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Introduction

During the last two decades research into ordered mesoporous materials has undergone extraordinary growth,¹ with some of the key developments being the discovery by the Mobil Oil Company of the M41S family of surfactant-templated mesoporous silicas (1992),^{2,3} the synthesis of periodic mesoporous organosilicas (PMOs) by three groups working independently of one another (1999),^{4–6} and the synthesis by Inagaki and coworkers of a phenylene-bridged PMO that showed not only a periodic arrangement of the mesopores but also molecular scale periodicity within the pore walls (2002).⁷ 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.⁷ The work by Bion *et al.*

Fax: +351 234 370084; Tel: +351 234 378190

^bDepartment of Materials and Ceramics Engineering, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

^cUniversity of Poitiers, CNRS, UMR 7285, Institut de Chimie des Milieux et

Preparation of crystal-like periodic mesoporous phenylene-silica derivatized with ferrocene and its use as a catalyst for the oxidation of styrene

Ana C. Gomes,^a Maria J. Ferreira,^b Sofia M. Bruno,^a Nicolas Bion,^{a,c} Paula Ferreira,^b Anabela A. Valente,^a Martyn Pillinger,^a João Rocha^a and Isabel S. Gonçalves^{*a}

The surface silanol groups in crystal-like mesoporous phenylene-silica have been derivatized with trimethylsilyl, benzyldimethylsilyl and dimethylsilyl(ferrocene) groups by performing a post-synthetic grafting reaction with the corresponding chlorosilane precursors. The success of the grafting procedure was demonstrated by transmission FT-IR spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and ¹³C and ²⁹Si magic-angle spinning (MAS) NMR spectroscopy. Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and N₂ adsorption data for the modified materials indicated preservation of the mesostructure as well as the molecular-scale periodicity in the pore walls. Ferrocene and the ferrocenyl-modified periodic mesoporous organosilica (PMO) were employed in the catalytic oxidation of styrene at 55 °C using either hydrogen peroxide or *tert*-butylhydroperoxide as an oxidant. The main reaction product was always benzaldehyde (BzCHO), and other products included styrene oxide, benzoic acid and 2-hydroxyacetophenone. Using a styrene : H₂O₂ molar ratio of 1 : 5, the highest BzCHO yields at 24 h were 65% (85% selectivity) for ferrocene (semibatch conditions involving stepwise addition of H₂O₂, 1 mol% Fe) and 34% (83% selectivity) for the modified PMO (batch conditions, 0.06 mol% Fe). The modified PMO could be recovered and reused, albeit with a drop in catalytic activity due to partial metal leaching during the first catalytic run.

showed that the pore diameter can be varied from 32 to 39 Å by changing the length of the hydrocarbon chain (C_{14} to C_{18}) of the alkyltrimethylammonium surfactant used.⁸ The family of crystal-like PMOs has since been extended to include materials containing 1,3-phenylene,⁹ biphenylene,¹⁰ ethylene,^{7,11} 1,4-divinylbenzene,¹² 2,6-naphthylene¹³ and pyridine bridging units.¹⁴

PMOs with molecular scale periodicity offer new possibilities for various kinds of modifications by post-synthesis derivatization. In particular, grafted species for catalytic or optoelectronic applications may be spatially organized along the wall surface.¹⁵ Shylesh et al. found that oxodiperoxomolybdenum complexes of the type (L-L)MoO(O₂)₂ tethered onto phenylene-bridged mesoporous organosilica showed up to a 10-fold increase in catalytic activity and a high stability in liquid phase olefin epoxidation reactions, with aqueous tertbutylhydroperoxide (TBHP) or H_2O_2 as the oxidant, compared to corresponding systems based on conventional ordered mesoporous silica (MCM-41) supports.¹⁶ This effect was attributed to the increased hydrophobicity of the framework walls due to the presence of phenylene bridges in defined positions. The authors proposed that the unique hydrophobic pores could facilitate the adsorption of olefins close to the active

^aDepartment of Chemistry, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. E-mail: igoncalves@ua.pt;

Matériaux de Poitiers (IC2MP), 4 rue Michel Brunet, 86022 Poitiers Cedex, France

sites, and/or reduce the adsorption of the more polar epoxide and by-products (*tert*-butanol or H_2O).

