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Post-synthetic modification of crystal-like periodic mesoporous phenylene-silica with ferrocenyl groups



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ABSTRACT

Amination of crystal-like 1,4-phenylene-bridged periodic mesoporous organosilica (Ph-PMO) was achieved with about 35% conversion of phenylene groups. Ferrocenylimine groups were subsequently anchored onto this material by condensation of acetylferrocene with amino groups. Elemental analysis indicated that about 15% of amino groups in PMO-NH₂ were derivatized, resulting in an iron loading of 0.21 mmol g⁻¹. Evidence for the presence of ferrocenylimine groups in the derivatized material (PMO-Fc) was obtained from ¹³C cross-polarization (CP) magic-angle spinning (MAS) NMR and FT-IR spectroscopies. PMO-Fc was further characterized by ²⁹Si MAS NMR spectroscopy, powder X-ray diffraction (XRD), N₂ adsorption—desorption, and thermogravimetric analysis (TGA). Powder XRD and N₂ adsorption—desorption data for PMO-NH₂ and PMO-Fc indicated that the mesoporous structure and molecular-scale periodicity in PMO-NH₂ were benzaldehyde (major) and styrene at 55 °C using hydroperoxides as oxidants. The reaction products were benzaldehyde (major) and styrene oxide (minor), with the aldehyde being formed in yields of 25–27% at 24 h. Recycling experiments indicated that the material was susceptible to leaching of catalytically active species into the liquid phase due to the pronounced water sensitivity of the azomethine linkage.

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1. Introduction

In 1999, a new family of nanoporous organic-inorganic hybrid materials termed periodic mesoporous organosilicas (PMOs) were reported [1–3]. These materials are synthesized by the hydrolysis and polycondensation of bridged organosilanes of the type $(ZO)_3Si-R-Si(OZ)_3$ in the presence of a micellar surfactant template [4–8]. Important features of PMOs include well-ordered mesostructures with narrow pore size distributions, homogeneous distribution of organic groups within the pore walls, high specific surface areas and high pore volumes. In 2002, Inagaki and co-workers reported a phenylene-bridged PMO that showed not only a periodic arrangement of the mesopores but also molecular scale periodicity within the pore walls [9,10]. The "crystal-like" 1,4-phenylene-bridged PMO has a unique surface structure with alternating hydrophobic phenylene and hydrophilic silica layers with a periodicity of 7.6 Å. Work by Bion et al. showed that the pore

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diameter can be varied from 32 to 39 Å by changing the length of the hydrocarbon chain ($C_{14}-C_{18}$) of the alkyltrimethylammonium surfactant used [11]. The family of crystal-like PMOs has since been extended to include materials containing 1,3-phenylene [12], biphenylene [13,14], ethylene [9,15,16], 1,4-divinylbenzene [17,18], 2,6-naphthylene [19] and pyridine bridging units [20].

PMOs with crystal-like pore walls offer new opportunities for various kinds of modification by post-synthetic derivatization. In particular, grafted guest species for catalytic or optoelectronic applications may be spatially organized along the wall surface [21-23]. To date, only a few studies have addressed the post-synthetic chemical modification of the organic groups in these materials. experiments performed for ethylene-Bromination and divinylbenzene-bridged PMOs showed that up to 35% of the organic groups were accessible for functionalization [16,18]. Crystal-like mesoporous phenylene-silica can be sulfonated in one step (by treatment with fuming sulfuric acid or chlorosulfonic acid) [9,24,25] or aminated in two steps (by nitration with HNO₃-H₂SO₄ followed by treatment with SnCl₂-HCl) [26]. N-Alkylation of the amino-functionalized material could be achieved with about 87% conversion by using a potassium iodide catalyzed method and



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microwave-assisted heating [27]. Phenylene-bridged PMO has been successfully modified with organometallic groups by treatment with $M(CO)_6$ (M = Mo, Cr; vapor or liquid-phase) to give supported arenetricarbonyl (-pHM(CO)_3-; pH = -C_6H_4-) complexes [28–31], and with [(CH_3CN)_3RuCp]PF_6 to give supported organoruthenium (-[pHRuCp]PF_6-; Cp = cyclopentadienyl) complexes [32].

