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Amino-modified periodic mesoporous biphenylene-silica

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ABSTRACT

The amination reaction of biphenylene moieties in crystal-like mesoporous silica (Bph-PMO) is successfully achieved with a density of 3.17 mmol g^{-1}. The amination occurs approximately in every aromatic ring of the biphenylene bridge in the position 2 and 2′, leading to above 50% of the biphenylene group di-aminated. The structural integrity of the synthetized material is preserved during the strong acid treatment to achieve the amine funcionalization of Bph-PMO. The aminated mesoporous organosilica is highly active (initial turnover frequency 2193 h^{-1} or 37 min^{-1}) and almost 100% selective in the Knöevenagel condensation. Moreover, the amine-modified periodic mesoporous biphenylene-silica is effective for direct metal coordination.

1. Introduction

Periodic mesoporous organosilicas (PMOs) [1] have been calling much attention due to their promising applications, such as catalysis, adsorption, molecular recognition, electronic and optical devices. PMO materials are remarkable for their high specific surface areas and pore volumes, narrow distribution of pore sizes and enhanced thermal stability [2–5]. The alternating hydrophobic/hydrophilic moieties along the mesochannel walls give to PMOs improved performance for example in catalytic reactions in which water may be formed and contribute to the deactivation of the catalytic site [6,7]. Furthermore, the organic bridge of the bisilylated precursor used to prepare the PMO can be changed promoting the creation of different features and interfacial interactions and tuning of the properties of the material for the desired application [8]. The ethane [2,9], ethylene [9,10], benzene [11], *p*-biphenylene [12] and thiophene [13] bridge were been successfully incorporated into the PMOs framework. Inagaki et al. [11] described the synthesis of phenylene PMO (Ph-PMO), in 2002. This material had a high impact due to the concomitant presence of both hexagonal bidimensional pore arrangement and molecular-scale order along the wall. Moreover, the post-synthesis sulfonation of the aromatic ring of Ph-PMO was demonstrated in the same report. In 2008, the same group reported the amination of 28% of phenylene moieties of PMO in a two-step chemical transformation procedure [14]. This functionalization reaction consists first on a strong acid treatment to introduce the nitro groups in the phenyl rings followed by their reduction to amines. Here, we describe for the first time the amination of the *p*-biphenylene-PMO (Bph-PMO) in a two-step reaction: (i) nitration of the aromatic rings of the biphenylene bridge, and (ii) reduction of the nitro groups to primary amines. Bph-PMO displays an equimolar ratio of aromatic rings to silica atoms, offering the opportunity to incorporate a large amount of functional groups on the material surface, which makes this material more interesting for catalysis or adsorption applications than the phenylene-PMO. Moreover, Bracco et al. [15] reported an amphidynamic behavior of the highly ordered hexagonal Bph-PMO and demonstrated the existence of parallel and aligned biphenylene bridge along the mesochannel axes. The introduction of functional groups, which possess polarity may turn this materials important for application as molecular rotors. This material is tested as catalyst in the Knöevenagel condensation and efficiency followed along consecutive cycles.

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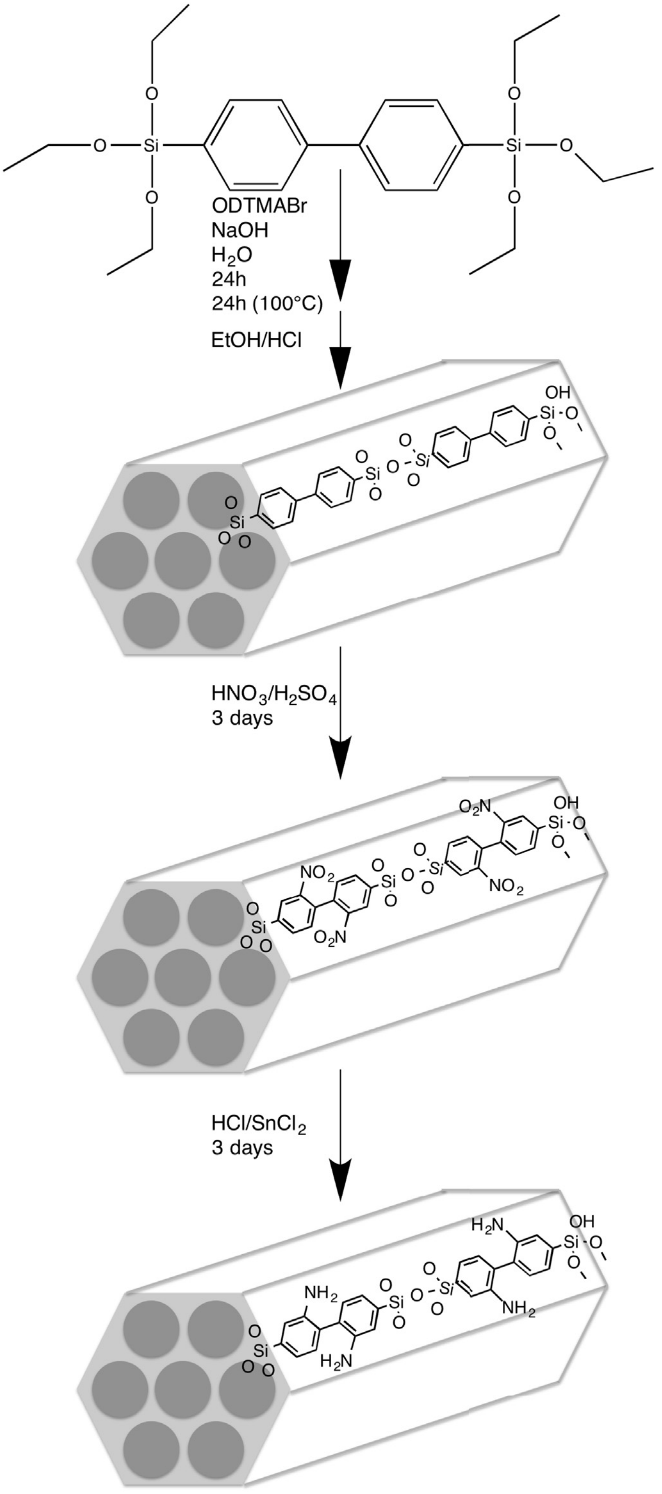
2. Experimental

