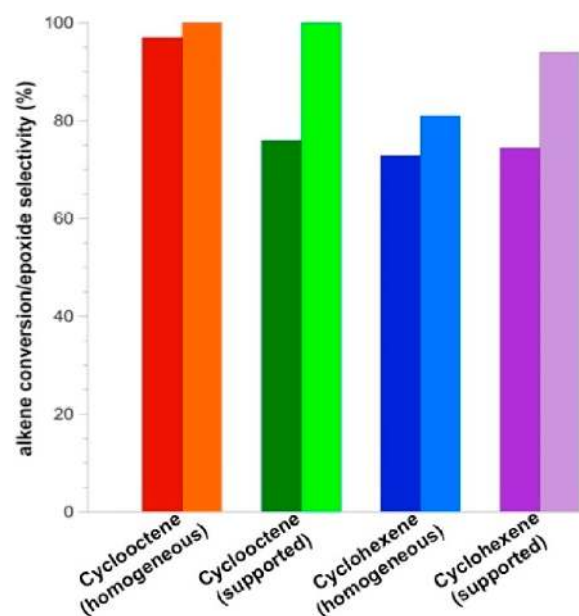
entry	catalyst	T (°C)	3 h	6 h	24 h
1	TBA <sub>3</sub> NaH(POM-CO <sub>2</sub> H)	20	59.5	88.5	96
2	TBA <sub>4</sub> H(POM-NH <sub>2</sub> )	20	2.6	74	97
3	TBA <sub>3</sub> NaH[AsW <sub>9</sub> O <sub>33</sub> { <sup>t</sup> BuPO} <sub>2</sub> ]	20	0	2.4	7.5
4	TBA <sub>3</sub> NaH[AsW <sub>9</sub> O <sub>33</sub> { <sup>t</sup> BuPO} <sub>2</sub> ]	50	20.6	97	100
5	TBA <sub>4</sub> H[PW <sub>9</sub> O <sub>34</sub> {PhPO} <sub>2</sub> ]	20	0.7	13.6	98
6	POM-CO <sub>2</sub> H@SBA-NH <sub>2</sub>	20	3.2	11.7	76
7	POM-CO <sub>2</sub> H@SBA-NH <sub>2</sub> (recycling)	20	10.2	23	81
8	POM-NH <sub>2</sub> @SBA-CO <sub>2</sub> H	20	1	3.5	19
9	POM-CO <sub>2</sub> H@MCF-NH <sub>2</sub>	20	1	9	41
10	POM-NH <sub>2</sub> @SBA-CO <sub>2</sub> H	50	29	53	87

<sup>a</sup>Conditions: catalyst, 24 μmol (homogeneous conditions) or 1.2 μmol (heterogeneous conditions); acetonitrile, 20 mL (homogeneous conditions) or 1 mL (heterogeneous conditions). Ratio cyclooctene/catalyst = 250; cyclooctene/H<sub>2</sub>O<sub>2</sub> (30%) = 1.

For the sake of comparison, we also tested the catalytic performances of two other compounds, TBA<sub>3</sub>NaH[AsW<sub>9</sub>O<sub>33</sub>{<sup>t</sup>BuPO}<sub>2</sub>] (Table 3, entries 3 and 4) and TBA<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{PhPO}<sub>2</sub>] (Table 3, entry 5) each related to (<sup>n</sup>-Bu<sub>4</sub>N)<sub>3</sub>NaH[AsW<sub>9</sub>O<sub>33</sub>{P(O)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>] (POM-CO<sub>2</sub>H) and (<sup>n</sup>-Bu<sub>4</sub>N)<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] (POM-NH<sub>2</sub>), respectively. The TBA<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{PhPO}<sub>2</sub>] complex contains the same A<sub>α</sub>-[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> anionic platform as [PW<sub>9</sub>O<sub>34</sub>{As(O)(*p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]<sup>5-</sup> (POM-NH<sub>2</sub> anion), and two {As(O)Ph} groups instead of the {As(O)(*p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)} ones. The catalytic behavior of this compound was analogous to that of TBA<sub>4</sub>H(POM-NH<sub>2</sub>), with a long induction time and a final conversion (after 24 h) close to 100% (Table 3, entry 5). We also compared the reactivity of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) with that of TBA<sub>3</sub>NaH[AsW<sub>9</sub>O<sub>33</sub>{<sup>t</sup>BuPO}<sub>2</sub>] based on a B<sub>α</sub>-[AsW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> subunit on which two {<sup>t</sup>BuPO} phosphonate groups have been grafted instead of the carboxypropyl functions in the POM-CO<sub>2</sub>H anion. In the present case, we found that, at room temperature, the behavior of both complexes was clearly different since the conversion after 1 day was found to be very low (7.5%) with TBA<sub>3</sub>NaH[AsW<sub>9</sub>O<sub>33</sub>{<sup>t</sup>BuPO}<sub>2</sub>] (Table 3, entry 3). It is noteworthy that an increase of the temperature up to 50 °C (Table 3, entry 4) led to a catalytic efficiency similar to that of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H). Regarding these results, we concluded that, at room temperature, the carboxylic functions of POM-CO<sub>2</sub>H anions could play a major role in the epoxidation process since the absence of these functions led to a dramatic decrease of the conversion of cyclooctene. These results could have been anticipated since the role of acids in general and of carboxylic acids in particular in epoxidation of alkenes (including cyclooctene) has been previously discussed in the literature, especially in POM chemistry.<sup>35–37</sup>