To the best of our knowledge there are only a few papers that describe the incorporation of ferrocene into PMOs [33–35]. Such materials may have interesting catalytic properties. In particular, ferrocene-containing PMO (prepared by co-condensation) [34] and mesoporous SBA-15 (prepared by post-synthesis grafting) [36] were found to be active catalysts for the hydroxylation of benzene (giving, in the former case, phenol with 65% selectivity at *ca.* 31% conversion).

The catalytic oxidation of olefins gives a variety of industrially important products such as epoxides, carbonyl compounds, diols and oxidative cleavage products of C=C [37]. For example, the oxidation of styrene gives styrene oxide, benzaldehyde, styrene glycol, benzoic acid, acetophenone and phenylacetaldehyde, which are useful intermediates or final products, e.g. as reactive diluent for epoxy resins, or for synthesizing fragrances, flavors and aromas [37,38]. Several iron-containing ordered mesoporous silicas (MCM-41 and SBA-15) have been applied as catalysts for the liquid-phase oxidation of styrene [38–43]. For example, a catalyst comprising ferric oxide nanoparticles supported on SBA-15 gave benzaldehyde as the main product in high selectivity, under mild reaction conditions (91–94% at 7–12% conversion, 50 °C) [38]. The catalyst was prepared by calcination of ferrocene-loaded SBA-15 (prepared by a physical-vapor-infiltration method). No catalytic results were reported for the uncalcined material.

Considering the above points, we set out to prepare a ferrocenylmodified PMO as a possible catalyst for the oxidation of styrene. A new approach for the incorporation of organometallic groups in crystal-like mesoporous phenylene-silica is reported, based on the further modification of the aminated material mentioned above. Specifically, the amino groups were condensed with acetylferrocene to give anchored ferrocenylimine moieties. The resultant material has been characterized by various techniques and examined as a catalyst for the oxidation of styrene using hydroperoxides as oxidants.

2. Experimental

2.1. Materials and methods

Acetylferrocene (Sigma–Aldrich), anhydrous toluene (99.5%, Panreac), 1,2-dichloroethane (99%, Sigma–Aldrich), dichloromethane (>99%, Sigma–Aldrich), sulfuric acid (95–97% v/v, Panreac), nitric acid (65% v/v, Panreac), tin chloride (98%, Aldrich), hydrochloric acid (37% v/v, Carlo Erba), isopropylamine (>99.5%, Aldrich) and ethanol (PA, Panreac) were purchased from commercial sources. The anhydrous toluene was stored over activated 4 Å molecular sieves prior to use. 1,2-Dichloroethane and dichloromethane were dried over CaH₂, distilled under inert atmosphere, and stored over activated 3 Å molecular sieves. The phenylenebridged PMO (Ph-PMO) was synthesized according to the literature procedure [9,11]. Subsequent derivatizations were performed using standard Schlenk techniques.

Microanalyses for N were performed at the Department of Chemistry, University of Aveiro. Fe was determined by ICP-OES at C.A.C.T.I., University of Vigo, Spain. Powder XRD data were acquired with a Rigaku Geigerflex D Max-C Series diffractometer using Cu-K α radiation. Samples were step-scanned in 0.02° 2 θ steps with a counting time of 60 s per step. Nitrogen adsorption–desorption

isotherms were recorded at -196 °C using a Micromeritics Gemini V 2380 surface area analyzer. Functionalized PMO materials were dehydrated overnight at 150 °C prior to analysis. TGA was carried out using a Shimadzu TGA-50 system with a heating rate of 5 °C min⁻¹ under a static air atmosphere. FT-IR (ATR) spectra were measured with a Bruker Tensor 27 spectrophotometer in the range of 4000 to 350 cm⁻¹ with 256 scans and 4 cm⁻¹ resolution. Solidstate MAS NMR spectra were recorded at 79.49 MHz for ²⁹Si and 100.62 MHz for ¹³C on a Bruker Avance III 400 spectrometer operating at 9.4 T. ²⁹Si MAS NMR spectra were recorded with 40° flip angle pulses, a spinning rate of 5.0 kHz, and 60 s recycle delays. 29 Si CP MAS NMR spectra were recorded with 4 μ s 1 H 90° pulses, a contact time of 8 ms, a spinning rate of 5 kHz, and 5 s recycle delays. 13 C CP MAS NMR spectra were recorded with 4 μ s 1 H 90° pulses, a contact time of 1 ms, a spinning rate of 9 or 15.0 kHz, and 4 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane.

