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Tuning the acid content of propylsulfonic acid-functionalized mesoporous benzene-silica by microwave-assisted synthesis

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ABSTRACT

Propylsulfonic-acid functionalized mesoporous phenylene-silicas have potential use in catalysis and applications demanding protonic conduction such as fuel cells. Their synthesis by conventional co-condensation is time consuming and with poor control of the incorporation of sulfonic acid. Here we report a fast, microwave-assisted synthetic route to prepare these materials with controlled acid load and structural order. It is found that the microwave energy strongly improves the kinetics of the various steps of the process, including the self-assembly of precursors (stirring), consolidation of the framework (hydrothermal treatment), surfactant extraction and the oxidation of the thiol to the sulfonic acid group. The concentration of incorporated acid groups increases linearly with the self-assembly time under microwave radiation, enabling the largest improvement of all synthetic steps. However, the mesopore order decreases significantly for microwave-assisted self-assemblies in excess of 6 h, and for microwave-assisted hydrothermal treatments longer than 3 h. The multivariate analysis of kinetic data is presented and used to derive kinetic parameters enabling the prediction of the acid load and the structural order of the materials as a function of the synthesis time under microwave radiation. For similar acid contents, full microwave synthesis is completed within 12 h, whereas nearly 84 h are needed with conventional heating sources. The protonic conductivity increases linearly with increasing acid load regardless of the used combination of synthetic steps, including MW or not. This is seen as a confirmation that the distribution of the acid groups in the pore surface is not affected by MW.

1. Introduction

Periodic mesoporous organosilicas (PMOs) were firstly reported in 1999 bringing the novelty of an organic-inorganic framework with high content of organic groups, uniformly distributed within the material walls and keeping the porosity free [1–3]. An important feature of the PMO materials is their “on-demand” channels. Prepared from bissilylated organic-bridged precursors, the organic moiety can be designed according to the potential application of the final material. In 2002, Inagaki et al. [4] reported the use of 1,4-bis(triethoxysilyl)benzene (BTEB) to achieve a material conjugating both meso- and molecular-scale periodicities. The phenylene-bridged PMO (Ph-PMO) possesses molecular-scale periodicity as a result of the layered arrangement of $O_{1.5}Si–C_6H_4–SiO_{1.5}$ units in the walls parallel to the pore channels. The molecular-scale periodicity was shown to be independent of the carbon chain length of the surfactant [5]. The synthesis of propylsulfonic acid-functionalized periodic mesoporous benzenosilica (Ph-PMO-SO_3H) was subsequently described by Yang in 2002 [6]. Ph-PMO-SO_3H was prepared with different acid content by co-condensation reaction of BTEB with 3-mercapto-propyltrimethoxysilane (MPTMS), using a cationic surfactant under basic conditions. The Ph-PMO-SO_3H has shown to be highly active as solid acid catalyst under water-based reaction conditions. The acid strength and the catalytic activity depend on the acid concentration [H^+] [7]. When the [H^+] is relatively low, the acid groups seem to be protected by the hydrophobic character of the aromatic ring. For [H^+] above a certain threshold (0.3 meq g^{-1}), the catalytic activity increases linearly with the acid content probably due to cumulative cooperative effect [7]. Recently, another group [8] and ourselves [9–11] have shown the potential of these materials as protonic conductors. The protonic conductivity

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increases with increasing temperature and humidity and is strongly enhanced in materials with high specific surface area and high concentration of sulfonic acid groups. The adsorption of large quantities of water molecules is possible on the large pore surface area, where they can be retained by electrostatic interactions promoted by the acidic groups. In Ph-PMO-SO_3H [12]. Furthermore this capacity increases with increasing $-SO_3H$ concentration. Both the protonated sulfonate ions and the water enable the necessary environment for the fast structural diffusion of protons, thus promoting high levels of protonic conductivity. Values as high as 0.3 S m^{-1} (at 100 °C and near 100% relative humidity) were obtained for Ph-PMO-SO_3H prepared using co-condensation method [10], which is three orders of magnitude higher than the value reported for a similar material obtained by grafting [8,11].

Considering the tremendous impact of porosity and acid load on the relevant functional properties of these materials, it would be interesting to reduce the very long synthesis cycles (between 80 and 100 h) [6,8], while keeping a tight control of the acid content, the surface area and the hierarchical meso- and molecular-scale order.

Microwave (MW) radiation has been used to carry out the self-assembly and the hydrothermal treatment of mesoporous silicas [13], as well as to shorten the synthesis time of periodic mesoporous benzene-silica [14]. Here, we report the use of MW radiation in all steps of preparation of sulfonic acid functionalized phenylene-PMO (Ph-PMO-SO_3H), namely on the self-assembly (stirring and hydrothermal treatment), extraction and oxidation steps. In addition, an attempt is made to extract kinetic parameters through a multivariate statistical analysis of the data, in order to correlate the synthesis time with the acid load and both the pore and structural order of Ph-PMO-SO_3H.