The post-synthetic modification of molecularly ordered PMOs has mainly involved the derivatization of the organic groups by, for example, bromination,^{11b,12b} sulfonation^{7,17} and amination,¹⁸ vapor or liquid phase treatment with $M(CO)_6$ (M = Mo, Cr) to give arenetricarbonyl complexes,¹⁹ and treatment with $[(CH_3CN)_3RuCp]PF_6$ to give $[C_6H_4RuCp]PF_6^-$ complexes.²⁰ Much less attention has been paid to the derivatization of residual silanol groups in crystal-like PMOs. This pathway was used by Shylesh *et al.* in the study mentioned above,¹⁶ and by Sharifi et al. to anchor SO₃H groups for enhanced proton conductivity.^{17b} In the present work, we have anchored ferrocene units onto phenylene-bridged PMO (PMO-Ph) by derivatisation of silanol groups. The incorporation of ferrocene into mesoporous materials has been a topic of considerable interest for several years,²¹ especially for the preparation of electrochemically-active²² and/or catalytically active materials.²³ The ferrocene-PMO described herein has been characterised by various techniques and examined as a catalyst for the oxidation of styrene using hydroperoxides as oxidants.

Experimental

Materials and methods

All chemicals used were of reagent grade or better and used as received from commercial sources. PMO-Ph^{7,8} and CpFe- $(C_5H_4SiMe_2Cl)^{24}$ were prepared according to literature procedures. Prior to use, PMO-Ph was vacuum-dried at 110 °C for 2 h.

Fe was determined by ICP-OES at C.A.C.T.I., University of Vigo, Spain. Powder X-ray diffraction (XRD) data were collected using a Philips X'pert MPD diffractometer equipped with an X'Celerator detector, a graphite monochromator (Cu-Ka radiation filtered by Ni (λ = 1.5418 Å)) and a flat-plate sample holder, in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Samples were step-scanned in $0.02^{\circ} 2\theta$ steps with a counting time of 10 s per step. Nitrogen adsorptiondesorption isotherms were recorded at -196 °C using a Micromeritics Gemini V 2380 surface area analyzer. Functionalized PMO materials were heated overnight at 150 °C under flowing N_2 and then placed under reduced pressure (<4 Pa) at ambient temperature prior to starting the analysis. The microstructures were analyzed by scanning electron microscopy (SEM) using a HITACHI SU-70 high resolution microscope equipped with a Bruker EDS detector, and by transmission electron microscopy (TEM) using a 300 eV HITACHI H9000-NA microscope. FT-IR transmission spectra were measured with a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a NICOLET 6700 FTIR spectrometer equipped with a Praying Mantis[™] High Temperature Reaction Chamber. The spectra were collected using an MCT detector with a resolution of 2 cm⁻¹ and 64 scans at room temperature and 50 °C under secondary vacuum (10⁻⁵ mbar). Raman

spectra were collected using a Bruker RFS100/S FT instrument with 2 cm⁻¹ resolution (Nd:YAG laser, 1064 nm excitation, InGaAs detector). Solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 79.49 MHz for ²⁹Si and at 100.62 MHz for ¹³C using a Bruker Avance 400 spectrometer. ²⁹Si MAS NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz, 60 s recycle delays and 8 ms contact time. ²⁹Si CP MAS NMR spectra were recorded with 4 μ s ¹H 90° pulses, 8 ms contact time with a spinning rate of 5 kHz and 5 s recycle delays. ¹³C CP MAS NMR spectra were recorded with 4 μ s ¹H 90° pulses and 2 ms contact time with a spinning rate of 9.0 or 15.0 kHz and 5 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane.

Preparation of PMO-Si(CH₃)₃ (1)

A toluene solution (20 mL) of chlorotrimethylsilane (0.5 mL, 3.9 mmol) was added to PMO-Ph (0.4 g) and the suspension was stirred at room temperature for 20 h. The white solid was filtered, washed with dichloromethane $(4 \times 20 \text{ mL})$, and vacuum-dried. FT-IR (KBr, cm⁻¹): $\nu = 3443$ (s), 3062 (m) (ν (C-H)), 2960 (m) (ν (CH₃)), 1935 (w), 1829 (w), 1634 (m), 1388 (m), 1254 (m) (δ (Si-CH₃)), 1160 (vs), 1101 (sh), 1065 (vs) (ν (Si-O-Si)), 1020 (sh), 915 (m) (ν(Si-OH)), 861 (m), 848 (m) (γ(Si-CH₃)), 813 (m), 762 (m), 554 (vs), 519 (s), 430 (m), 388 (m). Raman (cm⁻¹): ν = 3186 (w), 3043 (m), 2961 (w), 2901 (m), 1596 (s), 1530 (w), 1412 (vw), 1307 (w), 1204 (w), 1103 (m), 998 (w), 779 (m), 632 (w), 556 (w), 114 (w). ¹³C CP MAS NMR: δ = -0.4 (CH₃), 1.2 (CH₃), 133.5 (PMO-Ph). ²⁹Si MAS NMR: δ = 10.5 $(Si(CH_3)_3)$, -61.5 (T^1) , -71.4 (T^2) , -81.1 (T^3) $[T^m = RSi(OSi)_m$ - $(OH)_{3-m}$]. ²⁹Si CP MAS NMR: $\delta = 10.5$ (Si $(CH_3)_3$), -61.3 (T¹), $-71.1 (T^2), -81.1 (T^3).$

