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Catalytic epoxidation of styrene and methyl oleate over peroxophosphotungstate entrapped in mesoporous SBA-15†

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A new route for the heterogenization of peroxophosphotungstate species was developed for the epoxidation of olefins such as styrene and methyl oleate with hydrogen peroxide. The polyoxometalate based catalyst was entrapped inside the pores of a mesoporous SBA-15 support thanks to the grafting of octyl groups at the pores entrance allowing their convenient recycling.

Introduction

Epoxidation of alkenes is a highly relevant industrial reaction since epoxides find a broad range of applications in many fields of chemistry. One of the common and efficient routes consists in the use of mixture of formic acid/hydrogen peroxide (H₂O₂) or peracids/H₂O₂. This process is particularly efficient for the epoxidation of renewable fatty esters or vegetable oils. Comprehensive reports covering this topic can be found in the current literature.^{1–3} Although very high yields to the corresponding epoxides were reported in the presence of a stoichiometric amount of formic acids or peracids, formation of by-products and work-up procedures represent two serious drawbacks. In order to tackle these issues, few reports highlighted the possible use of tungsten-based derivatives, including polyoxometalates (POM), as catalyst for the direct epoxidation of alkenes in the presence of H₂O₂.^{4–12} Use of H₂O₂ as the oxidant is here of particular interest mainly because it is cheap, readily available in large scale and generates water as the sole by-product. These homogeneous POM catalysts were found to be highly active and usually exhibit a very high selectivity to epoxide offering a greener alternative to the utilization of formic acids or peracids.⁴ These POMs, also called Venturello's catalyst, are ionic and composed of a peroxophosphotungstate anion (PO₄[W(O)(O₂)₂]₄^{3–}) which is the active species in the oxidation

of alkenes with H₂O₂.⁴ The cation is generally a quaternary ammonium bearing long alkyl chains such as methyltrioctyl ammonium for instance. In such a case, POM also exhibits surfactant properties, thus favoring a better contact between alkenes and the aqueous H₂O₂ phase resulting in an enhancement of the reaction rate.

Previously, we and others have reported that epoxidation of methyl octadecenoate can be achieved with high yield in the presence of a peroxophosphotungstate catalyst.⁵ In particular, we have hypothesized that the high efficiency of these systems may rely on a synergetic effect between hydrogen peroxide and air (or oxygen) that favours the complete conversion of methyl octadecenoate into its epoxide form.⁶ Although high yields have been reported, separation and reuse of the homogeneous POM catalyst still remains a serious limitation. In this context, many groups have attempted the immobilization of POM over various solid supports.⁷

Neumann and Miller⁸ have first developed an insoluble catalytic complex consisting of a silicate xerogel covalently modified with phenyl groups and quaternary ammonium–polyoxometalate ion pairs. This catalyst is efficient for alkenes epoxidation with 30% aqueous H₂O₂ in the absence of any organic solvent. Later, same authors have reported a new route for immobilizing POM.⁹ Silica surfaces were covalently functionalized with polyethers which act as a supported liquid phase and/or ligands for the immobilization of homogeneous POM catalyst. This system led to the quantitative epoxidation of cyclooctene in the presence of 30% H₂O₂. The catalyst can be recycled without appreciable loss of activity. In 2007, Kovalchuk *et al.*¹⁰ have studied various supports for the heterogenization of the anion [HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}]₂^{2–}. To study the influence of the support on the catalytic efficiency, silica with different lipophilic properties has been synthesized by grafting various alkyl chains. Influence of lipophilic properties on the catalyst activity has been demonstrated in the epoxidation of limonene and cyclooctene in the presence of *tert*-butyl alcohol as the solvent and H₂O₂ as the oxidant. Mizuno and co-workers developed a concept of immobilization of POM species on an organic–inorganic hybrid support with covalently anchored *N*-octyldihydroimidazolium, leading to efficient catalysts for many types of oxidation reactions.¹¹ Previously, different peroxophosphotungstate catalysts supported onto amphiphilic resins were also prepared by ion exchange thanks to the grafting

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† Electronic supplementary information (ESI) available: Chemical compositions of the catalysts, N₂ adsorption–desorption isotherms, BJH pore size distribution and XRD patterns. See DOI: 10.1039/c2cy20082a

of an imidazole moiety on the support¹² leading to 30% of epoxide yield in the case of methyl oleate. The main drawback of this catalytic system was the low content of the POM species on the resin.