2. Materials and methods

2.1. Materials preparation

All air sensitive operations were carried out using standard Schlenk techniques under a nitrogen atmosphere. Octadecyltrimethylammonium bromide (ODTMA, 98%), (3-mercaptopropyl) trimethoxysilane (MPTMS, 95%) and dried solvents stored over molecular sieves were obtained from Aldrich and used as received. 1,4-Bis(triethoxysilyl)benzene (BTEB) was prepared following literature procedures [5,15].

2.2. Conventional synthesis

Propylsulfonic acid-functionalized periodic mesoporous benzene-silica (Ph-PMO-SO_3H) was prepared according to Yang et al. [6] by the co-condensation of BTEB and MPTMS in the molar ratio 1:1 under basic conditions, using ODTMA surfactant as structure directing agent (BTEB:ODTMA molar ratio 1:3). After the preparation of the gel, the precursors were allowed to self-assembly by stirring at room temperature for 24 h, followed by heat treatment at 90 °C for another 24 h. The surfactant was extracted using an ethanol/hydrochloric acid solution as solvent. The oxidation of the thiol to sulfonic acid group was achieved with concentrated HNO_3. This experimental procedure is based on the literature [6], with some minor adjustments. The extraction and oxidation steps were performed overnight (±12 h) and for 24 h, respectively. The total time spent in this synthesis is of 84 h.

2.3. Microwave-assisted synthesis

The syntheses were performed in a MW oven MARS-5 (CEM Corporation) with power output of 300, 600 and 1200 W at 2.45 GHz. Several samples were prepared by varying the synthetic conditions. The synthesis mixture was the same as for the conventional method. The first part of the self-assembly step was performed under conventional conditions (stirring and room temperature) for up to 24 h and under MW radiation (stirring at 40 °C) for up to 12 h. Subsequently, the mixture was hydrothermally treated in the proper vial (closed Teflon vial or opened round-bottom glass flask) at 100 °C under MW radiation for a maximum of 5 h. After washing the powder, the surfactant was removed by solvent extraction [6]. For the extraction step in the MW, 0.5 g of powder was suspended in 50 mL of 1:9 solution of HCl/ethanol, placed into a closed Teflon vial and heated for 15 min at 100 °C in the MW. The oxidation step was carried out using concentrated nitric acid. The mixture was placed in the Teflon vial and heated at 40 °C for 30 min in the MW oven.

Table 1 gives the full list of the prepared samples divided in three groups according to the source of heat in the self-assembly and hydrothermal steps. Group I comprises samples obtained by conventional heating in both synthetic steps (acronyms C*x*C*y* in which *x* and *y* represent the duration of each step in h), and control samples prepared in absence of surfactant (*no surf*) or MPTMS precursor (*no acid*). Group II includes samples prepared with a combination of conventional heating during the initial self-assembly and MW heating in the hydrothermal step (acronyms C*x*M*y*, where *x* and *y* represent the duration of each step in h). Finally, group III consists of samples synthesized using MW energy in both synthetic steps (acronyms M*x*M*y*).

2.4. Characterization methods

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Geigerflex D/Max – C diffractometer using Cu-Kα X-radiation (λ = 1.54056 Å) with a step of 0.02° in 2θ units scanned at 1° min^{-1}. The diffractograms are presented as raw data, but to effectively retrieve diffraction angles and the relative intensities of the two peaks, the baselines were subtracted. Transmission Electron Microscopy (TEM) images of powder dispersed on holey carbon-coated copper grids were recorded on a 300 eV Hitachi H9000-NA or in a 200 kV High Resolution (HR) and energy-filtered (EF) TEM JEOL 2200FS microscope. Microanalyses (C, H and S) on selected samples were measured by Elemental Analysis Service at the University of Vigo. The BET specific surface areas were calculated from the N_2 adsorption/desorption isotherms collected at −196 °C in a Micromeritics Gemini 2370 equipment. The pore size distribution was calculated with the adsorption branch using the BJH method with the KJS correction [16]. The Fourier Transform Infrared Spectroscopy (FTIR) measurements of KBr pellets were obtained on a FTIR Mattson-7000 infrared spectrometer with 2 cm^{-1} resolution. The acid load was measured by a simple acid-base back titration [17]. A weighted amount of dry sample (≈20 mg) was dispersed in 20 mL of 0.1 M KCl, ultrasonicated for 5 min and vigorously stirred for 30 min to allow the exchange of the proton for K^+. The suspension was then titrated with a 0.01 M KOH aqueous solution, following the pH evolution with a WTW Sentix 41 pH electrode wired to a WTW pH 330i pocket meter. The samples were also characterized by ^{13}C and ^{29}Si cross-polarization magic-angle spinning (CP-MAS) NMR and scanning electron microscopy, as described in ESI. The protonic conductivity (σ) of a few selected samples was assessed by impedance spectroscopy (Agilent 2980A LCR meter) at 94 °C and 98% relative humidity (RH) using a climatic chamber (ACS Discovery DY110). The spectra were