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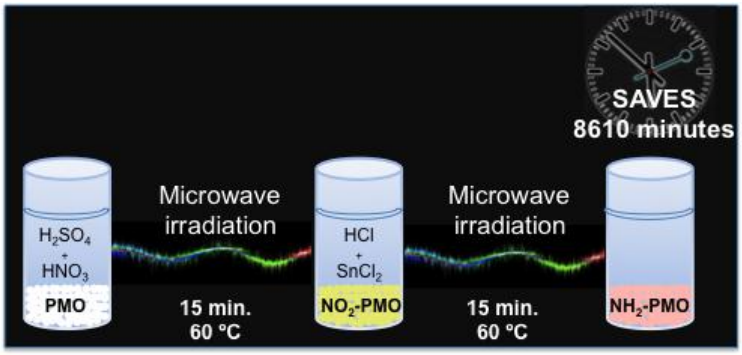
Table of Contents Entry



Fast Cooking:
Microwave-assisted synthesis allows the preparation of nitro- and amino-functionalized periodic mesoporous phenylene-silica in just 15 and 30 minutes, respectively, with tunable content and enhanced homogeneous distribution of functional groups.

Optimization of the time and temperature of the microwave-assisted amination of the phenylene-PMO

Mirtha A. O. Lourenço[a], José R. B. Gomes[b], Paula Ferreira*[a]

[a]*CICECO, Department of Materials & Ceramics Engineering, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.*

[b]*CICECO, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.*

*Corresponding author: *Fax: +351234401470; Tel: +351234401419; E-mail: pcferreira@ua.pt*

Abstract

In this paper we report a study on the optimization of the amination of periodic mesoporous phenylene-silica (PMO) using microwave heating. The optimization was carried out for two key steps in the reaction, namely, (1) nitration of the bissilylated phenylene bridge, and (2) reduction of the nitro group to primary amine. The temperatures of both reaction steps were varied between 37, 60, 75 and 90 °C. The reaction times studied were comprised between 15 to 360 minutes. Microwave heating lead to significant reductions in the times of reaction needed to achieve the maximum degree of nitration and amination compared to conventional means. After 15 minutes of reaction at 60 °C, it was observed a nitrogen density similar to that obtained for the same material synthesized conventionally, and after 240 minutes of reaction time at 60 °C the nitrogen density was exceeded. A complete reduction of the nitro to the amine groups was observed after 15 minutes of reaction at 60 °C, which demonstrates the great potential of the microwave irradiation in enhancing the kinetics of the post-synthesis functionalization of PMO materials, while preserving the molecular and mesoporous order.

Keywords: Nitration reaction, amination reaction, microwave-assisted synthesis, periodic mesoporous organosilicas, nanostructured materials

Introduction

Periodic mesoporous organosilicas (PMOs) have attracted much attention from the scientific community since 1999 due to their potential applications in a wide range of fields ranging from electronics and optical devices, to catalysis, gas separation and gas adsorption.[1] These materials possess high specific surface areas and pore volumes, narrow distribution of pore sizes, alternating hydrophobic-hydrophilic character, high thermal stability[2–5] and can be formed by a large variety of organic bridges which typically contain aromatic or unsaturated groups.[1,6,7] The properties of PMOs can be tailored by simple substitution of the organic bridge moiety of the bissilylated precursor[7,8] or by post-synthesis chemical modification of the organic moieties of PMO materials.[8] The first important example of the tunable character of PMOs by changing the organic group was reported by Inagaki *et al.*[9]. These authors synthesized a PMO with both meso and molecular-scale order using phenylene as the organic bridge. It was also shown the possibility of post-synthetic sulfonation of the aromatic rings to originate an acidic material with a concentration of sulfonic acid groups of 0.44 mmol·g^{-1}. In 2005, an ethylene bridge PMO was modified through a Diels Alder reaction with benzocyclobutene.[10] In 2008, a basic PMO was described by amination of the phenyl rings in a two-step reaction taking six days at room temperature, which yielded an amino group density of about 1.2 mmol·g^{-1}.[11] Very recently, we have further modified the amine functional group of the amine-phenylene PMO bridge (NH_2-PMO)[11] with iso-propyl group for improving the properties of the material for CO_2 capture. [12] In order to make these materials (e.g. NH_2-PMO) more interesting for applications in gas adsorption / separation, for example, it would be important to reduce the synthesis time of this material. This functionalization reaction consists first of a strong acid treatment to introduce the nitro group in the phenyl ring followed by its reduction to the amine.[11]

Due to the dielectric heating, chemical reactions under microwave radiation generally occur much faster.[13] Molecules possessing a permanent dipole moment tend to become aligned with the microwave electromagnetic field and, during this motion, they suffer frictions and collisions, with consequent heat generation. The efficiency of microwave heating is strongly dependent on the dielectric properties and on the relaxation times of the reaction components (namely reactants, functional groups and solvents).[14–16] Additionally, as the majority of the microwave ovens work at 2.45 GHz, the molecules exposed to this radiation are able to generate a strong internal heat with a heating rate up to 10 °C per second. Using conventional heating the temperature of the surface of reaction vessel is higher than the internal temperature and the transfer of the heating is made via thermal conduction. Therefore, the microwave radiation is a non-contact heating source allowing a more selective and effective heating than the conventional sources. Reaction vessels can be chosen to permit the microwave energy to go through it and heat only the reactants. Specific microwave effects can also occur during the reaction due to the presence of polar molecules in the mixture or if the polarity of the transition state is higher than the polarity of the ground state.[17],[18] To the best of our knowledge, there are only few reports using the microwave-assisted synthesis in PMOs, most in the preparation of the PMO material and only one in the post-synthesis *N*-alkylation of NH_2-PMO.[12,19–21] Smeulders *et al.*[19] demonstrated that this unconventional fast heating approach kept unchanged the structure of this kind of hybrid materials during the hydrothermal step synthesis. Additionally, when compared with the conventional synthesis, the usage of microwave irradiation promoted narrower distribution of pore sizes, higher surface area and larger pore volumes.[19] Recently, we found that faster *N*-alkyl functionalization of the NH_2-PMO at 170 °C without destroying the meso- and molecular-scale order was also achieved upon consideration of the alternative approach.[12]

