



Full Length Article

Mesoporous silica obtained with methyltriethoxysilane as co-precursor in alkaline medium



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ABSTRACT

Mesoporous silica particles have been synthesized by sol-gel method from tetraethoxysilane (tetraethylorthosilicate, TEOS) and methyltriethoxysilane (MTES), in ethanol and water mixture, at different ratios of the of the silica precursors. Ammonia was used as catalyst at room temperature and hexadecyltrimethylammonium bromide (cetyltrimethylammonium bromide, CTAB) as the structure directing agent. Nitrogen sorption, X-ray diffraction and small-angle neutron scattering gave information on the evolution of the gel structure and pore morphologies in the function of MTES/TEOS molar ratio. Thermogravimetric and differential thermal analysis showed that with addition of MTES the exothermic peak indicating the oxidation of the low molecular weight organic fragments shift to higher temperature. A room-temperature, one-pot synthesis of MCM-41 type materials is presented, in which the variation of the MTES concentration allows to change the hydrophobicity, preserving the specific properties materials, like the ordered pore structure, large specific surface area and high porosity. Specifically, the obtained materials had cylindrical pores, specific surface areas up to 1101 m²/g and total pore volumes up to 0.473 cm³/g. The obtained mesoporous materials are susceptible for further functionalization to improve their selective uptake of guest species in drug delivery applications.

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1. Introduction

Monodisperse spherical silica particles can be synthesized by the Stöber method, starting from tetraalkoxysilane in water and alcohol as solvent, and ammonia catalyst [1]. Mesoporous silica nanoparticles with surfactant templated pores became well known since their synthesis by Kresge et al. in Mobil Corporation laborato-

ries in the early 90s [2]. MCM-41 and related, surfactant templated materials are notable for their morphological properties such as large surface area, high porosity, and controllable mesopores with narrow size distribution [3]. Spherical, mesoporous MCM-41 like particles were first synthesized and reported by Grun et al., modifying the Stöber method by adding the cationic surfactant [4]. Regarding the order, the regularity and the thermal stability of the structure, the MCM-41 type materials obtained in basic medium at room temperature, usually are qualitatively inferior to those obtained by hydrothermal synthesis [5]. In the ordinary conditions of temperature and pressure, lower condensation grade of the silica can be reached [6,7]. On the other hand, the low temperature sol-gel method is cheaper and advantageous as scalable technol-

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Table 1
Sample names and synthesis conditions.

MTES/TEOS molar ratio	Drying at 60 °C	Calcination at 550 °C	Template extraction by ethanol
0/100	C0-60	C0-550	C0-EtOH
10/90	C1-60	C1-550	C1-EtOH
20/80	C2-60	C2-550	C2-EtOH
30/70	C3-60	C3-550	C3-EtOH
40/60	C4-60	C4-550	C4-EtOH
50/50	C5-60	C5-550	C5-EtOH

ogy. The presence of alcohol in the reaction mixture, as mutual solvent of water and alcoxide, facilitates homogenisation, favouring formation of spherical MCM-41 [8,9]. In surfactant templated spherical mesoporous silica, the channels are usually closed at one end, and the typical hexagonal long range order is much weaker compared to the classical MCM-41 materials [10].

For applications in adsorption and catalysis, the variation of surface hydrophobicity is required. Surface modifications of mesoporous materials are generally performed by two common ways: post-synthetic method and direct co-condensation method [11]. The latter involves a one-step co-condensation between tetraalkoxysilanes ($\text{Si}(\text{OR})_4$) with one or more organoalkoxysilanes ($\text{RSi}(\text{OR})_3$) through the sol-gel process in presence of a structure directing agent [12,13]. Inagaki et al. reported for the first time the synthesis of ordered mesoporous silica with organic groups evenly incorporated in the walls (so-called periodic mesoporous organosilicas, PMOs) using silsesquioxane precursor 1,2-bis(trimethoxysilyl) ethane as the silica source and octadecyltrimethylammonium chloride as the structure directing agent, under basic reaction conditions [14].