**Cyclohexene Epoxidation.** The epoxidation reaction of cyclohexene with aqueous H<sub>2</sub>O<sub>2</sub> was also studied, with the conditions being adapted from those used for cyclooctene. We first checked the activity of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) under homogeneous conditions in acetonitrile at room temperature. We thus found a good conversion of cyclohexene after 24 h (72.9%) and a final selectivity in the epoxide equal to 81.1%.<sup>38</sup> These results compare well with various other POM-based catalysts acting at room temperature (especially for the cyclohexene conversion rather than the selectivity).<sup>32</sup> For comparison, in acetonitrile at 50 °C, the Ishii–Venturello catalyst (<sup>n</sup>-Bu<sub>4</sub>N)<sub>3</sub>[PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>4</sub>] produced cyclohexene epoxide with 98% selectivity at 84% conversion after 6 h.<sup>39</sup>

**3.5.2. Epoxidation of Cyclooctene and Cyclohexene with H<sub>2</sub>O<sub>2</sub> by the Covalently Anchored Catalyst POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>.** The catalytic activity of the three different anchored catalysts (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>, POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>, and POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H, see descriptions in sections 3.2 and 3.3) toward cyclooctene epoxidation was also studied (Table 3, entries 6, 8, and 9) in the conditions used for their homogeneous counterparts (section 3.5.1). The most efficient precursor was POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> (Table 3, entry 6), in which the POM-CO<sub>2</sub>H anion was mostly grafted by only one carboxylic acid function, as established previously.<sup>19</sup> For this supported catalyst, the rate of cyclooctene conversion was still relatively high, even if it is lower compared to that obtained in homogeneous conditions (76% vs 96% after 1 day, see Figure 8). These differences were emphasized at an early stage (3.2% vs 59.5% after 3 h and 11.7% vs 88.5% after 6 h), reflecting an important delay probably due to different phenomena (lower diffusion rates of the substrate or different accessibility to the



**Figure 8.** Column diagram for the alkene conversion (left bar) and epoxide selectivity (right bar) for (respectively, from left to right) cyclooctene with TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) in homogeneous conditions and POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> in heterogeneous conditions and for cyclohexene with TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H) in homogeneous conditions and POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> in heterogeneous conditions.

593 active sites in heterogeneous conditions). A recyclability test  
594 was also performed with the POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> catalyst  
595 recovered after 24 h through filtration. Interestingly, we  
596 observed a similar (if not higher) cyclooctene oxide rate  
597 (81%) after 1 day, indicating an excellent stability of the  
598 catalyst.

599 The catalytic activity of the supported POM-CO<sub>2</sub>H anion  
600 covalently bound to SBA-NH<sub>2</sub> (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>) was  
601 also studied in the case of cyclohexene. Similarly to  
602 cyclooctene, significant delays were observed in the cyclo-  
603 hexene conversion at the early stage of the reaction. However,  
604 in the present case the final conversion was found to be on the  
605 same order (if not higher) as that observed in homogeneous  
606 conditions (72.9% for the homogeneous catalyst, i.e.,  
607 TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H), vs 74.5% for the supported one).  
608 Interestingly, the final selectivity into epoxycyclohexane was  
609 much higher after immobilization (94.0% vs 81.1%).