2.2. Preparation of PMO-NH₂ ($\mathbf{1}$)

The amination of the phenylene moieties in Ph-PMO was carried out by using the two step approach reported by Inagaki and coworkers [26]. First, a mixed acid solution of sulfuric acid (16.7 mL) and nitric acid (5.1 mL) was added slowly to Ph-PMO (1 g). After stirring for 3 days at room temperature, the mixture was poured into cold distilled water. The solid product was filtered and washed several times with a large amount of distilled water. The nitrated Ph-PMO (PMO-NO₂, 1.07 g) was obtained as a pale vellow powder. The aminated PMO (PMO-NH₂) was obtained by reduction of the nitro group. A solution of tin chloride (3.33 g) in hydrochloric acid (31.60 mL) was added slowly to PMO-NO₂ (1 g). The mixture was stirred for 3 days at room temperature and then mixed with 300 mL of distilled water. After filtration, the powder was washed with a large amount of distilled water followed by a mixture of isopropylamine (20 mL) in ethanol (100 mL). The PMO-NH₂ was obtained as a pale pink powder (1.04 g) after drying at 60 °C overnight. Anal. found: N, 2.09%. ¹³C CP MAS NMR: $\delta = 150.3$ (C1 (Ph-NH₂)), 133.5 (Ph-PMO, C3,5 (Ph-NH₂)), 123.9, 120.7 (C2,4,6 (Ph-NH₂)) (see Fig. 1 for atom numbering scheme). ²⁹Si MAS NMR: $\delta = -70.7 (T^2), -81.1 (T^3) [T^m = RSi(OSi)_m (OH)_{3-m}].$ ²⁹Si CP MAS NMR: $\delta = -70.7 (T^2), -80.8 (T^3).$

2.3. Preparation of PMO-Fc (2)

PMO-NH₂ (0.84 g) was predried under vacuum at 110 °C for 2 h. A dry toluene solution (20 mL) of acetylferrocene (3.28 g, 14.4 mmol) was then added and the suspension was stirred for 48 h at reflux. The cream colored solid was filtered, washed extensively with toluene (3 × 20 mL), 1,2-dichloroethane (4 × 20 mL) and dichloromethane (4 × 20 mL), and finally vacuum-dried. Anal. found: Fe, 1.15%. ¹³C CP MAS NMR: δ = 150.8 (C1 (Ph-N=C(CH₃)Fc)), 133.5 (Ph-PMO, C3,5 (Ph-N=C(CH₃)Fc)), 122.1 (C2,4,6 (Ph-N=C(CH₃)Fc)), 68.9 (Fc). ²⁹Si MAS NMR: δ = -71.8 (T²), -81.1 (T³). ²⁹Si CP MAS NMR: δ = -71.0 (T²), -80.9 (T³).

2.4. Catalysis

The catalytic reactions were carried out under air (autogenous pressure) and stirred magnetically (1000 rpm) in a closed borosilicate reactor (10 mL capacity) equipped with a valve for sampling, and immersed in an oil bath thermostated at 55 °C. Typically, the reactor was loaded with catalyst in an amount equivalent to 2.15 μ mol of iron, 3.4 mmol of styrene (Sty; 99%, Aldrich) and oxidant. Aqueous hydrogen peroxide (30 wt.% H₂O₂, Sigma–Aldrich), urea hydrogen peroxide (97%, Aldrich),



Fig. 1. Schematic illustration of Ph-PMO and its modification to give the aminated material PMO-NH₂ and the derivatized material containing anchored ferrocenyl groups (PMO-Fc).