The effect of the temperature and time of reaction together with the microwave radiation on the quantity of nitro groups incorporated in the phenyl bridge of the PMO and the their reduction to amines is an important aspect since it would make the synthesis of these materials faster and, consequently, PMOs would become more attractive for the several foreseen applications. However, the post-functionalization of PMO using microwave power was not addressed previously in the literature. In this report, we present a systematic optimization study of the nitration of PMO at four different temperatures and different reaction times using microwave heating treatment. The effects of microwave radiation, synthesis temperature and time on the chemical and structural stability of NO_2-PMOs were evaluated and correlated with the amount of nitro groups introduced in the phenylene moieties. The reduction reaction of the nitro group to the amine group was also made at four different temperatures during 15 minutes.

Experimental

Synthesis

The PMO was synthesized according to the procedure described in the literature[3,4,19,22], i.e., by condensation in basic medium of the 1,4-bis(triethoxysilyl)benzene (BTEB) precursor[23] in the presence of supra-molecular structure agent octadecyltrimethylammonium bromide (ODTMA, Aldrich). During the hydrothermal step, the autoclave was introduced in an oven preheated to 200 °C during 40 min, and then transferred to another oven at 100 °C, where it stayed for 23 h and 20 min. The surfactant template was extracted using an ethanol/HCl solution. The nitro functional groups were incorporated into the phenylene moieties of the PMO by treatment with a strong acid solution of HNO_3–H_2SO_4 using a modified literature procedure.[11] The NO_2-PMO was obtained by dropping a solution of HNO_3 (0.7 mL, 65% v/v, Panreac) and H_2SO_4 (2.2 mL, 95-97% v/v, Merck) into PMO (250 mg). Vials (10 mL) containing the previous mixtures were then sealed and heated at 37, 60, 75 and 90 °C for 15, 120 and 360 min in a CEM Discovery SP-D microwave apparatus, operating at a frequency of 2.45 GHz with continuous radiation power from 0 to 300W. By the end, the reaction mixtures were transferred into cold distilled water (150 mL) and were then filtered and successively washed with large amounts of water. All samples were dried overnight at 60 °C. The samples obtained in this first step of the work are named "NO_2-PMO_*x*/*y*", where *x* is the heating time expressed in minutes (min) and *y* is the heating temperature expressed in degree Celsius (°C). The reduction of the nitro to the amine group was accomplished by treatment of the different NO_2-PMO_15min/60°C with HCl/$SnCl_2$ solution.[11] The NH_2-PMO was obtained by drop wise of a solution of HCl (3.13 mL, 37%, Panreac) and $SnCl_2$ (0.33 g, 98%, Sigma-Aldrich) to the NO_2-PMO (100 mg). Vials (10 mL) having the above mixtures were then closed and heated at 37, 60, 75 and 90 °C during 15 min in a CEM

Discovery SP-D microwave apparatus. The reaction mixtures were poured into distilled water (100 mL) and were then filtered, washed with large amounts of water and followed by washing with a solution of isopropylamine (2.5 mL, 99.5%, Aldrich) in ethanol (25 mL). All samples were dried overnight at 60 °C. The different samples are denoted "NH_2-PMO_15min/*y*", where *y* is the heating temperature expressed in °C.

The conventional syntheses were performed according to Ref.[11] at room temperature during 72 h to obtain the NO_2-PMO followed by additional 72 h to attain the NH_2-PMO (in total 8640 min). The two samples resulting from the conventional synthetic procedure are named NO_2-PMO_C and NH_2-PMO_C, respectively. In order to further check the microwave effect on the nitration of the phenylene bridge of the PMO, a conventional reaction was performed during 15 minutes at 37 °C. The material was denoted NO_2-PMO_15min/37°C_C.

Characterization

^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 spectrometer operating at 9.4 T at 100.62 and 79.49 MHz, respectively. ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectra were obtained with 4 µs ^{1}H 90° pulse, contact time (CT) of 1 ms, a spinning rate (ν_R) of 8 and 7 kHz and a recycle delay (RD) of 4 s. ^{29}Si CP MAS NMR spectra were acquired with a 4 µs ^{1}H 90° pulse, a CT of 8 ms, a ν_R of 5 kHz and 5 s of RD. The ^{13}C and ^{29}Si NMR spectra were quoted in ppm from trimethylsilane.

Fourier transform infrared (FTIR) spectroscopies were performed in a FTIR Bruker Tensor 27 instrument with a Golden Gate ATR (Attenuated Total Reflectance). The different samples of the NO_2-PMO were dehydrated overnight at 100 °C before FTIR analyses. The FTIR spectra were collected in absorbance mode.

