



Polymer-grafted mesocellular silica foams: Influence of reaction conditions on the mesostructure and polymer content



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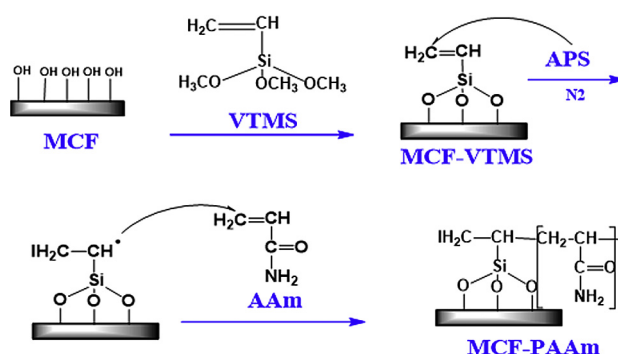
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HIGHLIGHTS

- Mesocellular silica foams (MCF) modified by covalent grafting of PAAm.
- Polymerization conditions tailored the content of PAAm into MCF.
- Hybrid material obtained using low monomer concentration at 4 h of reaction.
- Thermal stability of PAAm increases in presence of MCF.
- Modification with PAAm does not affect the morphology and mesostructure of MCF.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesocellular silica foam (MCF) was synthesized and modified by grafting polyacrylamide (PAAm) onto its surface. Grafting process was carried out by free radical polymerization using vinyltrimethoxysilane (VTMS) as coupling agent. The dependence of the final PAAm content with respect to monomer and initiator concentrations, reaction time, and temperature was evaluated. The PAAm contents in the hybrid material were determined by thermogravimetric analysis (TGA) and ranged from 15 to 64%. Diverse characterization techniques confirmed the grafting processes including small-angle X-ray scattering (SAXS), infrared spectroscopy, (FT-IR), nitrogen adsorption-desorption analyses, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). According with SAXS and N₂ adsorption-desorption studies, the grafting of polymer may cause pore blockage of mesopores channels being more evident for MCF silica with high content of PAAm.

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1. Introduction

The development of hybrid materials such as those based on mesoporous silicas and polymers have received much attention due to they have replaced a lot of polymeric materials in different applications. These materials combine the properties of their

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components giving as result composites with unique properties [1,2]. The inorganic part offers rigidity, thermal stability, large surface area ($\sim 1000 \text{ m}^2/\text{g}$), high pore volume as well as a uniform and narrow pore size distribution. On the other hand, the organic part endows chemical functionality, ductility and flexibility. These hybrid silica materials find application in diverse industrial fields as gas adsorbents [3,4], catalysts [5,6], sensors [7,8], drug delivery systems [9], etc.

Usually, the polymer-silica materials have been prepared by physical impregnation of silica with pre-synthesized polymers, blending and *in situ* polymerization methods [1,10–12]. In these methods, the polymer is bound to the silica by the force of many weak interactions, including hydrogen bonds, with silanol groups present in the inorganic material. However, for this hybrid materials, there is not a chemical link between inorganic and organic components causing a serious leaching problem when they are used as adsorbents or catalysts [5,11].

More recently, the post-grafting method has been used to attach covalently polymers onto inorganic materials [13,14]. The post-grafting is based on the condensation reaction between the silanol groups present in the surface of silica and the hydrolyzable groups on the silicon atom present in the coupling agent, usually an organosilane. This gives as result the covalent attachment of organic groups (amines, chloro, epoxy, vinyl, acrylic, etc) on the silica which play an important role in designing novel hybrid materials [15–17]. Also, this method allows to tailor the structure-property relationship of the hybrid materials by a proper selection of the grafting conditions.

In this work, polyacrylamide (PAAm) was covalently attached onto mesocellular silica foam (MCF) by radical polymerization. The synthetic path requires the previous silanization of MCF with vinyltrimethoxysilane (VTMS) which contains a vinyl group capable of radical polymerization. MCF is a new mesoporous material with very promising properties for sorption and catalysis and hence attracting considerable attention in recent years [18,19]. This siliceous material consists of a continuous 3-dimensional pore structure of large, spherical and uniform cells (20–40 nm) interconnected by uniform windows (10–15 nm) with high surface areas (500–1000 m^2/g), high pore volumes (up to $2.6 \text{ cm}^3/\text{g}$), and robust frameworks [20,21]. Due to their three dimensionally interconnected structure, large pore size and pore volume, this material is attractive for enzyme immobilization, catalysis, gas separation, drug and protein delivery where the diffusion within the pores plays an important role [22–26]. On the other hand, PAAm is a water-soluble polymer which finds applications in diverse industrial fields as adsorbent, and flocculant [27,28]. Thus, the combination of the properties from PAAm with those from MCF will allow the development of silica materials which could find application in diverse industrial processes.

