



Short communication

High-surface area spherical micro-mesoporous silica particles



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ABSTRACT

Submicrometer spherical micro-mesoporous SiO₂ particles have been synthesized with a Brunauer–Emmett–Teller specific surface area of up to 1600 m² g⁻¹, comparable with that of nanoporous carbon materials. The particles are constituted by densely packed SiO₂ channels, similarly to materials of the MCM-41 type. The particles have two pore subsystems: monodisperse cylindrical mesopores with controllably varied average diameter (2.5–3.5 nm) and micropores supposedly situated within the walls of the SiO₂ channels and between their outer surfaces. The particles with combined micro-mesoporous structure are obtained by hydrolysis of a mixture of tetraethoxysilane (TEOS) and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS) with molar ratio 5:1 in an alcoholic–aqueous–ammonia medium containing surfactant (cetyltrimethylammonium bromide + 1,3,5-trimethylbenzene). Negatively charged products of hydrolysis of silica precursors (TEOS and MPTMOS) are condensed near the positively charged amino groups situated on the surface of the cylindrical micelles of surfactant forming SiO₂ layer containing hydrophilic methacryloyloxypropyl (MP) groups in the interior. Due to the Van der Waals forces, these micelles coated with a SiO₂ layer are organized into surfactant–silica clusters forming identical spherical aggregates. Removing of surfactant micelles and MP groups leads to formation of mesopores and micropores consequently.

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1. Introduction

In the last decades, there has been strong interest in developing nanoporous materials with high specific surface area (SSA). The largest SSA values calculated by the Brunauer–Emmett–Teller method (BET SSA) (typically 1200–1900 m² g⁻¹) are observed in nanoporous carbon materials having subnanometer pores [1]. Nanoporous carbon materials are extensively used in, e.g., hydrogen storage devices, Li-ion batteries, and catalysts. However, numerous chemical processes (e.g., catalytic purification of vehicle exhaust gases to remove CO and NO_x) require incombustible supports. In the XX century, these were, in particular, synthetic zeolites (aluminosilicates) with an SSA of 400–600 m² g⁻¹ [2]. In the 1990s–2000s, various types of mesoporous silica were synthesized (M41S family, SBA, etc.) [3], which have replaced zeolites in numerous application areas.

The mesoporous silicas MCM-41 and SBA-15 are densely packed strands of amorphous SiO₂, with diameters of several to tens of nanometers and have a channel porous structure. Researchers are still trying to find methods for tailoring the mesostructure of these materials in order to optimize their properties (permeability, catalytic activity, etc.). To improve the application characteristics of materials, it is frequently necessary to increase the SSA and the pore volume. The MCM-41 silica is synthesized by the soft-template method, with cylindrical micelles of alkylamines serving as templates [3]. Silicas of the MCM-41 type have only cylindrical pores. The SSA is raised with surfactants having a short alkyl length (C₈, C₁₀) [3] and amine non-alkyl surfactants [4]. The so-far reached minimum pore diameter in M41S materials is ~2 nm, with the maximum BET SSA being ~1250 m² g⁻¹ [3,4].

In contrast to MCM-41, silicas of the SBA-15 type have not only monodisperse cylindrical mesopores with diameters in the range of 5–30 nm [3], but also micropores within the walls of the hexagonally packed SiO₂ channels, with the wall thicknesses being on the order of nanometers. In syntheses of SBA-15, the role of surfactants is played by triblock copolymers poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)–poly(ethylene oxide). At room temperature, the PEO

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chains are hydrophilic whereas the PPO chains tend to be hydrophobic, thus driving the formation of direct cylindrical micelles with the PEO chains on the outside [3,5]. When the micelles are coated with a hydrated amorphous silica layer, the PEO chains are situated within the silica layer, and, after the surfactant is removed by washing or annealing, micropores with sizes of fractions of a nanometer to 2–3 nm are formed within the channel walls [6,7]. The micropores make a considerable (up to 60% [3]) contribution to the SSA of SBA-15, which is $\leq 1000 \text{ m}^2 \text{ g}^{-1}$. Addition of hydrophilic organic substances (e.g., polyvinyl alcohol) to the reaction mixture provides an increase in the number of micropores and in the specific surface area of silicas of the SBA-15 type to $\sim 1250 \text{ m}^2 \text{ g}^{-1}$ [8].

The important characteristics of mesoporous silicas (mSiO_2) include the shape of particles and their size distribution. For example, with mSiO_2 used as a catalyst support or stationary phase in chromatography, the spherical shape and monodispersity of particles provide the same mass-transfer rates of substances within pores and outside the particles. In biomedicine, monodisperse spherical mSiO_2 particles with high SSA are promising carriers of toxic chemotherapeutics in drug delivery systems [9–11]. The narrow size distribution and the spherical shape of the particles result in their identical hydrodynamic properties in the blood vascular system and, consequently, in a controlled delivery time. A large SSA provides formation of an active internal surface, which enables binding and retention of drugs upon their introduction into the particles.

The goal of our study was to obtain high-surface-area sub-micrometer spherical particles of MCM-41 type silica with a narrow particle size distribution. The large values of SSA ($1300\text{--}1600 \text{ m}^2 \text{ g}^{-1}$) are obtained upon replacing 20 mol% of the silicon-containing precursor, tetraethoxysilane (TEOS), with [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS), which resulted in the formation of additional system of micropores within the mesoporous silica framework.