Elemental analyses were carried out at the University of Aveiro. To better observe the nitration of the PMO along time evolution and temperature, the NO_2-PMO samples were all reduced to NH_2-PMO using the conventional method proposed by Inagaki and co-workers[11], and the samples were dried at 100 °C for 24 h before the analyses.

Powder X-ray diffraction (PXRD) data were gathered with a Phillips X'Pert MPD diffractometer using Cu-Kα radiation.

Nitrogen adsorption-desorption isotherms data were collected at -196 °C using a Gemini V 2.00 instrument model 2380. NO_2-PMOs materials were dehydrated overnight at 120 °C to an ultimate pressure of 1024 mbar and then cooled to room temperature prior to nitrogen adsorption-desorption.

Thermogravimetric analyses (TGA) were obtained on a Shimadzu TGA-50 instrument with a heating rate of 5 $°C \cdot min^{-1}$ in air.

Scanning electron microscopy (SEM) images were acquired on a SEM-FEG Hitachi SU-70 microscope operated at 25 kV.

Transmission electron microscopy (TEM) images were recorded by a 300 kV Hitachi H9000 Instrument.

Results and Discussion

The nitration of phenylene bridges in PMO and the subsequent nitro reduction to the amine groups under microwave irradiation were successfully accomplished after reaction during a total time of only 30 min at 60 °C as confirmed by ^{13}C CP MAS NMR (Figures 1 and S1) and FTIR (Figures 2, 6, S2 and S3) spectroscopies.

The ^{13}C CP MAS NMR spectrum of the parent PMO displays one peak at 133.5 ppm assigned to the sp^{2} carbons from the phenylene bridge. The nitration reaction changes the chemical environment of the carbons of the phenylene group. In this way, the NO_2-PMO_15min/60°C presents four peaks at *ca.* 151, 137, 133 and 129 ppm. The reduction of the nitro group to the amine group is also accompanied by changes in the ^{13}C CP MAS NMR spectrum. Thus, the NH_2-PMO_15min/60°C exhibits five resonance peaks at 150, 133, 124, 122and and 119 ppm that are assignable to the carbons in the phenylene moieties with amine groups linked.

Thus, when compared with the conventional synthesis, microwave heating opens an avenue for faster functionalization of the phenylene moieties of PMO materials with nitro or amine groups. Using the microwave procedure, with only 15 min of reaction for each step at 60 °C, it was possible to achieve the same degree of amine functionalization as that obtained through after six days of the conventional synthesis, cf. Table 1.

The NO_2-PMO_*x*/*y* materials were also characterized by FTIR spectroscopy to corroborate the nitro functionalization of PMO, Figures 2 and S2. The PMO presents overtones of phenyl vibrations between 1300 - 2000 cm^{-1}, absorption modes assigned to the silanol stretching bands at 3200-3800 cm^{-1} and C-H aromatic stretching bands at 3028 and 3066 cm^{-1}. These values are similar to those described previously for PMO.[11]

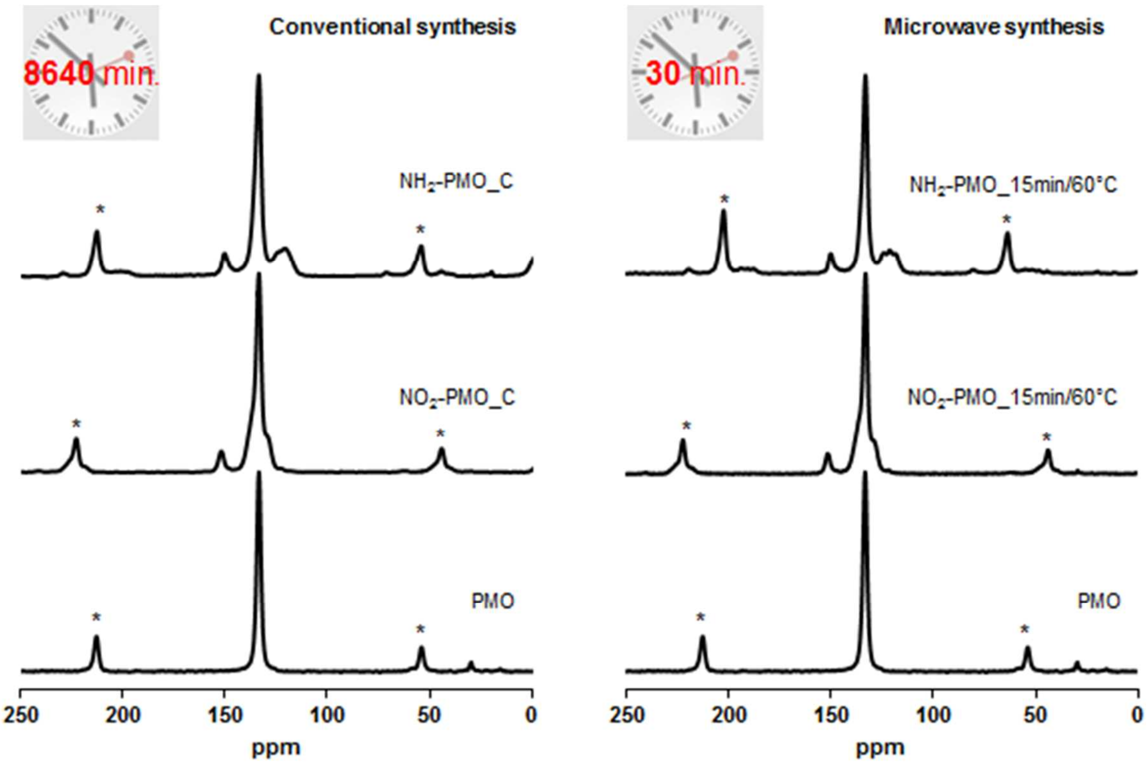


Figure 1. ^{13}C CP MAS NMR spectra of the PMO, NO$_2$-PMO_15min/60°C and NH$_2$-PMO_15min/60°C.