Preparation of PMO-Si(CH₃)₂(CH₂C₆H₅) (2)

Benzylchlorodimethylsilane (0.75 mL, 4.13 mmol) and toluene (20 mL) were added to PMO-Ph (0.63 g) and the suspension was stirred at 80 °C for 48 h. The solid was filtered, washed extensively with dichloromethane (4 × 20 mL), and vacuum-dried at 50 °C. FT-IR (KBr, cm⁻¹): ν = 3449 (s), 3066 (m) (ν (C–H)), 3011 (w), 2935 (w), 1938 (w), 1832 (w), 1641 (m), 1497 (w), 1458 (w), 1388 (m), 1254 (sh) (δ (Si–CH₃)), 1161 (vs), 1101 (sh), 1065 (vs) (ν (Si–O–Si)), 1020 (sh), 920 (m) (ν (Si–OH)), 845 (w) (γ (Si–CH₃)), 813 (m), 762 (m), 558 (vs), 520 (s), 430 (m), 392 (m). Raman (cm⁻¹): ν = 3186 (w), 3043 (m), 2986 (w), 2901 (w), 1596 (s), 1530 (vw), 1205 (w), 1104 (m), 1001 (w), 779 (m), 632 (w), 556 (w). ¹³C CP MAS NMR: δ = -4.2 (CH₃), 27.0 (CH₂), 127.4 (CH₂*Ph*), 133.1 (PMO-Ph). ²⁹Si MAS NMR: δ = 7.6 (PhCH₂Si(CH₃)₂–), -70.6 (T²), -80.9 (T³). ²⁹Si CP MAS NMR: δ = 8.1 (PhCH₂Si(CH₃)₂–), -61.6 (T¹), -70.8 (T²), -80.5 (T³).

Preparation of PMO-Si(CH₃)₂(C₅H₄)Fe(C₅H₅) (3)

 $(C_5H_5)Fe(C_5H_4)Si(CH_3)_2Cl (0.52 g, 1.87 mmol)$ and dry dichloromethane (20 mL) were added to PMO-Ph (0.27 g) and the suspension was stirred at room temperature for 48 h. The pale yellow solid was filtered, washed extensively with dichloromethane (4 × 20 mL), and vacuum-dried. FT-IR (KBr, cm⁻¹): ν = 3443 (s), 3062 (m) (ν (C-H)), 2965 (m) (ν (CH₃)), 1938 (w), 1829 (w), 1641 (m), 1385 (m), 1265 (m) (δ (Si-CH₃)), 1160 (vs), 1101 (sh), 1065 (vs) (ν (Si-O-Si)), 1020 (sh), 910 (m) (ν (Si-OH)), 848 (m) (γ (Si-CH₃)), 808 (m), 759 (m), 554 (vs), 519 (s), 428 (m), 388 (m). Raman (cm⁻¹): ν = 3043 (m), 2966 (w), 2907 (w), 1596 (s), 1530 (vw), 1307 (w), 1205 (w), 1104 (m), 1001 (w), 779 (m), 632 (w), 556 (w). ¹³C CP MAS NMR: δ = -15.4 (CH₃), 71.1 (C₅H₄), 67.8 (C₅H₅), 133.6 (PMO-Ph). ²⁹Si MAS NMR: δ = -19.4 (Si(CH₃)₂), -71.1 (T²), -80.7 (T³). ²⁹Si CP MAS NMR: δ = -20.5 (Si(CH₃)₂), -71.0 (T²), -80.7 (T³).

