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Some considerations to optimize the synthesis procedure and the structural quality of mesostructured silicas

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ABSTRACT

Two methods for the preparation of highly ordered MCM-41 silica are discussed. The quality of the structure was optimized by adequate stirring of the reaction mixture containing low concentration of surfactant, followed by heating at 70 °C for 3 h under stirring. Besides this energetically favorable procedure allowed to obtain structures very stable upon calcination. The role of the ethanol and the hydroxide source in the synthesis process is also analyzed.

1. Introduction

Nanotechnology will be one of the fields that will contribute the most to scientific and technological development along the 21st century. Nanostructured inorganic, organic or hybrid organic–inorganic materials present the ability to assemble and organize inorganic, organic and even biological components in a single material. This feature represents an exciting direction for developing innovative multifunctional advanced materials presenting a wide range of novel properties besides allowing an integration and miniaturization of devices.

Soft chemistry-based processes (i.e., chemistry at low temperatures and pressures, from molecular or colloidal precursors) clearly offer innovative strategies to obtain tailored nanostructured materials. The mild conditions of sol–gel chemistry provide reacting systems mostly under kinetic control. Therefore, slight changes of experimental parameters (i.e., pH, concentrations, temperatures, nature of the solvent, counterions) can lead to substantial modifications of the resulting supramolecular assemblies and give rise to solids with very different structures and properties [1,2]. Moreover, although the resulting nanostructures certainly depend on the chemical nature of their organic and inorganic components, they also rely on the synergy between these components. Thus, the tuning of the nature, the accessibility and the curvature of the hybrid interfaces are a key point for the design of new nanostructured materials.

The use of supramolecular assemblies (surfactant micellar aggregates) as structure directing agents in soft chemistry-based silica gelation processes resulted in the discovery of a new family of mesoporous silica compounds (M41S) [3–10]. These solid phases are characterized by a regular structure of mesopores (2–10 nm) with sharp pore size distribution, a high specific surface (up to 1500 m^2/g), a specific pore volume (up to 1.3 mL/g) and a high thermal stability. The M41S family includes a bidimensional hexagonal phase (MCM-41), a cubic phase (MCM-48) and several lamellar phases. These materials are potential candidates for a variety of promising applications in many fields: catalysis, optics, electronics, photonics, sensors, membranes, separation, sorption, biological applications (drug delivery, immobilization and recognition), etc. [11–16]. Particularly, the hexagonal packed array of unidirectional large channels in MCM-41 offers unique opportunities

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to be used as 'host porous structure' allowing the preparation of new nanostructured composite materials [17–19].

It is possible to synthesize M41S materials under a variety of concentration of surfactants and conditions [5,6,20–23]. At high concentrations of surfactant, it has been proposed that micellar aggregates are formed in solution, around which the silicate source polymerizes [5,6]. However, these materials can also be formed in mixtures with as little as 0.5 wt% of surfactant, which indicates that at these low concentrations a cooperative templating process may be in operation [20,24–26]. This self-assembly process is also sensitive to factors such as temperature, stirring and heating time, reactives nature and presence of cosolvents in the solution. Thus, finding a quick and easy method of synthesizing a particular mesostructure of this M41S family offers a significant advantage to the use of these materials. Other authors have made some efforts in this sense [27–28]. In this report, the preparation of a series of mesoporous silicas has been investigated in order to furnish more information about the influence of different synthesis conditions on the formed mesostructure. As part of these studies, the role of both the alkalinity source (supplied via alkali metal hydroxides or quaternary ammonium cation hydroxides) and the ethanol in the synthesis process was also discussed.

2. Experimental

The mesoporous silica materials were obtained by two different synthesis procedures (methods **A** and **B**). Following the first method, based on that reported previously by us to synthesize Ti-MCM-41 [29–30], 20 wt% solution of cetyltrimethyl ammonium bromide (95%) (CTABr) in water (previously heated at 35–40 °C to dissolve the surfactant) and 70% of the tetraethylammonium hydroxide 20 wt% aqueous solution (TEAOH) were added dropwise to tetraethoxysilane (98%) (TEOS) under stirring at room temperature and stirring was continued for 3 h. The remaining TEAOH and the water were further added dropwise to the milky solution and stirring was continued for 20 min. The pH of the resultant gel was 11.45 and the molar composition was as follows: TEAOH/Si = 0.30, CTABr/Si = 0.4, water/Si = 60. This gel was heated in a Teflon-lined stainless-steel autoclave under autogeneous pressure at 100 °C for 0–7 days. Sometimes, ethanol was used as solvent of CTABr in place of water.