Some changes in the FTIR spectra of PMO appear after the nitration reaction. The presence of nitro groups in the aromatic rings of the PMO is confirmed by the C-N stretching mode displayed at 1267 cm^{-1}, and by the appearance of strong bands due to N-O symmetrical and asymmetrical stretchings at 1352 and 1541 cm^{-1}, respectively. These two NO stretching bands are more intense in the case of nitrated PMOs with time reaction of 360 min than in the materials functionalized during 15 min. It is seen that the spectrum for NO$_2$-PMO_15min/60°C, presents NO stretching bands with similar intensities to that of the NO$_2$-PMO_360min/37°C material, cf. Figures 2a and 2b. The nitrated PMO with NO stretching bands with the highest intensities corresponds to that obtained with the largest reaction time and temperature, i.e., 360 min and 60 °C.

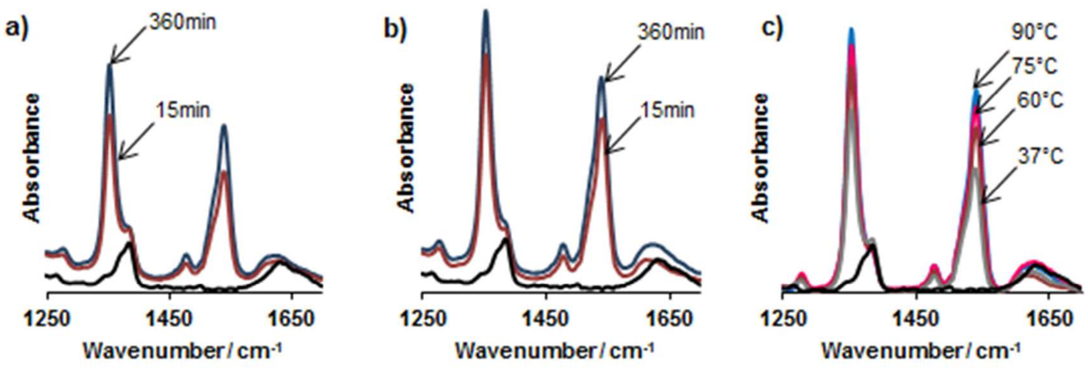


Figure 2. FTIR (ATR) spectra of NO_2-PMO_*x*/*y* at a) 37 °C and b) 60 °C for two different reaction times and c) NO_2-PMO_15min/*y* at different temperatures. The region of 1250 – 1700 cm^{-1} was chosen to better observe the main bands of functionalization. Black curves are for the parent Ph-PMO material.

Figure 2c displays the FTIR spectra of NO_2-PMO_15min/y materials in which it is possible to observe the increase of intensity of the two NO stretching bands with increasing temperature. Consequently, the increase of the number of nitrated phenylene moieties is directly correlated with the increase of temperature and in turn it can be correlated with the injection of microwave irradiation power. The microwave radiation effect is observed through the comparison of the FTIR spectra of NO_2-PMO_15min/37°C and the NO_2-PMO_15min/37°C_C, Figure S2d. The material prepared under microwave-assisted heating presents much intense NO stretching bands than the material prepared using conventional heating at the same temperature, which corroborates the favorable effect of the microwave irradiation on speeding up the nitration of the bissilylated phenylene bridge of the PMO.

Table 1 shows the results of the elemental analyses for the PMO parent material and for the materials aminated under different reaction conditions.

Table 1. Elemental analyses, nitrogen density and percentage of aminated phenylene bridges for PMO, NH_2-PMO_C (conventional synthesis) and NH_2-PMO_*x*/*y* (synthesized using microwave).

Sample	**% N**	**% C**	**% H**	**N Density /** mmol·g^{-1}	**% Phenylene bridges aminated**[a]
PMO	0.08	38.79	2.82	-	-
NH_2-PMO_C	2.49	34.29	3.32	1.78	41.5
NH_2-PMO_15min/37°C	1.62	33.16	2.98	1.16	27.0
NH_2-PMO_120min/37°C	2.22	33.57	3.05	1.59	37.0
NH_2-PMO_360min/37°C	2.50	34.48	3.27	1.79	41.7
NH_2-PMO_15min/60°C	2.50	33.58	2.84	1.78	41.5
NH_2-PMO_120min/60°C	2.83	33.30	3.24	2.02	47.2
NH_2-PMO_360min/60°C	2.95	31.18	3.26	2.11	49.2
NH_2-PMO_15min/75°C	2.99	31.54	2.90	2.14	49.8
NH_2-PMO_15min/90°C	3.16	31.20	2.95	2.26	52.6

[a] % of phenylene bridges aminated is calculated based on % N and assuming single amination, i.e., one amine group per phenylene bridge.