2. Experimental

We used the following reagents: cetyltrimethylammonium bromide $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$ (CTAB), 99+% (Acros); aqueous ammonia (NH_3), 24 wt%, $\geq 99.99\%$; ethanol ($\text{C}_2\text{H}_5\text{OH}$), 95 wt%; deionized water (H_2O) 10 M Ω ; TEOS $\text{Si}(\text{OC}_2\text{H}_5)_4$, 99+% (Acros); MPTMOS $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 98% (Aldrich); 1,3,5-trimethylbenzene $\text{C}_6\text{H}_3(\text{CH}_3)_3$ (TMB), 98% (Aldrich); and hydrochloric acid (HCl), 37 wt%, ACS reagent grade.

Nanoporous SiO_2 particles were synthesized by the method we developed via basic hydrolysis of TEOS in an $\text{NH}_3\text{--H}_2\text{O--C}_2\text{H}_5\text{OH}$ –surfactant mixture [12–14]. The solution weight was 1 kg for all the syntheses. The molar ratio of the reagents, TEOS: $\text{NH}_3\text{:H}_2\text{O:C}_2\text{H}_5\text{OH:CTAB}(\text{:TMB optionally})$, was 1:60:370:230:0.2:(0.6), respectively. To synthesize micro-mesoporous particles, we replaced 20 mol% of TEOS with MPTMOS. TEOS (or TEOS + MPTMOS) was introduced 10 min after the beginning of a vigorous stirring of the mixture of the rest of the components; the temperature of the reaction mixture was 65 °C. The synthesis duration was 1 h. To remove organics, the particles were washed with an alcoholic solution of HCl (0.01 M) and then were annealed in a flow of O_2 at a temperature of 400 °C for 5 h. The complete removal of organic contaminants was confirmed by FTIR [15].

Transmission electron microscopic (TEM) measurements were performed with a JEOL JEM-2100F microscope. An adsorption-structural analysis was made with a Micromeritics ASAP 2020 analyzer at a temperature of 77 K, with nitrogen as the adsorbate. The structure of the particles was subjected to a small-angle X-ray diffraction analysis on a Rigaku Geigerflex D/max-RC installation (CuK_α radiation).

3. Results and discussion

The approach we suggested for synthesis of MCM-41-like spherical porous silica particles (SPSP) with a narrow size distribution is based on the aggregative model of particle formation [12,13]. At a surfactant concentration exceeding the critical micelle concentration, rather short ($\sim 15 \text{ nm}$) rod-like surfactant micelles are formed under vigorous agitation [13]. Negatively charged products of TEOS hydrolysis are condensed near the positively charged amino groups situated on the surface of the micelles. As a result, this surface is covered by a hydrated amorphous silica layer with a thickness of 0.6–0.7 nm [12,13]. Due to the Van der Waals forces, these micelles coated with a SiO_2 layer are organized into surfactant–silica clusters with sizes of $\sim 15 \text{ nm}$. When a large number of these clusters are present in the reaction mixture, the system becomes aggregatively unstable, which leads to their coagulation into identical spherical aggregates [13]. SiO_2 particles synthesized with addition of MPTMOS also have a nearly spherical shape and small root-mean-square deviation of sizes (Fig. 1, Fig. S1, Table 1), which is indicative of the aggregative mechanism of their formation.

In joint hydrolysis of a mixture of TEOS + 20 mol% MPTMOS, a fifth of orthosilicate molecules contain a methacryloyloxypropyl

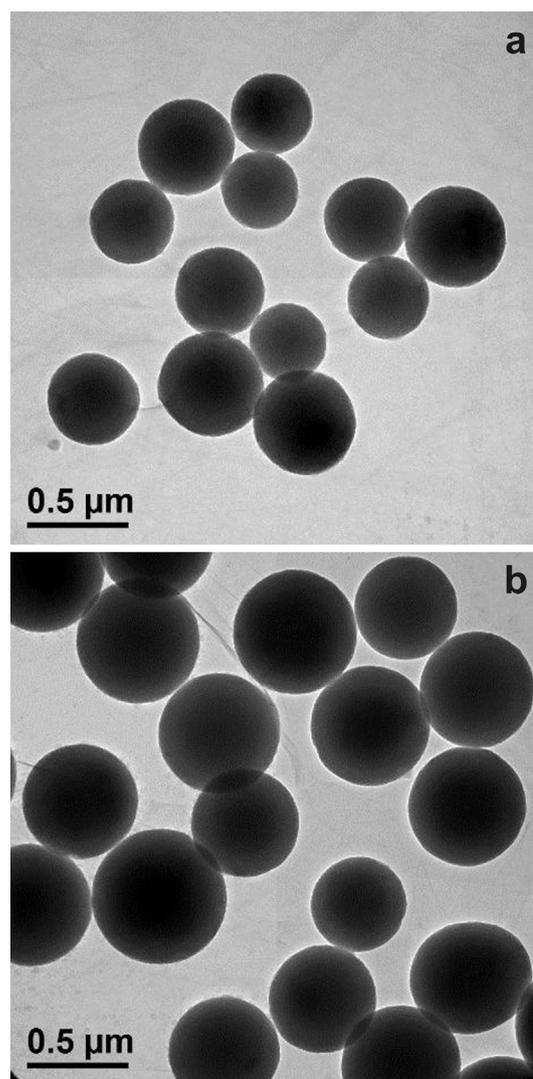


Fig. 1. TEM images of porous SiO_2 particles synthesized from TEOS + MPTMOS using CTAB (a) or CTAB + TMB (b) as surfactants.

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