2.1. Bph-PMO synthesis and functionalization

The Bph-PMO was prepared following a well-defined method (Scheme 1) [12]. 4,4′-bis(triethoxysilyl)biphenylene (BTEBP, Aldrich, 95%) precursor was hydrolyzed and condensed around a supramolecular structure agent, the octadecyltrimethylammonium bromide template (ODTMABr, Aldrich, 98%). After 24 h of stirring at room temperature, followed by 24 h hydrothermal treatment at 100 °C, the powder was recovered by filtration, washed with water and dried at 60 °C. The template was extracted using an ethanol–HCl solution. The incorporation of functional amino groups into the phenylene rings (to obtain NH_2-Bph-PMO) was achieved upon two-step treatment with very strong acid solutions of HNO_3–H_2SO_4 and $SnCl_2$–HCl using the same procedure of Ohashi et al. [14].



Scheme 1. Representation of the two steps functionalization reaction to achieve NO_2-Bph-PMO and NH_2-Bph-PMO materials.

2.2. Characterization of materials

The physical and chemical properties of Bph-PMO and functionalized materials were evaluated by powder X-ray diffraction (PXRD), low temperature (−196 °C) nitrogen adsorption–desorption isotherms, transmission electron microscopy (TEM), ^{29}Si MAS and CP MAS NMR, ^{13}C CP MAS NMR and FTIR spectroscopies. Description of the experimental conditions is presented at the Electronic Supplementary Information (ESI).

2.3. Catalytic experiments

All the catalytic reactions of the aminated material were performed in batch reactors at atmospheric pressure and with constant stirring. The Knöevenagel condensation was performed at 60 °C using 1.00 mmol benzaldehyde, 1.00 mmol malononitrile, 0.50 mmol of chlorobenzene (internal standard) and 30 or 80 mg of Bph-PMO in 4.00 ml of toluene, under inert atmosphere. The reaction was followed by gas chromatography (GC, Bruker 450 GC) by periodically withdrawing aliquots from the reaction mixture. At the end of the reactions the material was isolated by filtration over 0.22 μm nylon membranes and extensively washed with toluene, dried under vacuum at 60 °C and reused in another cycle using the same experimental procedure. A control experiment was also performed using the same experimental procedure, but without addition of the mesoporous organosilica. The reaction product was confirmed by GC–MS.

3. Results and discussion

3.1. Structural and morphological characterization

The Bph-PMO was prepared and its aromatic rings were modified according to Scheme 1 to form NO_2-Bph-PMO and NH_2-Bph-PMO. PXRD, TEM and N_2 sorption isotherms were used to evaluate the structural order and the textural physical properties of the pristine and functionalized Bph-PMO materials.

Fig. 1 shows the PXRD patterns of Bph-PMO, NO_2-Bph-PMO and NH_2-Bph-PMO. All patterns are assigned a 2D hexagonal porous lattice with a space group *p*6*mm*. The first strong low angle peak is assigned to the (100) reflection is observed at a spacing $d = 4.96$ nm for the parent Bph-PMO and at $d = 4.70$ nm for the NH_2-Bph-PMO (Table S1, ESI). The hexagonal unit cell lattice parameters, a, were calculated from the d_{100} reflection using the equation $a = 2d_{100}/\sqrt{3}$ and are equal to 5.73 nm for the Bph-PMO and 5.42 nm for the NH_2-Bph-PMO showing that a slightly contraction of the unit cell occurs during the amination reaction.

The molecular-scale periodicity for the Bph-PMO is observed through the peaks at $d = 1.197$, 0.596, 0.396, 0.297 and 0.242 nm, highlighted by arrows. Similar peaks are observed for the NO_2-Bph-PMO and NH_2-Bph-PMO. Both meso- and molecular-scale periodicity are preserved after nitration and subsequent reduction of the nitro to the amine group.