NH_2-PMO sample from conventional synthesis holds an amino group density equal to 1.78 mmol·g^{-1} (1.78 % of N). Assuming an incorporation of just one amine group per phenylene bridge, this density value indicates that ~42% of phenylene bridges were successfully functionalized. Under microwave irradiation at 37 °C, such a high value of functionalization (maximum was 1.16 mmol·g^{-1}) could not be reached. It is also concluded that the irradiation time strongly influences the nitration reaction at 37 °C since an increase in the density of amine groups from 1.16 to 1.59 mmol·g^{-1} is obtained with the increase of the nitration reaction from 15 to 120 min, respectively. The increase in the density of amine groups obtained upon incrementing the time of reaction from 120 to 360 min is less evident, i.e., a slight increase of 0.20 mmol·g^{-1} is found in the latter. When the synthesis is carried out at 60 °C, the density of amine groups in the PMO after 15 min of reaction reaches a value of 1.76 mmol·g^{-1} which is similar to the density in the sample obtained by conventional synthesis. This demonstrates that the reaction is extremely dependent on the temperature and heating source. Note that the microwave injected 230 W of power to achieve 60 °C, which is 140 W higher than the value required to reach 37 °C. The higher amount of amine groups introduced into the phenylene moieties may be due to the faster diffusion of the amine contents into the PMO at 60 °C. The increase of amine groups in the phenylene moieties takes place when the time is raised from 15 to 120 min with a difference of 0.26 mmol·g^{-1}, corresponding to a percentage of phenylene bridges nitrated close to 6%. The difference is even lower when the time is extended to 360 min, with a density of amine groups of approximately 2.11 mmol·g^{-1}, i.e., an increase of only 0.09 mmol·g^{-1} when compared to the NO_2-PMO_120min/60°C material (Table 1). The use of microwave power to reach 60 °C leads to a higher nitro content than the use of conventional heating to reach the same temperature. This was observed for the synthesis of the material NO_2-PMO_C_4320min/60°C (conventional synthesis during 3 days made at 60 °C) which has similar amount of nitro groups than the material NO_2-PMO_240min/60°C. Moreover, the NO_2-PMO_C_4320m/60°C material loose the meso-scale periodicity (not shown) which is a huge disadvantaged comparing with the similar material made by using microwave heating.

Table 1 also reveals the amount of nitro groups incorporated in the phenylene moieties of the PMO material with the increase of the temperature for similar reaction time (15 min). The consideration of high temperature is found to promote the introduction of higher amounts of nitro groups into the PMO channels. Since NH_2-PMO_15min/75°C presents a nitrogen density of 2.11 mmol·g^{-1} which is similar to that for NH_2-PMO_360min/60°C, it suggests that the temperature is very important to control the nitrogen density into the PMO for short times of reaction. By increasing the temperature reaction to 90 °C resulted in a PMO material having the highest content of nitro groups linked to the phenylene bridge of the PMO. The nitrogen density of 2.26 mmol·g^{-1} determined for NH_2-PMO_15min/90°C corresponds to a total of nitrated phenylene moieties of more than 50%.

The ^{29}Si MAS and CPMAS NMR spectra of Ph-PMO, NO_2-PMO_15min/37°C and NO_2-PMO_360min/60°C are shown in Figure 3. The pure PMO exhibits peaks at *ca.* 81, 71.5 and 61.5 ppm, which correspond to T^3, T^2 and T^1 organosiliceous species, respectively. As expected taking into account the literature, significant changes are introduced in the ^{29}Si NMR spectra of NO_2-PMO_*x*/*y* materials upon the nitration reaction.[11] Peaks related with the presence of Q^n species are absent in the ^{29}Si spectra for all materials, which is a strong evidence that carbon-silicon bond cleavage is not happening during the nitration reaction under microwave conditions.

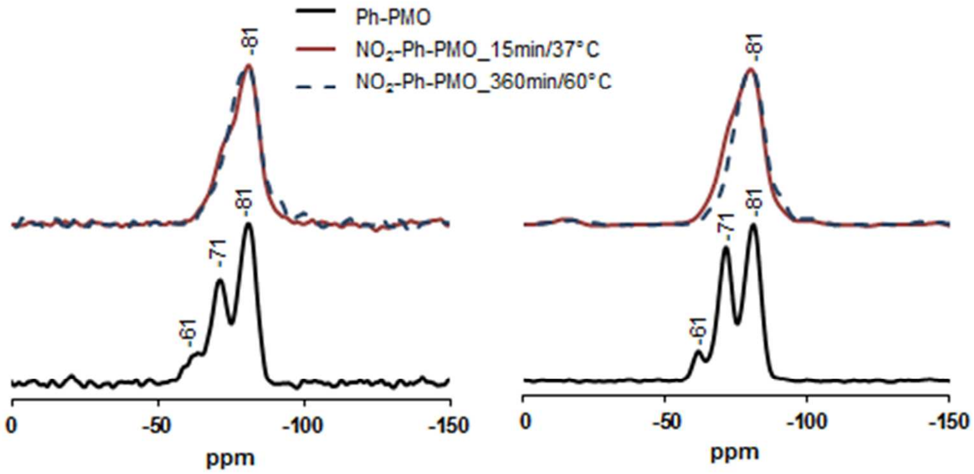


Figure 3. ^{29}Si MAS (left) and CP MAS NMR (right) spectra of Ph-PMO (bottom) and NO_2-PMOs_*x*/*y* (top) obtained at two different reaction times and temperatures.