610 Regarding the important delay observed at the beginning of  
611 the reaction in both experiments using POM-CO<sub>2</sub>H@SBA-  
612 NH<sub>2</sub> and despite the fact that the experimental conditions used  
613 here (acetonitrile during 1 day at room temperature) were  
614 much more gentle than the initial catalyst treatment before its  
615 use (Soxhlet for 2 days in refluxing acetonitrile), it was  
616 important to determine the true nature of the catalysis. In other  
617 words, did POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> behave as a supported  
618 catalyst or a homogeneous one obtained through (partial)  
619 leaching processes? Indeed, it is now admitted that a simple  
620 conventional catalyst recycling experiment showing no  
621 significant loss of activity (Table 3, entry 7) is by no means a  
622 sufficient proof of heterogeneity in itself. According to the  
623 procedures defined by R. A. Sheldon and co-workers,<sup>40</sup> the  
624 strong immobilization of the catalyst was proven through  
625 another experiment where (i) the POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>  
626 catalyst was removed (filtration after 5 h with 0.2 μm porosity  
627 filters) before completion of the reaction (at room temper-  
628 ature) and (ii) the activity of the resulting filtrate was checked  
629 after 24 h. We then observed a dramatic lowering of the  
630 catalytic activity (see Figure 9) compared to the reference  
631 experiment (without filtration, see also Table 3, entry 6).  
632 Indeed while cyclooctene conversion was approximately 13.9%  
633 at the time of the filtration (at 5 h), the final conversion (at 24  
634 h) within these experimental conditions hardly reached 25%  
635 versus 76% with the nonfiltered heterogeneous catalyst (Figure  
636 9). We assume that the slight increase in the conversion after  
637 filtration (between 5 and 24 h) was probably due to the  
638 existence of remaining silica grains whose size was lower than  
639 200 nm (size of the filter) in the solution, as observed by HR-  
640 TEM, instead of potential active species leached into solution.  
641 Nevertheless, regarding the results of the recyclability test and  
642 of the present experiment, one can be confident that the POM-  
643 CO<sub>2</sub>H@SBA-NH<sub>2</sub> material can be considered as a truly  
644 anchored catalyst.

645 **3.5.3. Epoxidation of Cyclooctene with H<sub>2</sub>O<sub>2</sub>. Comparison**  
646 **between Homogeneous and Covalently Anchored Catalysts.**  
647 Concerning the catalytic activity of the other anchored  
648 catalysts, the scenario was surprisingly different with POM-  
649 CO<sub>2</sub>H@MCF-NH<sub>2</sub> (Table 3, entry 9). After 1 day, only partial  
650 conversion of cyclooctene (41%) was observed, as the results of  
651 POM-CO<sub>2</sub>H anion grafting onto a MCF-NH<sub>2</sub> instead of SBA-  
652 NH<sub>2</sub> support. With this experiment, we thus highlighted an  
653 effect of the support on the reaction rate. With the structure of  
654 the porosity being the main difference between SBA-NH<sub>2</sub> and  
655 MCF-NH<sub>2</sub> supports, it was tempting to hypothesize that

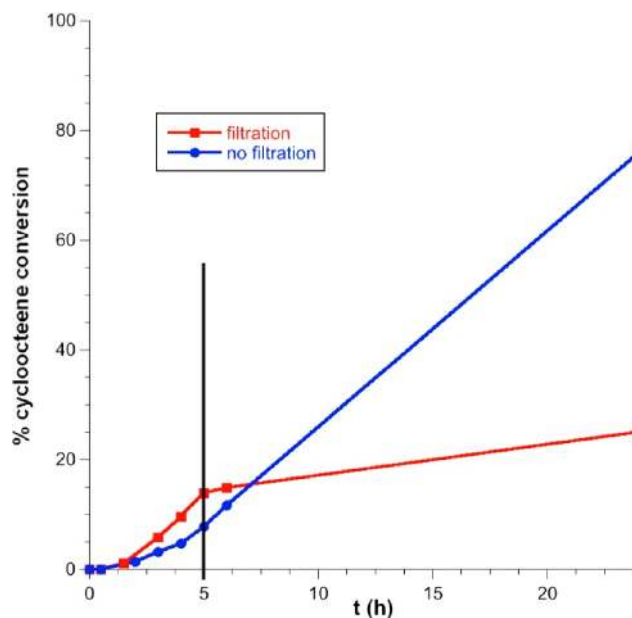


Figure 9. Catalytic activity of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> for the epoxidation of cyclooctene with aqueous H<sub>2</sub>O<sub>2</sub> with (in red) or without (in blue) filtration. The black vertical line indicates the time for filtration.