Kholdeeva *et al.*¹³ have also prepared different polyoxometalate-based heterogeneous catalysts for liquid phase oxidations. For example, they have prepared a catalyst by embedding it into a silica matrix by (i) a sol-gel method, (ii) by an irreversible adsorption of POM on active carbon or (iii) by incorporation within nanocages of a metal-organic framework MIL-101. Li and co-workers¹⁴ have studied the encapsulation of homogeneous catalyst in the mesoporous cage of SBA-16 and showed that the catalytic performances of these catalysts are as good as the homogeneous catalysts. They have also studied the direct immobilization of polyoxometalate catalyst in layered double hydroxide.¹⁵

Recently, Inumaru and co-workers¹⁶ reported an efficient way for the wet impregnation of a homogeneous catalyst over mesoporous silica followed by a silylation of the material with a long alkyl chain alkoxy silane. The grafting of alkoxy silane led to the entrapment of the homogeneous catalyst within the mesoporous framework. Indeed, during the grafting process, silanol groups located at the pore entrance first react with the alkoxyorganosilane inducing a pore blockage.

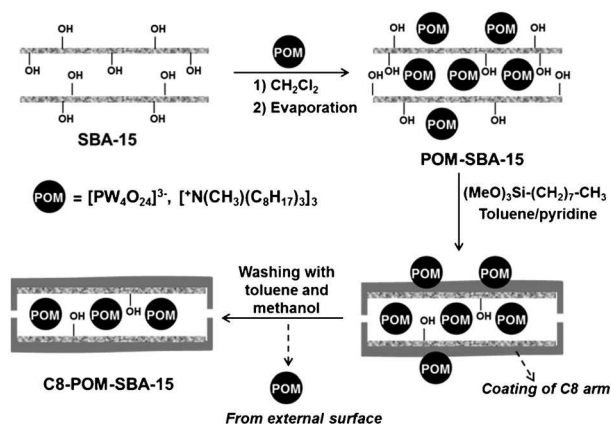
Inspired by this methodology, we report here the entrapment of homogeneous POM catalyst within the mesoporous framework of SBA-15. In particular, using this strategy, we found that POM encapsulated in the mesopores of SBA-15 was capable of epoxidizing styrene or methyl oleate with more than 50% selectivity while no leaching of POM was observed, thus offering an environmentally friendly route to valuable epoxides.

In a first set of experiments, the POM catalyst and SBA-15 were separately prepared as described elsewhere.¹⁷ Entrapment of POM within the porous framework of SBA-15 was achieved in a three step procedure. Typically, 5 g of POM was dissolved in 20 mL of dichloromethane in the presence of 4 g of SBA-15. Then, dichloromethane was gently removed under reduced pressure allowing the adsorption of POM over SBA-15. Note that at this stage, POM is impregnated either within the pores or on the external surface of SBA-15 leading to the so-called POM-SBA-15 material. As described in the literature, POM-SBA-15 was then reacted with *n*-octyltriethoxysilane in a mixture of toluene/pyridine (10:1) with the aim of blocking the pores and entrapping the homogeneous POM catalyst in the mesopores of SBA-15. Next, the recovered C8-POM-SBA-15 was extensively washed with toluene and methanol in order to remove POM that was impregnated on the external surface. The procedure is illustrated in Scheme 1.