PXRD was used to evaluate the structural order of all materials. Figure 4 shows the PXRD patterns of the PMO and NO_2-PMO-*x*/*y* obtained at different reaction conditions (temperature and time). All prepared materials displayed an intense low angle reflection and two much less intense peaks all corresponding, respectively, to the (100), (110) and (200) reflections characteristic of the two-dimensional hexagonal symmetry (*p6mm*) lattice.

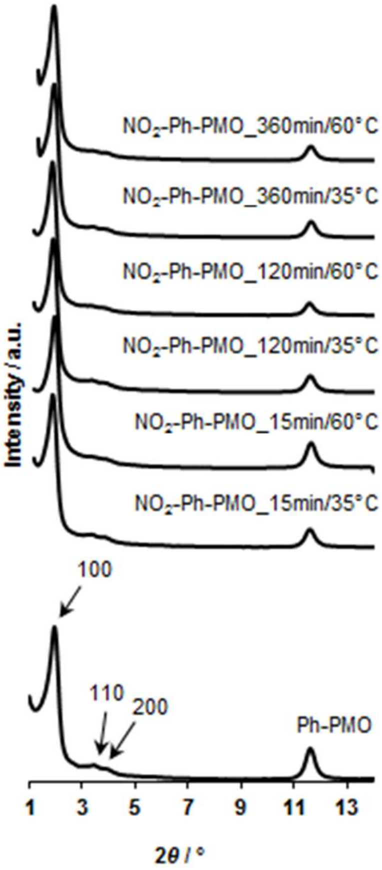


Figure 4. PXRD patterns for PMO and NO_2-PMO-*x*/*y* materials showing the typical low angle reflections characteristic of the 2D hexagonal mesoporous order and the medium-range reflection typical of the molecular-scale order in PMO materials.

The PMO and the two most extreme NO_2-PMO samples, i.e., NO_2-PMOs synthesized during 15 minutes at 37 °C or during 360 min at 60 °C, exhibit the first strong characteristic low angle (100) reflections at d = 4.55 nm, 4.70 nm and 4.55 nm, respectively. From the spacing (d) of the (100) peak it can be calculated the hexagonal unit cell lattice parameter, a, which is equal to $2d_{100}/\sqrt{3}$ (Table S1). For the samples PMO, NO_2-PMO_15min/37°C and NO_2-PMO_15min/60°C, the first sharp diffraction at medium-range reflection can be detected at d = 0.761, 0.762 and 0.758 nm, respectively, which is attributed to the periodic arrangement of the organic bridge within the pore walls of these materials. Thus, both meso- and molecular- scale periodicities are preserved after nitration reaction under the conditions described and this is also valid for the other materials obtained under different conditions. Attempts were made for fast synthesis (15 min) of materials with more than 50% of phenylene moieties mono-nitrated into the PMO channels by increasing the temperature of the nitration reaction to 75 and 90 °C. Figure S4 shows PXRD patterns for the materials obtained under these conditions. The 2D hexagonal symmetry (*p6mm*) lattice is attained for all the materials as supported by the observation of the first strong peak corresponding to the (100) reflection and two less intense peaks corresponding to the (110) and (200) reflections. The PMO and the NO_2-PMOs synthesized at 37, 60, 75 and 90 °C exhibit the first strong characteristic low angle (100) reflection at d = 4.55 nm, 4.70 nm, 4.70 nm, 4.82 nm and 4.82 nm, respectively, Table S1. From the d_{100} peaks it can be calculated the hexagonal unit cell parameter $a = (2d_{100}/\sqrt{3}) = 5.25$ nm for the PMO and a values between 5.20 nm and 5.57 nm were obtained for the nitrated PMO (Table S1).

TEM images obtained for the material NO_2-PMO_15min/60°C (Figure 5) show the order along the channel and the hexagonal arrangement of pores.

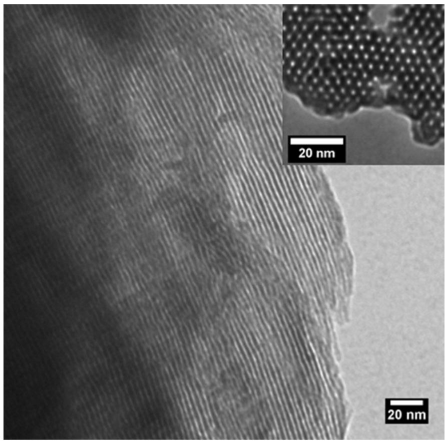


Figure 5. TEM micrographs of NO_2-PMO_15min/60°C. The inset displays a micrograph perpendicular to the pores where it is clear their 2D hexagonal arrangement.

The low temperature (-196 °C) N_2 sorption isotherms and pore size distribution (PSD) curves (Figure S5) confirm the characteristic type IV isotherms and narrow distribution of pore sizes for the pure PMO and NO_2-PMO_*x*/*y* materials commonly seen in mesoporous materials.[9] A decrease of the specific surface area and pore volumes upon increase of the temperature and reaction times is consistent with the enhancement of the degree of functionalization with nitro groups. The BET surface area of the materials synthetized at 37 °C decreases with the increase of the reaction time. The increase in the reaction temperature from 37 to 60 °C is also accompanied by a decrease of the surface area. The N_2 sorption isotherms display the increase of the BET surface area with the increase of the reaction time for the nitrated materials prepared at 60 °C (Table S1), which is the opposite of what is expected. This can be attributed to the splitting of the large aggregates into small particles due to the microwave irradiation as observed before by Smeulders *et al.*[19] in the microwave-assisted synthesis of PMO under long reaction times.