656 variations of activity between POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub> and  
657 POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> might be due to a poorer accessibility  
658 of the active sites in the particular case of MCF-NH<sub>2</sub>. However,  
659 regarding the textural data, it is difficult to correlate *a priori* this  
660 decrease of the catalytic activity at the molecular level to the  
661 S<sub>BET</sub> measured for both systems (lower for POM-CO<sub>2</sub>H@SBA-  
662 NH<sub>2</sub> compared to for POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>, see Table 1).  
663 Another explanation could be related to the irregular  
664 organization of the active sites inside POM-CO<sub>2</sub>H@MCF-  
665 NH<sub>2</sub> (see Figure 5) compared to those inside POM-CO<sub>2</sub>H@  
666 SBA-NH<sub>2</sub> (see Figure 4) as shown by TEM micrographs.  
667 Existence of a tighter linkage (two carboxylic groups instead of  
668 one) between POM-CO<sub>2</sub>H and MCF-NH<sub>2</sub> as the result of a  
669 surface geometry more adapted for multiple anchorage could  
670 also be invoked to explain the decrease of the reactivity of  
671 POM-CO<sub>2</sub>H in POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>.

672 The existence of small aggregates as well as the irregular  
673 organization of POM-NH<sub>2</sub> in the third anchored catalyst,  
674 POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H, as shown in Figure 6, also had  
675 negative effects on cyclooctene conversion (Table 3, entry 8).  
676 Indeed, while in homogeneous conditions, we obtained a fair  
677 value after 1 day (97%), the conversion dramatically fell to 19%  
678 at ambient temperature in the case of POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H.  
679 Such a decrease is apparently due to a reduction of the exposed  
680 surface area of the active component of the catalyst and  
681 consequently a decrease of the contact between reactants and  
682 catalysts. POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H also culminated in the  
683 lowest POM loading of the three different anchored  
684 homogeneous catalysts so that significantly larger amounts of  
685 powder had to be used, leading to strong diffusion limitations.  
686 It is noteworthy that, for this specific solid material, a significant  
687 catalytic activity can be recovered at higher temperature (Table  
688 3, entry 10).

689 The very encouraging results of the present study compare  
690 well with those obtained by Stein and co-workers.<sup>17</sup> Indeed, in  
691 their work, the incorporation of POM hybrids (derived from  
692 the γ-[SiW<sub>10</sub>O<sub>36</sub>]<sup>8-</sup> platform) by covalent links into porous 692



693 silica materials had led to moderate yields (up to 28%) in the  
694 epoxidation of cyclooctene (at room temperature, after 24 h).  
695 Such comparison consequently validates the use of bi-  
696 sphosphonate derivatives of trivacant POMs for the preparation  
697 of anchored homogeneous catalysts. Indeed, we observed the  
698 persistence of fairly good catalytic activity after immobilization  
699 of the latter (probably due to the presence of “lacunary” oxygen  
700 atoms after grafting), provided that the best POM organization  
701 on the chosen support may be found.

#### 4. CONCLUSION

702 In this work, we have prepared and characterized three POM-  
703 containing mesoporous silica supports and studied their  
704 catalytic activity in the epoxidation of cyclooctene and  
705 cyclohexene in the presence of hydrogen peroxide. These  
706 POM-anchored materials (POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>, POM-  
707 CO<sub>2</sub>H@MCF-NH<sub>2</sub>, and POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H) were ob-  
708 tained through amide coupling reactions between POMs  
709 hybrids and functionalized silica supports bearing each  
710 complementary pending group.

711 Two different POMs, with either carboxylic acid (TBA<sub>3</sub>NaH-  
712 [As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>]) or alkylamine func-  
713 tions (TBA<sub>4</sub>H[PW<sub>9</sub>O<sub>34</sub>{As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>]}<sub>2</sub>]), were used.  
714 Both POMs were shown to be efficient catalysts for cyclooctene  
715 epoxidation with aqueous H<sub>2</sub>O<sub>2</sub> at room temperature in  
716 homogeneous conditions (acetonitrile). The bis-carboxylic  
717 acid derivative TBA<sub>3</sub>NaH[As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)-  
718 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)}<sub>2</sub>] showed also interesting properties for  
719 the epoxidation of cyclohexene at room temperature, either in  
720 homogeneous conditions or after covalent immobilization on  
721 the SBA-NH<sub>2</sub> support, with an increased selectivity into  
722 epoxy cyclohexane in the latter case.