Experimental section

Experimental synthesis of the catalysts

The sample of SBA-15 was prepared according to the literature.¹⁷ 12 g of pluronic 123 (triblock copolymer) were dissolved in 360 g of distilled water and 43 g of 32% HCl were added under vigorous stirring prior to heating at 308–313 K. After total dissolution of P123, 24 g of TEOS (tetraethyl orthosilicate) were added; the mixture was stirred at 308–313 K for 24 h. The resulting gel was



Scheme 1 Procedure for the synthesis of the catalyst.

transferred to a Teflon autoclave and kept at 323 K for 24 h. The autoclave temperature was decreased to room temperature; the solid product was filtered off, washed with water and calcined at 823 K for 3 hours under air with a heating rate of 1 K min⁻¹.

The peroxophosphotungstate catalyst (POM) ($[(C_8H_{17})_3N^+ - CH_3]_3 [PW_4O_{24}]^{3-}$) was prepared according to a typical procedure;⁴ a suspension of 5 g of tungstic acid in 14 mL of 35% H₂O₂ w/v was stirred and heated at 333 K until a colourless solution was obtained. After filtration and cooling the solution to room temperature, 1.24 mL of 40% H₃PO₄ w/v was added and the mixture was further diluted with 60 mL of distilled water. To the resultant solution, 4.18 g of methyltriocylammonium chloride in 80 mL of dichloromethane was added dropwise (2 min) under vigorous stirring. Then, the mixture was stirred for another 15 min. After the decantation, the organic phase was dried over MgSO₄ and gently evaporated on a rotary evaporator under reduced pressure at 308–313 K yielding a slightly yellow syrup.

Next, 4 g of the prepared SBA-15 and 5 g of the POM were dissolved in 20 mL of dichloromethane. After stirring the mixture at room temperature for 1.5 h, the solvent was evaporated very slowly in order to include the catalyst by solvophobic effect. The solid (A) was dried overnight at 318 K.

Finally, 4.5 g of *n*-octyltriethoxysilane, 3 g of pyridine in toluene (30 mL) were added to solid A. The mixture was stirred 24 h at 333 K. The solid was washed two times with toluene (30 mL) and four times with methanol (30 mL). Then it was dried in an oven overnight at 311 K leading to the so-called C8-POM-SBA-15 catalyst (Scheme 1). POW trapping efficiency was estimated to be approximately 15 mole%.

Characterization of the catalysts

The XRD analyses for the SBA-15 were carried out with a Bruker D5005 diffractometer. Data were collected stepwise over the $0.75^\circ \leq 2\theta \leq 5^\circ$ angular region, with steps of 0.02° , 20 s per step accumulation time, and Cu K α (1.54178 Å) radiation.

The ICP analyses were performed with an ICP/ES Perkin Elmer Optima 2000 DV.

Textural properties were determined by nitrogen isotherms at liquid N₂ temperature using a Micromeritics Tristar apparatus (static volumetric technique). Samples (0.2 g) were first out gassed overnight at 373 K under vacuum.

Epoxidation procedure

Epoxidation of methyl oleate (MO) was carried out in a double-walled reactor. Typically, 0.5 g of catalyst and methyl oleate (99% Aldrich, 3.37 mmol) were introduced under vigorous stirring (400 rpm) and with an O₂ flow (10 mL min⁻¹). When a temperature of 338 K was reached, 35% H₂O₂ w/v (990 μL) was added in 3 portions (330 μL at *t*₀, *t*_{4h} and *t*_{8h}). At the end of the reaction, the mixture was filtered in order to recover the catalyst. The reused catalyst was then washed with 3 mL of ethyl acetate and recycled without other purification. The organic phase was then extracted with 20 mL of ethyl acetate (99% Carlo-Erba) and dried on MgSO₄. After evaporation of the solvent, products were analyzed by GC.^{5,6}

A similar procedure was used for the epoxidation of styrene with only a slight modification *i.e.* the catalyst was separated by centrifugation instead of filtration.

Results

The immobilized POM was then characterized by means of different analytical methods. XRD patterns of SBA-15 and C8-POM-SBA-15 were similar and show three well-resolved peaks at 2θ lower than 4° supporting that the mesoporosity of SBA-15 is preserved after entrapment of the POM (Fig. 1). However, from Fig. 1, it clearly appears that the *d*100 diffraction line of C8-POM-SBA-15 (1,1° - 2,1° - 2,7°) is shifted to higher 2θ than that of SBA-15 (1,0° - 2,0° - 2,6°) suggesting a contraction of the mesoporous structure during the entrapment of the POM.