2. Materials and methods

2.1. Materials

Deionized water obtained from a system of two ionic exchange columns, Cole-Parmer Instruments was used in all experiments. All materials were used as received from the chemical vendor (Aldrich) without further purification. Non-ionic block copolymer surfactant EO₂₀-PO₇₀-EO₂₀ Pluronic 123, ammonium fluoride (NH₄F $\geq 98\%$), 1,3,5-trimethylbenzene (98%), and tetraethyl orthosilicate (TEOS, 98%) were used for the preparation of MCF silica. On the other hand, vinyltrimethoxysilane (VTMS, 98%), ammonium persulfate (APS, 98%), and acrylamide (AAM 99.8%) were used for the modification of MCF.

2.2. Preparation of MCF silica

In a typical synthesis, 1.0 g of Pluronic 123 was dissolved in 37 mL of 1.6 M HCl at room temperature. After, 3.8 mL of 1,3,5-trimethylbenzene (TMB) and 10 mg of NH₄F were added. The resulting solution was stirred at 40° for 1 h followed by the addition of 2 mL of TEOS and stirring for another 24 h. Then, this solution was transferred to an oven under static conditions for 24 h at 90 °C. After that, the resulting solid was filtered and washed with deionized water. Finally, the MCF silica was calcined at 550 °C for 6 h.

2.3. Functionalization of MCF with VTMS

The functionalization of MCF silica with VTMS was carried out as follows: 1 g of calcined MCF (previously dried at 100 °C) was added to 50 mL of toluene containing VTMS (1 or 2 g). The resulting mixture was sonicated to disperse the MCF silica particles. Then, the reaction mixture was vigorously stirred under reflux temperature for 8–24 h. After that, the solution was filtered and the remaining solid was washed three times with 10 mL of toluene for 20 min under magnetic stirring in order to remove the free VTMS. The functionalized MCF silica was dried at room temperature and then stored at 80 °C.

2.4. Modification of MCF with PAAm

VTMS-modified MCF (0.25 g) was added to an aqueous solution containing acrylamide (1.4–7.0 mmol) and ammonium persulfate (0–0.4 mmol). The mixture was sonicated and purged with nitrogen (N₂) for 20 min. Polymerization reaction was carried out by varying temperature from 60 to 80 °C at different reaction time. After polymerization, the solution was filtered and the hybrid material was washed three times with deionized water under stirring to remove residual monomer and non-grafted PAAm.

2.5. Characterization

Thermogravimetric analyses were carried out under nitrogen atmosphere at heating rate of 10 °C min⁻¹ using a TGA Q500 (TA Instruments). FTIR spectra were acquired in an FTIR Nicolet Magna 550 spectrophotometer by using the KBr pellet method in the frequency region of 4000 to 500 cm⁻¹. Small angle X-ray scattering (SAXS) data were recorded in a SWAXS equipment model SAXS esmc² from Anton Paar in the 2 θ range of 0.5–8°.

The morphology of the samples was examined using a scanning electron microscope (JEOL JSM-7401F) and a transmission electron microscope (HRTEM Fei Titan 80-300). Textural properties (surface area, pore volume) were obtained using a Quantachrome AS1Win equipment at –196 °C. Before experiments, samples were degassed under vacuum at 150 °C. The specific surface area of the sample was calculated using the Brunauer–Emmett–Teller (BET) method in the range of P/P₀ of 0.1–0.3 while the total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99.

3. Results and discussion

3.1. Functionalization of MCF silica with VTMS

MCF silica with three-dimensional structure and well-defined mesopores was obtained by the procedure used in this work. Then, this silica was functionalized with VTMS in order to obtain a siliceous material with vinyl groups. The modification with VTMS was carried out in anhydrous toluene and the effect of organosilane

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