Organic modification of the silicate allows precise control over the surface properties and pore sizes of the mesoporous sieves and at the same time stabilizing the materials towards hydrolysis. Using organically modified precursors, like methylalkoxysilanes, the hydrophobicity of the materials can be changed in an easily controllable way. Various examples for using methyltriethoxysilane (MTES) as a hydrophobic reagent for xerogel preparation were presented in the literature attempting to achieve superhydrophobic surfaces. The character of the sol-gel derived hybrid film surface shifts from hydrophilic to superhydrophobic due to the incorporation of CH_3 groups in the silica surface from MTES precursor [15]. An enhancement of the surface hydrophobicity is retarding the leaching [7] and improves also the hydrothermal stability [16]. S-shape leaching curves have been obtained with an induction time increasing with the MTES content, while the more hydrophilic samples prepared without MTES exhibited immediate rapid release [16].

In a recent study, ordered mesoporous silica was synthesized at 60 °C with NaOH catalyst, by using MTES together with TEOS, as silica precursors, in different molar ratio, without adding alcohol in the reaction mixture. It has been shown that the increased amount of MTES destroyed the mesoporous channels and the materials became amorphous at 30% MTES content [17].

In our present work, we prepared mesoporous particles, by room temperature sol-gel synthesis, using tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) at various molar ratios, a cationic surfactant as templating agent, ammonia catalyst and adding alcohol into the reaction mixture. Spherical mesoporous particles of MCM-41 type have been obtained in a cost-effective way in one pot synthesis at room temperature. The hydrophobicity of the pore walls could be efficiently tuned varying the proportion of the hydrophobic silica precursor. Template removal was carried out using two methods: by calcinations and by extraction with solvent, and the morphology of the resulted materials has been characterized by several experimental techniques.

2. Experimental

2.1. Synthesis

All chemicals were commercially available: Tetraethyl orthosilicate (TEOS), (99%, for analysis, Fluka); Methyltriethoxysilane (MTES 97%, Merck); Ethanol Absolute (Riedel de Haen); NH_4OH aq (25%, SC Silal Trading SRL); Hexadecyltrimethyl-ammonium bromide (CTAB, Sigma).

The reactants molar ratio was: (TEOS + MTES): Ethanol: H_2O : NH_3 = 1:58:144:11. The molar ratio Si:CTAB was kept constant at 0.3 and through the series where TEOS was partially replaced with MTES. Typically, 4.92 g CTAB were dissolved in a mixture of 116.64 mL distilled water and 152.4 mL of ethanol. Subsequently 37.1 mL of ammonia 25% were added; the mixtures were vigorously magnetic stirred in a closed vessel at room temperature for 30 min. Then, the sol-gel precursors (10 mL TEOS or TEOS + MTES mixed in advance) were slowly dripped (in 10 min) into the reaction mixture and the resulting mixture was vigorously stirred for 2 h (rotation speeds 250 rpm). The formed gel was aged for 16 h, in static condition. In the next day, the resulted suspension was several times washed with distilled water and then centrifuged at 9000 rpm (2 times, 5 min each and two times, 10 min each) until the pH of the supernatant approached neutral value. To the decanted precipitate, ca. 110 mL ethanol was added and left for 48 h; then, the samples were dried at 40 °C for 1 h, and then at 60 °C for 21 h. These xerogel samples were labeled as Cx-60 (Table 1).

Template removal was carried out using two methods: by calcination and by extraction with ethanol.

For calcination, a part of each dried sample has been further heated up to 550 °C and kept for 5 h, and were labeled as Cx-550 (Table 1).

In the extraction procedure, 1 g of Cx-60 samples were mixed with 200 mL of acidified ethanol (1 mL of concentrated HCl: 100 mL of ethanol) under magnetic stirring (350 rot/min) for one hour, at room temperature following the slightly modified method of Du et al. [18]. Then, the samples were dried at 60 °C for 12 h. These samples were labeled as Cx-EtOH (Table 1).

2.2. Characterization

FTIR spectra were taken on KBr pellets with a JASCO –FT/IR-4200 apparatus.

Measurements of specific surface area of the composite silica samples were performed by low temperature nitrogen adsorption using Quantachrome Nova 1200e analyzer. Before measurements the samples were outgassed at 120 °C for 18 h in vacuum. Surface area S_{BET} was determined by Brunauer–Emmett–Teller (BET) method. When the BET plot produces either a too large, or negative C constant, the Langmuir surface area may be considered [19]. The total pore volume is measured at a relative pressure of $P/P_0 = 0.99$. The pore diameter was calculated from adsorption by BJH method. Pore size distribution was calculated from nitrogen adsorption isotherms by DFT, assuming cylindrical pore shape and NLDFT model.

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