With the aim of supporting this hypothesis, textural properties of the starting SBA-15 and C8-POM-SBA-15 materials were investigated using the BJH method (Fig. S1 and S2, ESI†). Results are presented in Table 1.

During the entrapment stage of POM within SBA-15, a significant decrease of the specific area (from 515 to 357 m² g⁻¹) and the porous volume (from 0.55 to 0.38 cm³ g⁻¹) was

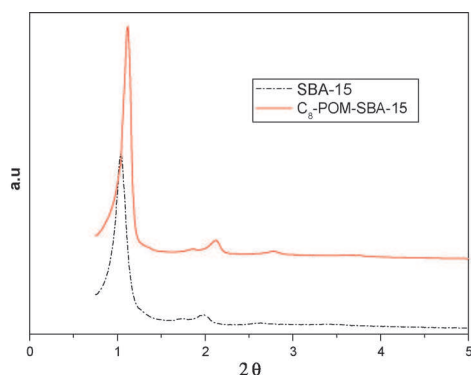


Fig. 1 XRD patterns of the initial SBA-15 and the final material C8-POM-SBA-15.

Table 1 Textural properties of prepared materials^a

Material	<i>S</i> _{BET} /m ² g ⁻¹	<i>V</i> _p /cm ³ g ⁻¹	Pore diameter/nm
SBA-15	515	0.55	5.4
C8-POM-SBA-15	357	0.38	4.7

^a Measured by the BJH method, from the adsorption branch of the N₂ isotherm.

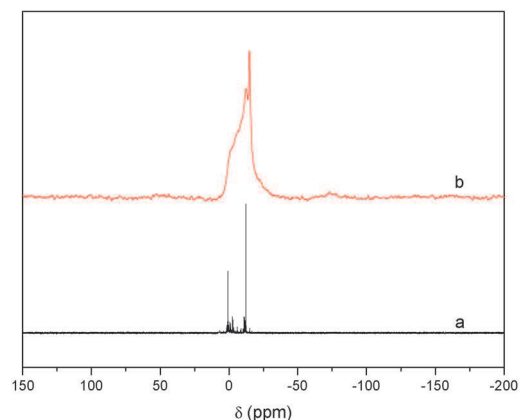


Fig. 2 ³¹P NMR analysis of the liquid POM (a) and the catalyst C8-POM-SBA-15 after three runs (b).

observed in accordance with the presence of POM within the mesopores of SBA-15. After entrapment of the POM, the pore diameter of the SBA-15 support was decreased from 5.4 to 4.7 nm confirming the contraction of the mesoporous structure observed by XRD.

³¹P and ¹³C NMR analyses performed on C8-POM-SBA-15 and homogeneous POM were similar suggesting that the chemical structure of POM was not modified during the entrapment procedure (Fig. 2 and 3). Additionally, the P/W and P/N mole ratio were 0.22 and 0.27, respectively, which is in accordance with the theoretical mole ratio for the homogeneous POM (P/W_{theo} = 0.25 and P/N_{theo} = 0.33), further demonstrating the integrity of the chemical structure of POM after its entrapment within the pores of SBA-15 (Table S1, ESI†). On the basis of elemental analysis, the loading of POM in the SBA-15 is 0.065 mmol g⁻¹. Moreover carbon and hydrogen amounts strongly increase after grafting of octyl chains and stay stable after 3 recycling proving that the alkyl chains are efficiently grafted on the mesoporous SBA-15 silica.