Figure S6 shows the TGA curves for PMO and NO_2-PMO at 37 and 60 °C for two different time extremes. The first weight loss for all materials corresponds to desorption of physisorbed water occurring below 100 °C. The PMO material presents a thermal stability up to 550 °C. Above this temperature, all materials suffer decomposition due to the degradation of the phenylene bridges from the framework. The nitro group introduction in the phenylene moieties decreases the thermal stability of all materials and a new weight loss, corresponding to the cleavage of nitro group in the phenylene bridge of the material, is observed at approximately 400 °C.

Scanning electron microscopy (SEM) images for NO_2-PMO materials obtained using different synthetic conditions are shown in Figure S7. The SEM images reveal the high order along the channels for all materials. The particle size of the different materials as a function of the reaction conditions could not be determined due to formation of ordered aggregates.

The reduction of the nitro groups is a very important step for obtaining the aminated compounds and the decrease of the reaction time will have obvious implications for the consideration of these materials in catalysis and adsorption applications.

The nitro to amine reduction was followed by ATR-FTIR spectroscopy, Figure 6. Upon treatment with $SnCl_2$–HCl, the N–O stretching vibrations disappeared completely in the case of reaction at 60 °C while new bands attributable to the bending and stretching modes of N–H appeared at 1633 and 3340–3487 cm^{-1}, respectively. It was also possible to observe the importance of the microwave heating in this reaction. The reduction of the nitro to the amine groups at 37 °C was made using microwave and conventional heating and the samples were labelled NH_2-PMO_15min/37°C and NH_2-PMO_15m/37°C_C, respectively. The use of microwave heating promotes the reduction of a larger content of nitro groups, which causes a significant diminution of the intensity of the N–O stretching vibrations bands.

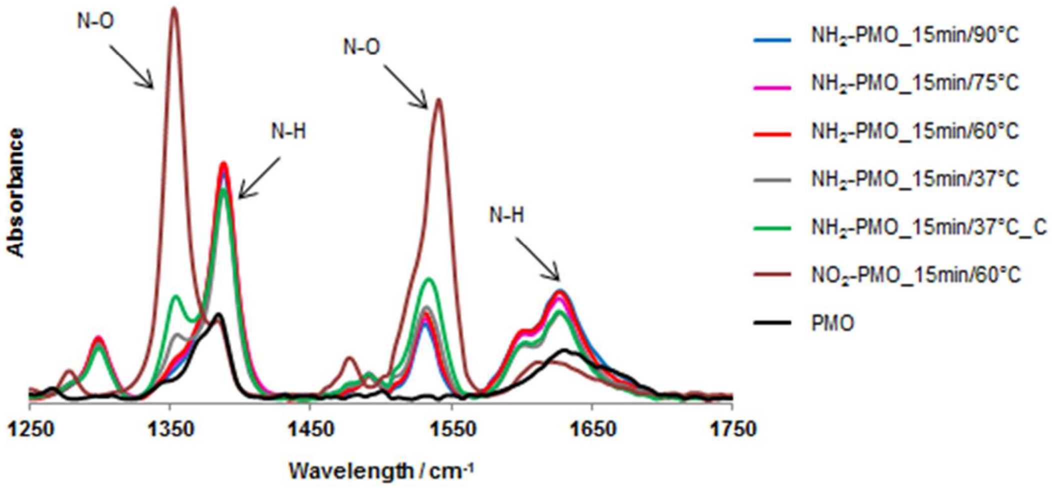


Figure 6. FTIR (ATR) spectra in the 1250 – 1700 cm^{-1} region of PMO, NO_2-PMO_15min/60°C and the NH_2-PMO_15min/*y*.

The ^{29}Si MAS and CP MAS NMR spectra of the NH_2-PMO_15min/60°C sample are presented in Figure S8. The peaks at *ca.* -81, -71 and -61 ppm are assigned to the T^3, T^2 and T^1 organosiliceous species of the NH_2-PMO material. The ^{29}Si spectrum also shows that no Si-C bond cleavage is observed.

Figure 7a shows PXRD patterns for PMO, NO_2-PMO_15min/60°C and NH_2-PMO_15min/*y*.

All materials display the first strong peak corresponding to the (100) reflection and two less intense peaks corresponding to the (110) and (200) reflections corresponding to the 2D hexagonal symmetry (*p6mm*) lattice. The intensity of these two peaks decreased with the reduction of the nitro groups. The molecular periodicity is preserved with the increase of the reaction temperature.