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. Unless otherwise stated, the reactor was loaded with 6.3 mg (34 µmol) of ferrocene or 40 mg (equivalent to 2.15 µmol of iron) of material 3, substrate (3.4 mmol) and oxidant (5.1-17.2 mmol). The oxidants tested were aqueous hydrogen peroxide (30 wt% H₂O₂, Sigma-Aldrich) or aqueous tert-butylhydroperoxide solution (70 wt% in water, Sigma-Aldrich). The total amount of oxidant was added initially or gradually throughout the first 5 h of the reaction. The cosolvents tested were 1,2-dichloroethane (1.0 mL, DCE, Aldrich, 99%), acetone (1.5 mL, Fluka, 99.5%) or acetonitrile (3.0 mL, Aldrich, 99%), added in sufficient amounts to obtain a single liquid phase. The olefin and cosolvent were preheated in separate vessels (10 min at the reaction temperature) and then the corresponding desired amounts were transferred to the reactor (with preheated walls) containing the catalyst. The instant the reaction began 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 was 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 undecane as the internal standard. After 24 h of reaction, polystyrene (PS, identified by FT-IR) was sometimes isolated by the following procedure: the reaction mixture was centrifuged and the solid obtained was washed with *n*-hexane (Sigma-Aldrich, PA), and dried at room temperature overnight. The isolated yields of PS were in general less than 4%, but may be underestimated due to the partial solubility of PS in the reaction mixtures.

Results and discussion

Synthesis

Phenylene-bridged PMO (PMO-Ph) was prepared by the hydrothermal synthesis reported by Inagaki *et al.* using octadecyltrimethylammonium bromide and 1,4-bis(triethoxysilyl)benzene as starting materials.^{7,8} The powder XRD pattern of PMO-Ph shows one strong low-angle peak at a *d*-spacing of 48.5 Å, which is assigned to the (100) reflection of a two-dimensional hexagonal symmetry (*p*6*mm*) lattice with a lattice constant *a* =



Fig. 1 Low angle powder XRD patterns of PMO-Ph (a), and the derivatized materials 1 (b), 2 (c) and 3 (d).

56.0 Å (Fig. 1). The broad, weak shoulder on this peak toward higher angles (3–4° 2 θ) 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 PMO-Ph pore walls along the channel direction.^{7,8}

As mentioned in the introduction, the post-synthetic modification of PMO-Ph may be performed by derivatization of the phenylene groups and/or the residual silanol groups. The DRIFTS spectrum of PMO-Ph reveals the presence of non-condensed isolated surface silanol groups *via* the SiO–H stretching vibration at 3728 cm⁻¹ (Fig. 2).^{25 29}Si MAS NMR spectroscopy shows the presence of organosilica species of the type [RSi-(OSi)(OH)₂] and [RSi(OSi)₂(OH)] (in addition to fully condensed [RSi(OSi)₃] sites), with the latter single silanol species being much more abundant than the geminal silanol species.⁸

Treatment of PMO-Ph with chlorotrimethylsilane, benzylchlorodimethylsilane and chlorodimethylsilyl-ferrocene in either toluene or dichloromethane gave the derivatized materials 1-3, respectively (Fig. 3). A decrease in the population of isolated OH groups in the three materials (relative to PMO-Ph) was revealed by a pronounced decrease in the relative intensity of the sharp IR absorption band at 3728 cm⁻¹ in the DRIFTS spectra, especially noticeable for 1 and 3 (Fig. 2). The presence of methylsilyl groups in all three materials was confirmed by the three new absorption bands at 845–850 (γ (Si– CH₃)), 1255–1265 (δ (Si–CH₃)) and 2960–2965 cm⁻¹ (ν (CH₃)) in the IR spectra (Fig. 2 and 4), resonances between -15 and 2 ppm in the ¹³C CP MAS NMR spectra (Fig. 5), and resonances between -20 and 10 ppm in the ²⁹Si MAS NMR spectra (Fig. 6). Additional ¹³C NMR signals at 27.0 and 127.4 ppm for 2 are assigned to the carbon atoms of the benzyl group. The



Fig. 2 DRIFTS spectra in the range 2500–4000 $\rm cm^{-1}$ of PMO-Ph (a), and the derivatized materials 2 (b), 1 (c) and 3 (d).



Fig. 3 Schematic illustration of PMO-Ph, showing the three grafting reactions carried out to give materials **1–3**.

presence of ferrocenyl species in 3 is supported by the weak peak at 67.8 ppm and the broad shoulder at 71.1 ppm in the ¹³C CP MAS NMR spectrum, which are attributed to C_5H_5 and C_5H_4Si , respectively.^{21*d*,26} The low intensity of these signals is consistent with the low Fe content of 0.3 wt%. All three materials exhibit the expected strong ¹³C NMR resonance at 133.5 ppm for the phenylene groups of the PMO support.