tert-butylhydroperoxide (TBHP) in decane (5–6 M. Sigma-Aldrich: dried over activated 4 Å molecular sieves prior to use), or aqueous TBHP (70 wt.% aqueous, Sigma-Aldrich) were tested as oxidants (6.9 mmol) under batch conditions. In a different approach, aqueous H₂O₂ was added gradually to the reactor throughout the first 5 h of reaction (system referred to as semicontinuous). The cosolvents (3 mL) tested were acetonitrile (99%, Aldrich) and tetrahydrofuran (THF; 99.99%, Fischer Scientific), which allowed a single liquid phase to be obtained. For the reaction using TBHPdec as oxidant, CH₃CN was predried using activated 4 Å molecular sieves. The substrate was preheated in a separate vessel for 10 min at 55 °C, and then the desired amount was transferred to the reactor (with preheated walls) containing the catalyst and cosolvent. The instant t = 0 was taken as the instant the preheated mixture of the substrate, cosolvent and catalyst was put into contact with the oxidant.

The course of the reactions were monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m \times 0.25 mm; 0.25 µm) and a flame ionization detector, using H₂ as the carrier gas and cyclododecane oxide (95%, Aldrich) as internal standard. After a 24 h batch run, the solid phase was separated from the reaction mixture by centrifugation, washed with *n*-hexane (PA, Sigma–Aldrich), and dried at room temperature overnight to give the recovered solids referred to in the discussion.

3. Results and discussion

3.1. Synthesis

The phenylene-bridged PMO (Ph-PMO) was prepared by the hydrolysis and polycondensation of 1.4-bis(triethoxysilyl)benzene in the presence of octadecyltrimethylammonium bromide [9,11]. After synthesis the template was extracted with an ethanol/HCl solution. The amination of phenylene moieties in Ph-PMO was achieved by a two-step procedure involving treatment with very strong acid solutions of HNO₃-H₂SO₄ to give a nitrated material, followed by treatment with SnCl₂-HCl [26]. The final material is denoted PMO-NH₂. Elemental analysis of PMO-NH₂ gave an amino group density of close to 1.5 mmol g^{-1} , indicating that 35% of phenylene moieties in the parent PMO were functionalized with the amino group. Condensation of amino groups in PMO-NH₂ with acetylferrocene gave the modified material PMO-Fc containing anchored ferrocenylimine moieties (Fig. 1). ICP-OES analysis gave an iron content of 0.21 mmol g^{-1} . Hence, overall, about 5% of the phenylene moieties in the PMO were derivatized with ferrocenyl groups.

Evidence for the presence of ferrocenvlimine groups. $[Fe(C_5H_4C(CH_3)N-Ar)(C_5H_5)]$, in PMO-Fc was obtained from the ¹³C CP MAS NMR and FT-IR (ATR) spectra. The ¹³C CP MAS NMR spectrum of Ph-PMO displays a single resonance at 134 ppm for the 1,4substituted phenylene carbon atoms. After the two-step functionalization to give PMO-NH₂, resonance peaks at 121, 124, 134 and 150 ppm are observed (Fig. 2), in agreement with that reported previously [26,27]. The latter peak is assigned to the aromatic carbon atom directly bonded to NH₂ groups, while the overlapping peaks at 121 and 124 are assigned to the C2,4,6 carbons of aminosubstituted phenylene groups. The intense resonance at 134 is assigned to unmodified phenylene moieties and C3,5 carbons of amino-substituted phenylene groups. The subsequent treatment of PMO-NH₂ with acetylferrocene resulted in only slight changes to the ¹³C CP MAS NMR spectrum in the chemical shift range of 120-150 ppm. A new peak at 69 ppm is attributed to cyclopentadienyl carbon atoms of ferrocenyl groups.

Owing to the low iron content of 0.21 mmol g⁻¹, resonances due to the imine (expected in the range 150–170 ppm) and methyl group (expected at ca. 25 ppm) carbon atoms could not be observed in the ¹³C CP MAS NMR spectrum of PMO-Fc. The presence of methyl groups was, however, supported by FT-IR spectroscopy (Fig. 3). The ATR FT-IR spectra of PMO-NH₂ and PMO-Fc are similar



Fig. 2. ^{13}C CP MAS NMR spectra of (a) PMO-NH $_2$ and (b) PMO-Fc. Spinning sidebands are denoted by asterisks.

in the range of 400–4000 cm⁻¹ except that the latter shows an additional weak band at 1460 cm⁻¹, which is assigned to an asymmetric deformation mode of methyl groups. A band for the azomethine (C=N) stretching vibration, generally found between 1620 and 1650 cm⁻¹, may be present but is obscured by the absorption centered at 1625 cm⁻¹, which has contributions from the in-plane N–H bending vibration ("scissoring" mode) of aromatic primary amine groups, and a water bending vibration.