723 POM-anchored materials showed various catalytic perform-  
724 ances in the epoxidation of cyclooctene, with conversions in the  
725 range 19–97% after 24 h. These differences cannot be  
726 explained in terms of textural data since POM-CO<sub>2</sub>H@SBA-  
727 NH<sub>2</sub>, which presented the lowest S<sub>BET</sub>, was also the best  
728 anchored catalyst. The POM organization throughout the  
729 materials appeared to be a determining parameter. The  
730 structure of the POMs at the pore (SBA-15) or cell (MCF)  
731 level of the materials that could be observed by HR-TEM (after  
732 microtome cutting) showed a decrease of the POM  
733 nanostructure from POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> to POM-NH<sub>2</sub>@  
734 SBA-CO<sub>2</sub>H materials with some aggregates in the latter case.  
735 Trends emphasized for the catalytic activity of the anchored  
736 homogeneous catalysts were identical, i.e., the best activity for  
737 the material with the most ordered POMs.

738 Finally, recyclability experiments and a filtration test  
739 performed in the case of the POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> (before  
740 completion of the cyclooctene epoxidation reaction) clearly  
741 indicated that this material can be considered as a truly  
742 anchored catalyst, thus precluding the hypothesis of significant  
743 leaching of the active species.

#### ■ ASSOCIATED CONTENT

##### ● Supporting Information

746 Thermogravimetric analyses (TGA), weight losses, DTA curves  
747 and nitrogen adsorption/desorption isotherms of SBA-NH<sub>2</sub>,  
748 SBA-COOH, and MCF-NH<sub>2</sub> materials. Powder X-ray  
749 diffraction patterns and TEM micrographs of SBA-NH<sub>2</sub>, SBA-  
750 CO<sub>2</sub>H, and POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>. <sup>13</sup>C CP-MAS NMR  
751 spectra of SBA-COOH, POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H, and POM-  
752 CO<sub>2</sub>H@MCF-NH<sub>2</sub>. <sup>31</sup>P CP-MAS NMR spectra of POM-

CO<sub>2</sub>H@SBA-NH<sub>2</sub> and POM-CO<sub>2</sub>H@MCF-NH<sub>2</sub>. Raman  
spectra of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub> and POM-CO<sub>2</sub>H@MCF-  
NH<sub>2</sub> compared to that of TBA<sub>3</sub>NaH(POM-CO<sub>2</sub>H). Details  
(HR-TEM) of the zones of POM-CO<sub>2</sub>H@SBA-NH<sub>2</sub>, POM-  
CO<sub>2</sub>H@MCF-NH<sub>2</sub>, and POM-NH<sub>2</sub>@SBA-CO<sub>2</sub>H function-  
alized silica grains studied by XEDS and tables indicating the  
W/Si contents. The Supporting Information is available free of  
charge on the ACS Publications website at DOI: 10.1021/  
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##### Author Contributions

The manuscript was written through contributions of all  
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the manuscript.

##### Notes

The authors declare no competing financial interest.

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853 CO<sub>2</sub>H and POM-NH<sub>2</sub> are different: B<sub>3</sub>α-[AsW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> for POM-  
854 CO<sub>2</sub>H, and A<sub>3</sub>α-[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> for POM-NH<sub>2</sub>. The choice of these  
855 compounds has been done in order to maintain the presence of a <sup>31</sup>P  
856 nucleus in each POM hybrid for its characterization (<sup>31</sup>P NMR), with  
857 the aniline function in POM-NH<sub>2</sub> being introduced through  
858 organoarsenate {As(O)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)} groups, commercially available  
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882 *trans*-cyclohexane-1,2-diol (that came from the opening of  
883 epoxy-cyclohexane with H<sub>2</sub>O), a product typical of two-electron  
oxidation mechanisms, along with the classical allylic products (such as  
2-cyclohexene-1-ol and 2-cyclohexene-1-one). It is noteworthy that the  
mass balance for this reaction (which was calculated after taking  
account of the initial reactive and all observed products in the  
chromatogram) was systematically found to be higher than 90% for  
each sampling, with a final mass balance after 1 day of 94%.
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