The powder XRD patterns for 1–3 are similar to those for PMO-Ph, which indicates retention of the mesoporous structure as well as the molecular-scale periodicity (Fig. 1). SEM studies for all three materials revealed very large aggregates of irregular, thin and mostly elongated particles (Fig. 7). Material 3 was further characterized by TEM and N₂ adsorption–desorption isotherms measured at –196 °C. In accordance with the XRD results, TEM shows a locally well-ordered 2D hexagonal mesostructure (Fig. 8). Materials 1–3 exhibit a type IV nitrogen adsorption–desorption isotherm. Condensation inside the mesopores occurred at p/p_0 in the range of 0.1–0.4, and multilayer adsorption was noticeable as p/p_0 tended to unity,



Fig. 4 FT-IR spectra (KBr) of (a) PMO-Ph and the modified materials **1** (c), **2** (d) and **3** (e), and of the solids recovered from a 24 h catalytic run using an Fe : Sty : oxidant molar ratio of 0.06 : 100 : 500, and semibatch conditions for (b) PMO-Ph and (f) **3**. Spectrum (g) is of the solid recovered from a second run using **3**. The bands indicative of Si–CH₃ groups are highlighted by the yellow bars.



Fig. 5 ¹³C CP MAS NMR spectra of PMO-Ph (a), and the derivatized materials 1 (b), **2** (c) and **3** (d). Spinning sidebands are indicated by asterisks. The signals marked with $+(\delta$ 15.9, 58.3) are due to residual ethoxy groups present in the starting material PMO-Ph.



Fig. 6 ^{-29}Si MAS (a, c, e) and CP MAS (b, d, f) NMR spectra of the derivatized materials 1 (a, b), 2 (c, d) and 3 (e, f).

indicating that the samples possessed significant external specific surface area. Similar features were observed for the starting material PMO-Ph, confirming that the mesostructure was essentially preserved during the modification treatments. The BET specific surface areas (calculated for p/p_0 in the range 0.01–0.1) for 1–3 were 655, 627 and 738 m² g⁻¹, respectively, and the pore size distribution curves (BJH algorithm applied to the adsorption branch) had maxima (D_p) for 1–3 at *ca.* 3.7, 3.5 and 3.6 nm of pore width, respectively. The S_{BET} and D_p for 1–3 are lower than those for PMO-Ph (999 m² g⁻¹ and 3.9 nm, respectively, in agreement with the literature data⁸), most likely due to filling of the internal void spaces by the anchored species.

Catalytic oxidation of styrene

The catalytic performances of ferrocene and material **3** were investigated in the oxidation of styrene. To the best of our knowledge, there is only one very recent report on the application of ferrocene in oxidation catalysis.²⁷ Specifically, Shul'pin *et al.* described the oxidation of (cyclo)alkanes into alkyl hydroperoxides using a catalytic system consisting of a mixture of ferrocene and pyrazine-2-carboxylic acid (PCA) or 2,2'-bipyridine, and H₂O₂ as an oxidant. These catalytic oxidation systems were effective under relatively moderate reaction conditions (50 °C). In turn, supported ferrocene catalysts have been previously tested in oxidation reactions, specifically the hydroxylation of phenol or benzene, but not the oxidation of styrene.^{23*a*-*g*}

The oxidation of styrene to benzaldehyde involves bond cleavage. Oxidative cleavage of olefins is a useful synthetic tool



Fig. 7 Representative SEM images of the derivatized materials ${\bf 1}$ (a), ${\bf 2}$ (b) and ${\bf 3}$ (c).

in organic chemistry, allowing, for example, oxygen atoms to be introduced into molecules (*e.g.* forming carbonyl compounds) or to fragment large molecules.²⁸ The classical methods used for oxidative cleavage of olefins involve the use of ozone and/or heavy metals, posing serious safety/environmental concerns.²⁹

The catalytic performance of ferrocene was investigated in the reaction of styrene (Sty) using either DCE, CH_3CN or acetone as cosolvents, at 55 °C (Fe:Sty:oxidant molar ratio of 1:100:150). Under these conditions, benzaldehyde (BzCHO) and polystyrene (PS, less than 4 mol%) were detected as products, although less than 14% conversion was reached at 24 h



Fig. 8 TEM micrograph of the derivatized material **3**. The inset displays the (001) projection, which proves the hexagonal arrangement of pores.