The materials PMO-NH₂ and PMO-Fc were further characterized by ²⁹Si MAS NMR spectroscopy (Fig. 4). The ²⁹Si MAS and CP MAS NMR spectra of PMO-NH₂ are in agreement with those reported previously [27], showing signals for single silanol organosilica species of the type [RSi(OSi)₂(OH)] (T²) and fully condensed [RSi(OSi)₃] sites (T³). No significant changes were observed upon treatment of PMO-NH₂ with acetylferrocene to give PMO-Fc. None of the spectra display Qⁿ signals corresponding to silicon atoms connected entirely to OSi and/or OH units, which indicates that all silicon atoms are covalently bonded within the PMO network and no Si–C bond cleavage took place during the chemical modifications.

Powder XRD and N₂ adsorption-desorption data for PMO-NH₂ and PMO-Fc indicated that the mesoporous structure and the molecular-scale periodicity in PMO-NH₂ were largely retained upon treatment with acetylferrocene. Thus, the powder XRD pattern of Ph-PMO shows one strong low-angle peak at a *d*-spacing of 48.5 Å, which is assigned to the (100) reflection of a twodimensional hexagonal symmetry (p6mm) lattice with a lattice constant a = 56.0 Å (Fig. 5). The broad, weak shoulder on this peak towards higher angles $(3-4^{\circ} 2\theta)$ comprises the overlapping (110) and (200) reflections. In addition to the low-angle peaks, a medium-range reflection is observed at d = 7.6 Å, which arises from the molecular-scale periodicity in the Ph-PMO pore walls along the channel direction [9–11]. The patterns for PMO-NH₂ and PMO-Fc are similar except that the (110) and (200) reflections are no longer clearly resolved, and the (100) reflection is relatively weaker when compared with that for Ph-PMO. These changes may be due to a reduction in the XRD scattering contrast (between the pores



Fig. 3. FT-IR (ATR) spectra of (a) acetylferrocene, (b) PMO-NH₂ and (c) PMO-Fc. The arrow marks the appearance of a band at 1460 $\rm cm^{-1}$, which is assigned to an asymmetric deformation mode of methyl groups.



Fig. 4. 29 Si MAS (a, c) and CP MAS (b, d) NMR spectra of PMO-NH₂ (a, b) and PMO-Fc (c, d).

and organosilica framework) due to the functionalization of the material (which results in a slight loss of surface area and pore volume, as described below).

The N₂ adsorption isotherm for PMO-Fc indicated that capillary condensation inside mesopores occurred in the p/p_0 range of 0.2–0.4, and multilayer adsorption occurred as p/p_0 tended to unity (Fig. 6). Hence, PMO-Fc possesses a mesoporous structure and significant external specific surface area. Similar features were observed for PMO-NH₂, indicating that the pore structure was essentially preserved during the modification treatment. Material



Fig. 5. Low angle powder XRD patterns of (a) Ph-PMO, (b) PMO-NH₂ and (c) PMO-Fc.



Fig. 6. N₂ adsorption isotherms of PMO-NH2 (\bigcirc) and PMO-Fc (\times).

PMO-Fc possessed a BET specific surface area (calculated for p/p_0 in the range of 0.01–0.1) of 434 m² g⁻¹, and pore widths (calculated from the BJH algorithm applied to the adsorption branch) in the range of 2.8–3.4 nm. The S_{BET} and pore sizes for PMO-Fc are lower than those for PMO-NH₂ (580 m² g⁻¹ and 3–3.5 nm, respectively), most likely due to the filling of the internal void spaces by the anchored organometallic species.