Next, we investigated the catalytic activity of the C8-POM-SBA-15. In a first set of experiments, catalytic activity of C8-POM-SBA-15 was tested in the epoxidation of styrene in the presence of hydrogen peroxide. Typically, 3.37 mmol of styrene were mixed with 0.5 g of C8-POM-SBA-15 and heated at 50 °C prior to addition of 990 μL of H₂O₂. Note that H₂O₂ was added in three portions in order to by-pass its

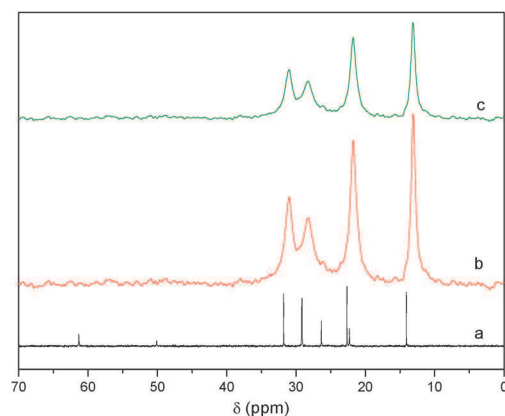


Fig. 3 ¹³C NMR analysis of (a) POM, (b) the catalyst C8-POM-SBA-15, and (c) the catalyst after three runs.

Table 2 Epoxidation of styrene with the C8-POM-SBA-15 catalyst^a

Entry	Catalytic run	Time/h	Epoxide selectivity ^b (%)	W leaching ^c /ppm
1	1	1	59	nd
2	1	2	100	0.5
3	2	1	29	nd
4	2	2	59	<0.1
5	2	3	59	<0.1
6	3	2	56	<0.1
7	4	2	60	<0.1

^a 100% conversion, 2 h, 338 K, H₂O₂/styrene (3/1), O₂ 10 mL min⁻¹.
^b Determined by gas chromatography. ^c Determined by ICP.

decomposition. The reaction progress was monitored by gas chromatography. Results are presented in Table 2. After 1 h of reaction, styrene was completely converted while the selectivity to the corresponding epoxide was 59% (entry 1).

Upon prolonged reaction time, up to 2 h, the selectivity to epoxide was increased from 59% to 99% which is consistent with the formation of reaction intermediates (entry 2).

After the first catalytic cycle, the C8-POM-SBA-15 was recovered by filtration and reused as collected in order to investigate its possible recycling. Although after 1 h conversion of styrene was complete, like observed in the first catalytic run, the selectivity was lowered (29% vs. 59% for the first run, entry 3). As observed in the first catalytic run, upon prolonged reaction time (2 h), the selectivity to epoxide increased from 29% to 59% but this selectivity then remained constant even after stirring after 3 h (entries 4 and 5). It is noteworthy that during the third and fourth catalytic cycle, complete conversion and same selectivities were obtained showing that the C8-POM-SBA-15 catalyst can be successfully recycled (entries 4, 6, and 7). This surprising change of catalytic behavior observed only after the first catalytic run might be ascribed either (1) to a partial leaching of POM during the first catalytic run or (2) to a chemical modification of the POM located in the pores of SBA-15.

In order to get more insight on this phenomenon, used C8-POM-SBA-15 was characterized by means of different analytical methods. First, no change of XRD patterns was observed before and after catalysis indicating that the mesoporous structure of SBA-15 was not damaged during the catalytic reaction (Fig. S3, ESI[†]). ICP analysis performed on the liquid phase after removal of C8-POM-SBA-15 revealed a contamination of W lower than 0.5 ppm while contamination of P was found below the detection limit of apparatus suggesting that leaching of POM did not occur in a large extent during the catalytic reaction. To further support this hypothesis, the C8-POM-SBA-15 was removed after 20% of conversion and the liquid phase was heated (hot filtration test). No significant increase of the styrene conversion and selectivity to epoxide was observed confirming that leaching of POM can be ruled out for explaining this sudden change of selectivity observed after the first catalytic run. Additionally, determination of the P/W, P/N, C/N mass ratio of the C8-POM-SBA-15 catalyst before and after catalytic experiments were similar indicating that the chemical composition of POM was not changed after the first catalytic cycle (Table S1, ESI[†]). Such information was also supported by solid ¹³C NMR that did not reveal significant changes in the structure of POM before and after catalytic experiments (Fig. 3). Taken together, these results