of reaction. Using TBHP as an oxidant instead of H_2O_2 did not improve the catalytic results (<3% conversion at 24 h). PS was only isolated when the oxidant was H_2O_2 (for TBHP, no PS was isolated). Increasing the Sty : oxidant molar ratio from 1 : 1.5 to 1 : 5 (CH₃CN as a cosolvent) led to an increase in the conversion at 24 h from 7% to 37% for H_2O_2 (Table 1), whereas for TBHP the reaction remained slow (<3% conversion at 24 h). The main reaction product was always BzCHO (formed in 26% yield and 72% selectivity at 24 h), and other products included styrene oxide (StyO), 2-hydroxyacetophenone (HAP) and PS. A similar trend was reported for the oxidation of cyclohexane in the presence of ferrocene–PCA using CH₃CN as a solvent at 50 °C, in that much better catalytic results were obtained for H_2O_2 than for TBHP.²⁷

Table 1 Reaction of styrene with ${\rm H_2O_2}$ in the presence of ferrocene or material ${\bf 3}^a$

				Selectivity ^d (%)			
Catalyst	Operation mode ^b	Time (h)	Conv. ^c (%)	BzCHO	StyO	BzA	HAP
Ferrocene	Batch	5	17	93	7	_	_
		24^e	37	72	6	_	3
Ferrocene	Semibatch	5	10	91	9	_	
		24	77	84	6	3	6
$Ferrocene^{f}$	Semibatch	5	7	100	_	_	_
		24	33	81	13	_	4
3	Batch	5	14	100	_	_	_
		24	41	81	9	4	4
3	Semibatch	5	8 (4)	100 (100)	-(-)	-(-)	-(-)
		24	40 (23)	71 (85)	10 (11)	7 (—)	8 (—)

^{*a*} Reaction conditions: a Fe:Sty molar ratio of 1:100 for ferrocene and 1:1667 for 3, a Sty: H_2O_2 molar ratio of 1:5, 3 mL CH₃CN as a solvent, 55 °C. ^{*b*} Batch mode when the total amount of oxidant was added at the initial instant of the reaction, and semibatch mode when the total amount of oxidant was added gradually during the first 5 h of reaction. ^{*c*} Values in parentheses are for the second run. ^{*d*} Identified products: BzCHO = benzaldehyde, StyO = styrene oxide, BzA = benzoic acid and HAP = 2-hydroxyacetophenone. Polystyrene was sometimes identified as product at 24 h of reaction. ^{*e*} PS was detected with 19% selectivity. ^{*f*} A ferrocene : Sty molar ratio of 1 : 1667 was used.

A possible explanation for the poor catalytic results for ferrocene is the "non-productive" catalytic decomposition of the oxidant. Wang et al. reported significant decomposition of H₂O₂ by iron-containing silica materials, tested as catalysts in the reaction of Sty at 70 °C.³⁰ In order to check this hypothesis, ferrocene was mixed with each oxidant in separate experiments (without Sty and cosolvent, using a Fe: oxidant molar ratio of 1:150) for 3 h at 55 °C, and subsequently the concentration of the unreacted oxidant was measured by iodometric titration. Ferrocene nearly completely decomposed H₂O₂ (98%), whereas TBHP decomposition was negligible (2%, which is within the range of experimental error). These results are consistent with the release of gas bubbles observed from the reaction mixtures using H₂O₂ (this decomposition gives water plus molecular oxygen), which was not observed for TBHP. However, these results do not correlate with the higher catalytic activity with H₂O₂ as an oxidant in comparison to TBHP. Possibly, different mechanisms are involved for the two oxidants. It has been reported for the catalytic oxidation system ferrocene-PCA-H₂O₂ that ferrocene-PCA adducts are formed and react with H₂O₂ to give strong oxidizing hydroxyl radicals.²⁷ This is somewhat consistent with a previous work reporting that protonated ferrocene can react with H2O2 forming water and hydroxyl radicals.³¹ On the other hand, a free radical reaction mechanism has been proposed for iron-containing silicas tested as catalysts in the reaction of Sty with H2O2 to give BzCHO and StyO.³⁰ For ferrocene (and 3, discussed below, using a Sty: H_2O_2 molar ratio of 1:5) StyO was detected as a product at 24 h of reaction (Table 1). The conversion of Sty to BzCHO may involve StyO as an intermediate or the direct oxidative cleavage of the double bond of the olefin. Using StyO as the substrate instead of Sty, and ferrocene as the catalyst, led to 96% conversion at 24 h of reaction, and BzCHO was formed in 30% yield; the reaction products included benzoic acid (BzA) and HAP formed in 25 and 15% yields, respectively. Based on these results, it seems that for ferrocene the conversion of Sty to BzCHO involves StyO as an intermediate at least to a certain extent. Nevertheless, we cannot rule out that the direct oxidative cleavage of the double bond of Sty takes place via a parallel pathway. No PS was isolated for the reaction using StyO as the substrate, suggesting that the polymer product is formed via free radical polymerization of Sty possibly involving hydroxyl radicals as initiators.³²