A typical TEM image of PMO-NH₂ along the pore channel axis is shown in Fig. 7(a). The image shows a locally well-ordered 2D hexagonal mesostructure. Accordingly, the corresponding FFT shows bright diffraction spots in a hexagonal arrangement (inset of Fig. 7(a)). TEM images of PMO-NH₂ perpendicular to the pore channel axis showed large domains of ordered stripe-like arrangements of the long parallel cylindrical channels. Similar images were obtained for PMO-Fc (Fig. 7(c)).

The TGA curves for Ph-PMO, PMO-NH₂ and PMO-Fc exhibit a weight loss below 100 °C due to desorption of physisorbed water (Fig. 8). For Ph-PMO [9,27], PMO-NH₂ and PMO-Fc, the decomposition and release of organic moieties from the framework takes places in one step, starting at ca. 530 °C for PMO (DTG_{max} = 620 °C), 350 °C for PMO-NH₂ (DTG_{max} = 610 °C) and 200 °C for PMO-Fc (DTG_{max} = 505 °C). Hence there is a progressive decrease in thermal stability upon amination and subsequent anchoring of ferrocenyl groups. Decomposition of the ferrocenyl groups in PMO-Fc



Fig. 8. TGA curves of acetylferrocene $(- \cdot - \cdot - \cdot)$, Ph-PMO $(\cdot \cdot \cdot \cdot \cdot)$, PMO-NH₂ (- - -) and PMO-Fc (--).

above 200 °C may lead to the iron-promoted decomposition and release of phenylene groups at a temperature significantly lower than that observed for PMO-NH₂. For PMO-NH₂, the mass loss (on a dry basis, i.e., after correcting for the physisorbed water content) is 35.9% in the temperature range of 350–775 °C, while the mass loss for PMO-Fc in the range of 200–650 °C is 38.6%. Assuming that in 1 g of PMO-NH₂ 0.22 mmol of NH₂ groups were derivatized with ferrocenyl groups as shown in Fig. 1 (to give a final Fe loading of 0.21 mmol g⁻¹), the calculated increment in mass loss for the decomposition step is 2.8% (assuming that Fe will be thermally removed alongside organic moieties), which is in agreement with the observed value of 2.7%.

3.2. Catalytic oxidation of styrene

PMO-Fc was tested as a catalyst for the oxidation of styrene (Sty) with different types of oxidants, at 55 °C, using CH₃CN as solvent (Fe:Sty:oxidant molar ratios of 0.06:100:200). The oxidants used were aqueous hydrogen peroxide (H₂O₂), urea hydrogen peroxide, and *tert*-butylhydroperoxide in decane or water. Of the tested oxidants, H₂O₂ led to the highest Sty conversion at 24 h reaction (8%)



Fig. 7. TEM images of PMO-NH₂ (a, b) and PMO-Fc (c). The inset in (a) is the corresponding fast Fourier transform (FFT).

with benzaldehyde (BzCHO) as the only reaction product; for the remaining oxidants the reaction did not occur.

The catalytic performance of PMO-Fc was further explored using H₂O₂ as oxidant, and CH₃CN or THF as solvent, at 55 °C (the oxidant was added gradually throughout 5 h reaction, to give Fe:(initial Sty):(total added oxidant) molar ratios of 0.06:100:500). The Sty conversion at 24 h reaction was 16% and 19% for CH₃CN and THF as solvents, respectively, and BzCHO was always the only reaction product (Table 1). Using PMO-NH₂ instead of PMO-Fc as catalyst under similar conditions led to 3% conversion at 24 h reaction. These results indicate that the active species contain iron. Iodometric titration of the mixture of PMO-Fc/H₂O₂/CH₃CN (without substrate) obtained after stirring for 5.5 h at 55 °C gave a "nonproductive" decomposition of H₂O₂ which lied within the range of experimental error (5%). A four-fold increase in the catalyst loading led to higher Sty conversion at 24 h: 28% and 30% conversion, for CH₃CN and THF, respectively. The reaction products were BzCHO and styrene oxide (StyO), with BzCHO formed in 25% and 27% yield for CH₃CN and THF, respectively. It is noteworthy that the two solvents tested led to similar catalytic results. The conversion of Sty to BzCHO may involve StyO as intermediate (with subsequent hydrolysis) or the direct oxidative cleavage of the double bond of the olefin (involving a radical mechanism) [40,42,44-46]. Using StyO as substrate instead of Sty, and the same catalytic conditions, led to 100% conversion at 24 h reaction, and BzCHO was formed in 55% yield (additionally, 2-hydroxyacetophenone was formed in 33% vield). Based on these results, the conversion of Stv to BzCHO involves StvO as intermediate at least to a certain extent.