demonstrate that the mesoporosity and chemical structure of POM remained unchanged after the first catalytic run. Therefore, one may suspect that this surprising change of selectivity observed after the first catalytic cycle might be ascribed to a change of the POM geometry presumably due to the reorganization of the C8 arm when the C8-POM-SBA-15 catalyst was first immersed in water. Indeed, the C8-POM-SBA-15 was prepared in an organic solvent. Because of the hydrophobicity of the C8 arm, one may suspect that the molecular organization of the C8 arm on the SBA-15 can be affected when the C8-POM-SBA-15 was placed in an aqueous phase, thus inducing a slight change of configuration of the entrapped POM. These aspects definitely deserve further investigations.

Having demonstrated that the C8-POM-SBA-15 can be recycled without significant leaching of POM, we next investigated its activity in the epoxidation of methyl oleate. This reaction is of great importance since it provides a direct access to renewably-sourced epoxidized fatty esters which find nowadays a broad range of applications especially in the field of polymer chemistry. Experimentally, epoxidation of methyl oleate by H₂O₂ in the presence of C8-POM-SBA was performed similarly than starting from styrene. Results are presented in Table 3. As compared to styrene, the reaction rate is much lower since 15 h of reaction were required to observe 85% of conversion of methyl oleate vs. only 1 h for styrene (entry 1). A similar trend is observed in the current literature and was ascribed to the very low solubility of methyl oleate in the aqueous phase. Similarly to what was observed from styrene, the selectivity of the reaction was dramatically changed after the first catalytic cycle. Indeed, whereas the selectivity to the fatty epoxide was only 5% after the first run, the selectivity was increased to 50% during the second cycle which is in the same range as the selectivity observed from styrene (entry 2). Then, the selectivity remains constant cycle after cycle (entries 2–4). Here again, the mesoporosity of the C8-POM-SBA-15 catalyst and the chemical composition of POM were unchanged after reuse while no appreciable leaching of the POM was observed further supporting a plausible change in the geometry of the POM during the first catalytic cycle. Note that the yield of fatty epoxide (44%) obtained with our system is slightly higher than those reported in the current literature (30%) further demonstrating the effectiveness of this work.⁴

Finally, in order to show the effect of the C8 arm for the entrapment of POM, we next investigated the catalytic activity of the POM-SBA *i.e.* in the absence of C8 arm. In such a case, a catalytic amount of POM was directly impregnated over the mesoporous SBA-15 support. In this case, the conversion of methyl oleate (also observed in the case of styrene) rapidly decreased since after only three catalytic cycles the conversion

Table 3 Epoxidation of methyl oleate with the C8-POM-SBA-15 catalyst^a

Entry	Catalytic run	Conv. ^b (%)	Epoxide selectivity ^b (%)	W leaching ^c /ppm
1	1	85	5	<0.1
2	2	87	51	0.2
3	3	86	47	0.3
4	4	86	50	0.2

^a 338 K, 15 h, H₂O₂/MO (3/1), O₂ 10 mL min⁻¹. ^b Determined by gas chromatography. ^c Determined by ICP.

of methyl oleate was decreased to less than 20% while an important decrease of the W and P content of the catalyst was observed (77.4% loss of W and 77.3% loss of P). This result confirms that C8 arms are essential for the entrapment of POM within the mesoporous structure of SBA-15.

Conclusions

We report here an efficient route for the non-covalent immobilization of POM within the mesoporous framework of SBA-15. Remarkably, no appreciable leaching of POM in the aqueous phase was observed allowing the successful recycling of the C8-POM-SBA-15. Although the selectivity is different after the first catalytic cycle, presumably due to a change of the POM geometry during the first catalytic cycle, no appreciable loss of activity and selectivity was observed after the second recycling further demonstrating the efficiency of such a solid catalyst for the epoxidation of alkenes. Interestingly, the C8-POM-SBA-15 catalyst is also capable of epoxidizing methyl oleate with similar selectivity than that observed from styrene, thus providing a straightforward route for the synthesis of renewably-sourced monomers.

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