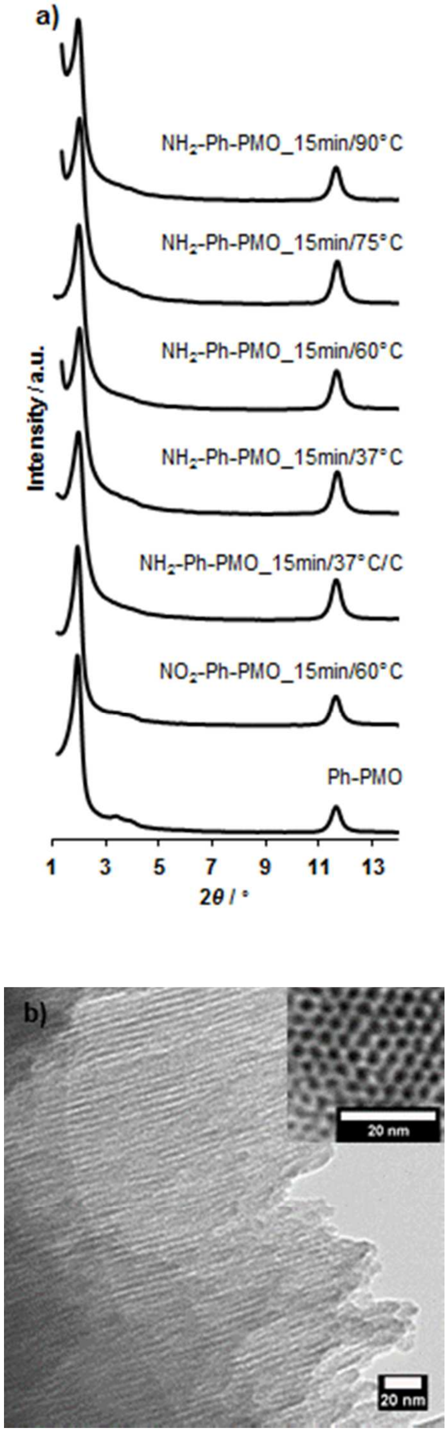


Figure 7. a) X-ray diffraction patterns for Ph-PMO, NO_2-PMO_15min/60°C and NH_2-PMO_15m/*y* and b) TEM images of NH_2-PMO_15min/60°C.

The TEM images observed in Figure 7b support the preservation of the order along the channels and also the 2D hexagonal arrangement of the pores of the NH_2-PMO_15min/60°C material.

The PMO and the NH_2-PMO_15min/*y* synthesized at 37, 60, 75 and 90 °C exhibit the first strong characteristic low angle (100) reflection at d = 4.55, 4.37, 4.41, 4.37 and 4.46 nm, respectively, Table S2.

The low temperature (-196 °C) N_2 sorption isotherms shown in Figure S9 confirm the type IV isotherms for the synthetized NH_2-PMO_15min/*y* materials and pore size distribution (PSD) curves confirms the narrow distribution of pore sizes.

The thermal stability of the amine PMO is similar to the thermal stability of the PMO nitrated, Figure S10. The cleavage of the amine group in the phenylene bridge of the aminated material, is observed at approximately 400 °C. The thermal stability of the NH_2-PMO is not affected by the use of different reaction temperatures using the microwave heating. The thermal stability is similar to the aminated PMO material prepared conventionally.[11]

Conclusions

This study shows that the time and the temperature of reaction are essential factors in the nitration of phenylene moieties of PMO materials and subsequent reduction of the nitro groups to amines. The information gathered from different experimental techniques, namely elemental analysis, TGA, and ^{13}C CP MAS NMR, ^{29}Si CP MAS NMR and FTIR spectroscopies, shows that changing the time and temperature of the nitration reaction under microwave irradiation has a huge influence on the amount of nitro groups incorporated into the Ph-PMO without cleavage of the Si-C bond. Both meso- and molecular- scale periodicities are preserved after strong acid treatment under microwave heating (observed by PXRD patterns and TEM images).

The temperatures used in the microwave heating (37 and 60 °C) are accompanied by different kinetic profiles behaviors. It was possible to find a clear dependence of the amount of nitro groups incorporated into the PMOs with the reaction time (up to 120 min) for reactions carried out at 37 °C comparing with reactions made at 60 °C. SEM does not show differences on the particles of parent and functionalized materials. A significant reduction in the time required for the nitration of phenylene bridges in PMO was observed upon microwave irradiation. Characterization with several different techniques suggests that nitration occurs without modification of the structural properties of the parent PMO. Importantly, in some cases, e.g. microwave assisted reaction at $T = 60$ °C and $t = 120$ min, the nitro groups content incorporated into the PMO channels was larger than that achieved under conventional conditions (3 days at room temperature), while similar contents between microwave-assisted and conventional heating were found when the synthesis used microwave irradiation during 15 min at 75 °C. Furthermore, the nitration reaction carried out at 90 °C during 15 min resulted in a content of nitrated phenylene moieties above 50%.

The microwave synthesis method presents clear advantages when compared with the conventional synthesis approaches, both in time and in the amount of nitro groups incorporated in the phenylene moieties of the PMO material. The use of the microwave heating promotes a high control of the nitro groups incorporated into the phenylene moieties of the PMO material. Additionally, the reduction of the nitro to the amine groups was also successfully achieved after treatment with $SnCl_2$/HCl under microwave irradiation with preservation of the structural order.

The use of microwave heating speeds up the nitration of the phenylene-PMO probably due to the presence of polar intermediate species, such as nitronium ion and water molecules. Moreover the transition state of the material should be more reactive under microwave irradiation when compared to thermal heating due to the specific microwave absorption by the polar reactants. In addition, we believe that the diffusion of the reactant species through the mesochannels of the phenylene-PMO is improved using the microwave irradiation, allowing a fast access of the nitronium ion to the phenylene bridges for the nucleophilic attack, which is a determinant rate step.

Although phenylene-PMO is considered an apolar substance, i.e. being a weaker microwave irradiation absorber, we must consider that the silanols and the delocalization of the electrons by the approximation of the positive nitronium ion can play a beneficial role in the local heating. In the amination step, the nitro groups attached to the phenylene bridges are also important for the generation of local heating which will speed-up the reaction.

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