In an attempt to improve the catalytic performance of ferrocene, the operation mode was changed from batch to semibatch in which the total amount of oxidant was added gradually during the first 5 h of reaction (CH₃CN as a solvent, at 55 °C, and the total amount of added H₂O₂ corresponded to a Sty: H₂O₂ molar ratio of 1:5). The conversion at 24 h was much higher for the semibatch conditions (77%) than for the batch ones (37%), Table 1. The main reaction product was always BzCHO (formed in 65% yield and 84% selectivity at 24 h), and other products included StyO, BzA and HAP (formed in 5%, 2% and 5% yield, respectively), and PS (smaller amounts were isolated compared to the batch conditions). Iodometric titration of the mixture of ferrocene–

 $\label{eq:Table 2} Table 2 \quad The literature data for iron-containing heterogeneous catalysts tested for the oxidation of styrene with H_2O_2$

Catalyst ^a	Reaction conditions ^b	Fe:Sty (mol%)	Conv. ^{<i>c</i>} (%)	BzCHO sel. ^{d} (%)	Other products ^e	Ref.
3	1:5, CH ₃ CN, 55 °C, 24 h	0.06	40	71	StyO, BzA, HAP	This work
Fe-SBA-15	1:1, Acetone, 50 °C, 24 h	65	7	94	StyO	23h
Fe-SBA-15	1:1, Acetone, 50 °C, 24 h	240	11	92	StyO	23h
Fe(acac)-SBA-15	1:3, CH ₃ CN, 30 °C, 24 h	7.8	22	72	StyO, BzA, diol	33 <i>a</i>
Fe(acac:salen)-SBA-15	1:3, CH ₃ CN, 30 °C, 24 h	7.8	45	>99	StyO, BzA, diol	33 <i>a</i>
Fe(salen)-clay	1:13, CH ₃ CN, rt, 24 h	nm^{f}	nm	nm ^g	nm	33 <i>b</i>
$(FeO_x)/SBA-15$	1:1, water, 100 °C, 4 h	3	95	100	_	35
Fe-SBA-1	1:1, CH ₃ CN, 80 °C, 4 h	0.18	66	73	StyO	36
Fe-SBA-1	1:1, CH ₃ CN, 80 °C, 4 h	0.36	68	74	StyO	36
Fe-SBA-1	1:1, CH ₃ CN, 80 °C, 4 h	0.54	66	72	StyO	36
Fe-MCM-41(s-g)	1:1, DMF, 60 °C, 2 h	0.18	22	35	StyO	34 <i>a</i>
Fe-MCM-41(imp)	1:1, DMF, 60 °C, 2 h	0.18	9	45	StyO, styrene glycol	34 <i>a</i>
Fe-MCM-41	1:3, CH ₃ CN, 50 °C, 2 h	0.06	14	80-96	nm	34 <i>b</i>
Fe-MCM-41	1:0.98, DMF, 73 °C, 2 h	0.32	14	37	StyO, BzA, diol, MA	30
Fe-ZSM-5	1:0.98, DMF, 73 °C, 2 h	0.21	5	63	StyO	30

^{*a*} Salen = N,N'-ethylenebis(salicylideneaminato), acac = acetylacetonate, clay = K10-montmorillonite, s–g = catalyst synthesized *via* the sol–gel technique, imp = catalyst synthesized *via* the impregnation technique. ^{*b*} Styrene : H₂O₂ molar ratio, solvent, reaction temperature, reaction time (rt = room temperature). ^{*c*} Sty conversion. ^{*d*} BzCHO selectivity. ^{*e*} StyO = styrene oxide, BzA = benzoic acid, diol = 1-phenylethanediol, and MA = mandelic acid. ^{*T*} nm = not mentioned. ^{*g*} BzCHO yield of 30%.