Following the method **B**, based on that proposed by Gallis et al. [31–32], CTABr was dissolved in water and 2 M sodium hydroxide aqueous solution (NaOH) (97%). After heating slightly (35–40 °C) to dissolve the surfactant, the TEOS was added. The ratios of the reactants were as follows: NaOH/Si = 0.50, CTABr/Si = 0.12, water/Si = 132, and sometimes TEAOH was used in place of NaOH. The resulting mixture (pH 11.25) was stirred at room temperature for 2–4 h. Then, this gel was heated at 70 °C under stirring in a closed flask or at 100 °C and 150 °C in a Teflon-lined stainless-steel autoclave. In both methods, the typical amount of TEOS used for the synthesis was 10 ml.

The final solid was then filtered, washed with distilled water and dried at 60 °C overnight. To remove the template, the samples were heated (heating rate of 2 °C/min) under N_2 flow up to 500 °C maintaining this temperature for 6 h and subsequently calcined at 500 °C under air flow for 6 h.

The materials were characterized by powder X-ray diffraction (XRD) and nitrogen adsorption. XRD patterns were collected in air at room temperature on a diffractometer using CuKα radiation of wavelength 0.15418 nm. Scans were performed between $2\theta = 1.5°$ and 7° at an interval of 0.01° and a scanning speed of 2°/min was used. The N_2 adsorption–desorption isotherms and surface area measurements were carried out at 77 K on a sorption equipment with an accuracy higher than 3% and a reproducibility of +0.5%. Prior to the measurement the sample was outgassed for 12 h at 573 K to a residual pressure below 10^{-4} atm.

3. Results and discussion

3.1. Method *A*

3.1.1. Effect of the hydrothermal synthesis time

XRD spectra of calcined samples produced by method **A** with different hydrothermal treatment times at 100 °C and using water as solvent are shown in Fig. 1. As it can be observed, a mesostructure was formed without hydrothermal treatment. This sample exhibits an intense low-angle reflection peak at approximately 2.4° and other broader and less intense one between 4° and 5°, which is characteristic of mesoporous silicas. Moreover, the sample also shows a high surface area around 1400 m^2/g typical of mesoporous materials (Table 1). A subsequent hydrothermal treatment of the gel appears to cause a partial collapsing of the pore array, giving rise to a notable decrease of the long-range order of the structure. In addition, the surface area of the samples decreases with the hydrothermal treatment up to a 50%, which is clearly correlated to the decrease in the structural order observed.

3.1.2. Effect of solvent

To examine the role of ethanol in our synthesis process, ethanol was used in place of water to dissolve the surfactant. Interestingly, this yielded a material with only a single broad peak in the diffraction pattern (Fig. 1) and lower surface area (Table 1). This result confirms that ethanol is involved at the silicate–surfactant inter-

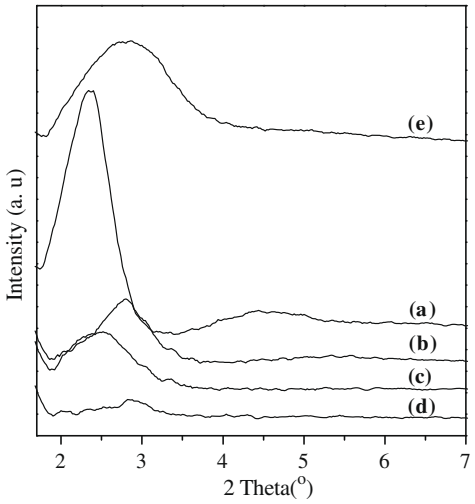

Fig. 1. XRD spectra of calcined samples prepared by method **A,** using water as solvent: (a) without hydrothermal treatment, (b) with hydrothermal treatment of 1 day, (c) 4 days, (d) 7 days and (e) using ethanol as solvent, without hydrothermal treatment.

Table 1
Surface areas of the samples synthesized by method **A**.

Hydrothermal treatments time (days)	Solvent	Area (m^2/g)
0	Ethanol	1056 (5)
0	Water	1398 (6)
1	Water	1245 (6)
4	Water	1016 (5)
7	Water	817 (4)

The estimated deviations of the parameters are given in parentheses as uncertainty in the last digit.