As mentioned in the Introduction, one related published work on the oxidation of styrene is that of Zhang et al. [38], who used mesoporous SBA-15-supported ferric oxide nanoparticles (6.5– 24 mol% Fe content; H₂O₂ as oxidant; acetone as solvent), prepared by calcination of a ferrocene-loaded precursor. With a catalyst loading equivalent to 65–240 mol% of Fe relative to Sty, and a Sty:H₂O₂ molar ratio of 1:1, at 50 °C, 7–12% conversion was reached at 24 h reaction, and BzCHO was the main product (91–94% selectivity). Based on these results, PMO-Fc seems to be a fairly active and more selective catalyst than the Fe-containing SBA-15 material reported by Zhang et al.

The catalytic stability of PMO-Fc was investigated using CH₃CN as solvent, by reusing the recovered solid for two consecutive 24 h batch runs (Fe:Sty:oxidant molar ratios of 0.06:100:500). A decrease in the catalytic activity from run 1 to run 2 was observed (16% and 10% conversion, respectively), and BzCHO was always the only reaction product. A hot-filtration test (using a 0.2 μ m PTFE GVS membrane) was carried out for PMO-Fc, at 55 °C, in which the filtrate obtained at 5.5 h reaction was left to react until 24 h at the same temperature. The increment in Sty conversion between 5.5

Table 1

Reaction of styrene with H₂O₂ in the presence of PMO-Fc.^a

Solvent	Fe:Sty (mol%)	Time (h)	Conv. (%) ^b	Selectivity (%) ^{b,c}	
				BzCHO	StyO
CH₃CN	0.06	5	5 (2)	100 (100)	0 (0)
		24	16 (10)	100 (100)	0 (0)
CH₃CN	0.24	5	11	87	13
		24	28	91	9
CH₃CN	0.06	5	2	100	0
		24	19	100	0
THF	0.24	5	2	100	0
		24	30	92	8

^a Reaction conditions: Sty: H_2O_2 molar ratio of 1:5, 3 mL CH₃CN or THF as solvents, 55 °C, with the total amount of oxidant being added gradually during the first 5 h of reaction.

^b Values in parentheses are for the second run.

^c BzCHO = benzaldehyde, StyO = styrene oxide.

and 24 h reaction was comparable to that for the typical catalytic test (without filtration), suggesting that active species were leached from PMO-Fc into solution during the catalytic reaction. A likely explanation is that in the presence of water the imine group hydrolyses back to the ketone and the amine, resulting in the release of acetylferrocene into the liquid phase. The instability of the imine group was noted previously for the ordered mesoporous silica MCM-41 functionalized with a pyridylimine ligand, used for complexation with molybdenum tetracarbonyl [47] and bischlor-ocopper(II) [48] species.

4. Conclusion

In the present study we have demonstrated that crystal-like mesoporous phenylene-silica can be derivatized by performing a condensation reaction between phenylene-substituted amino groups and acetylferrocene. A ferrocenylimine-modified PMO was obtained and characterized in the solid state by various techniques. Although the ferrocene-PMO hybrid is effective in the ironcatalyzed oxidation of styrene with H₂O₂ under mild conditions at 55 °C, giving benzaldehyde as the major product with a selectivity typically greater than 90%, active species are leached from the modified PMO into solution during the catalytic reaction, probably due to the pronounced water sensitivity of the azomethine linkage. Other applications can be envisaged for the ferrocene-PMO hybrid, such as in the field of optical and electro-optical materials. The post-synthetic derivatization method reported here may be generally applicable for incorporating a wide range of functional species into crystal-like phenylene-bridged PMOs.

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