H₂O₂-CH₃CN (without Sty) indicated that for the semibatch conditions the decomposition of the oxidant after 330 min was not complete (50%), in contrast to that observed for the batch operation mode. Based on these results it seems that the catalytic performance and the productive consumption of the oxidant (or oxidant efficiency) may be improved by using the semibatch conditions. These results are in agreement with those reported by Wang *et al.* for the oxidation of Sty with H₂O₂ in the presence of iron-containing silica catalysts, where the efficiency of the oxidant was improved by gradually adding it to the reaction mixture.³⁰

The catalytic performance of material 3 was investigated using batch and semibatch conditions, with H₂O₂ as an oxidant and CH₃CN as a cosolvent, at 55 °C. In contrast to that observed for ferrocene, with 3 the catalytic results for the semibatch and batch conditions were comparable (40% and 41% conversion at 24 h, respectively) with BzCHO as the main reaction product formed in 28% and 33% yield, respectively (Table 1). Additional products were StyO, BzA and HAP (for semibatch conditions phenylacetaldehyde was also formed). In contrast to that observed for ferrocene, no measurable amount of PS was isolated in the case of 3. The reaction using PMO-Ph (without iron) instead of 3, under similar semibatch conditions, led to 3% conversion at 24 h, indicating that the iron species play a determining catalytic role. A comparative study of ferrocene and 3 under similar reaction conditions (using a Fe:Sty molar ratio of 1:1667, and semibatch conditions) showed that the latter led to somewhat higher conversion (33% and 40% for ferrocene and 3, respectively) and BzCHO yield at 24 h (27% and 28% for ferrocene and 3, respectively), Table 1.

A fair comparison of the catalytic performance of **3** with those reported in the literature for other catalysts tested in the same reaction is not trivial due to the different ranges of reaction conditions used. Based solely on the reported conversions and BzCHO yields, the catalytic results for **3** seem to be either comparable or superior to those reported for supported iron complexes bearing organic ligands^{23*h*,33} or iron-containing silicas and zeolites (Table 2).^{30,34} However, much better catalyst results have been reported for iron oxide nanoparticles supported on mesoporous silica.³⁵

The catalyst stability of **3** was investigated by using the semibatch conditions (CH₃CN-H₂O₂, 55 °C) and performing a second run. After the first run, the catalyst was separated by centrifugation, washed with *n*-hexane and dried at room temperature overnight. The reaction rate decreased from the first to the second run; 40% and 23% conversion at 24 h for runs 1 and 2, respectively, and BzCHO was always the main product (Table 1). The FT-IR spectra of the recovered solids are similar to those for the respective PMO-Ph and **3** (Fig. 4). In particular, for the derivatized material **3**, the bands at about 850 and 1260 cm⁻¹ due to methylsilyl groups are still present even after the second catalytic cycle.

The drop in catalytic activity of 3 from run 1 to run 2 may be due to metal leaching. In order to check this hypothesis a hot-filtration test was performed at 55 °C. The solid catalyst was filtered through a 0.2 µm PTFE GVS membrane after 330 min of reaction and the filtrate was left to stir at 55 °C until 24 h (counting from the initial instant of the hot-filtration test). The increment in Sty conversion between 330 min and 24 h of reaction was 25%, which is considerable in comparison to the increment of 32% observed for the typical catalytic test (without filtration). Hence, active species were leached from 3 into solution during the catalytic reaction. Superior catalyst stabilities (based on the evaluation of the catalytic activity in consecutive batch runs and metal leaching tests) have been reported for Fe(acac:salen) complexes and iron oxide nanoparticles supported on SBA-15, 33a, 35 and for iron-containing MCM-41 with an iron content lower than 0.8 wt%.³⁰

Conclusion

In the present study we have demonstrated that crystal-like mesoporous phenylene-silica can be derivatized by performing a grafting reaction between the surface silanol groups and chlorosilanes. A ferrocenyl-modified PMO was obtained and shown to be effective in the iron-catalyzed oxidation of styrene with H₂O₂ under mild conditions at 55 °C, giving benzaldehyde as the major product. However, active species are leached from the modified PMO into solution during the catalytic reaction. To the best of our knowledge, there is only one very recent report on the application of ferrocene in oxidation catalysis, namely oxidative alkane functionalization with H₂O₂ in the presence of pyrazine-2-carboxylic acid or 2,2'-bipyridine.²⁷ We report that catalytic amounts of ferrocene also promote the oxidation of styrene to benzaldehyde with quite high selectivity and, depending on the reaction conditions, moderate activity. Further studies are underway on the application of ferrocene and ferrocenyl-modified mesoporous materials in oxidation catalysis.

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