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One-pot synthesis of two different highly porous silica materials

Patrycja Krasucka, Wojciech Stefaniak, Agnieszka Kierys, Jacek Goworek*

Maria Curie-Sklodowska University, Faculty of Chemistry, Department of Adsorption, M. Curie-Sklodowska sq. 3, 20-031 Lublin, Poland

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ABSTRACT

A new method, which combines the swelling of preformed porous polymer particles in silica precursor and sol–gel procedure at the presence of cetyltrimethylammonium bromide (CTAB), is used to prepare spherical, highly porous silica particles and polymer-silica composites. As a by-product, MCM-41 silica is formed. The resulting products are the effect of two simultaneous and competing processes: the swelling of polymer in silica precursor tetraethoxysilane (TEOS) and the adsorption of CTAB on polymer with simultaneous desorption of TEOS. The paper presents the formation mechanism of final silica particles as well as the structural properties of composites and silicas derived from them. All materials are characterized by scanning electron microscopy (SEM), transmission electron microscopy, (TEM), atomic force microscopy (AFM), nitrogen adsorption and X-ray diffraction (XRD). This study is supplemented by the Naproxen desorption measurements for the selected composites and silicas.

1. Introduction

Silica particles of well-defined morphology and size are of considerable interest due to a wide variety of their applications in many processes involving adsorption, flow of media, separation techniques, chromatography and catalysis [1–5]. For such applications, it is desirable to control the particle size, particle size distribution and porosity. Among these materials, the most important are spherically shaped silica particles of high porosity, which results in their low density, high surface area and high pore volume.

Sol–gel synthesis is widely used in preparation of regularly shaped silica species. Starting from Stober's et al. method [6] of synthesis of monodisperse silica particles, dozens of new methods for producing high quality silica spheres have been developed until the present [7–9]. In recent years, new methods of synthesis for the purpose mentioned above have been proposed, based on templating with organic polymers. The method consists of assembling the silica layer onto a colloid or polymer particle and subsequently removing the template through its calcination or dissolution [10–15]. Finally, totally hollow silica microspheres are obtained. These materials may serve as an initial structure for further deposition of various substances due to their high pore volume. Xu et al. [16] used cross-linked polystyrene microspheres as a template in preparation of hollow silica microspheres. Silica source was introduced into polymer spheres in supercritical CO_2. Kan et al. [17] used porous polystyrene particles as a template for preparation of silicalite-1 microspheres. Li et al. [18] used dual soft-template system comprising the asymmetric triblock copolymer poly (styrene-b-2-vinylpyridine-b-ethylene oxide) (PS-b-P2VP-b-PEO) and the surfactant (CTAB) to synthesize hollow mesoporous silica (HMS) nanoparticles. The silica product was obtained by initial impregnation of preformed polymer particles by TEOS, followed by its condensation. In all procedures, the polymer template was removed after synthesis by heating at ca. 550 °C in air. A different strategy was presented by Yoo et al. [19], who used Na_2SiO_3 spray-dried radical hollow microspheres followed by their transformation to SiO_2.

In the course of the past five years, we have proposed the synthesis of a polymer-silica composite and through its further processing at high temperature, silica gels with spherically shaped particles. The silica component was introduced into polymer by swelling in silica gel precursor TEOS [20–22]. The porosity of final material was determined by the adjustment of pH of the solution in which the precursor is transformed into silica gel. It appears that moderately polar acrylic resin Amberlite XAD7HP is an excellent polymer matrix for preparing the polymer-silica composite as well as highly porous silica at either acidic or basic conditions.

The present paper focuses on how the presence of surfactant in reacting solution influences the composite structure as well as the silica derived from the composite by calcination. Controlling the amount of surfactant in solution and pH is of practical importance

* Corresponding author.
E-mail addresses: jacek.goworek@umcs.lublin.pl, jacek.goworek@poczta.umcs.lublin.pl (J. Goworek).

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because the adsorption of surfactant is a deciding factor regulating the distribution of silica species within polymer particles and/or in the whole system.

In the last decade, mesoporous silica materials such MCM-41, MCM-48, SBA-15 and others silicas have been examined for various biomedical applications, especially as carriers for drugs in advanced drug delivery system DDS. Such great interest stems from their properties i.e. non-toxicity, biocompatibility, high sorption capacity and its ease modulating structure [23,24]. Furthermore, it has been shown recently that the use of mesoporous silica carriers improves the solubility of poorly water-soluble drugs such as naproxen. This effect results from the transition of the drug from the crystalline to non-crystalline form in the narrow pores of the siliceous material [25]. An additional advantage of using these materials for hosting pharmaceuticals is the ability to control drug loading and the kinetics of its release by the selection of proper morphological parameters, such as surface area, diameter and pore volume or surface modification. It was proved that narrower pores of MCM-41 or its amino-functionalization delay the desorption of ibuprofen and allow controlling its release rate [23].

In order to assess whether the synthesized materials may be useful due to their high adsorption capacity as carriers in the controlled drug delivery systems, the desorption/release experiment in the liquid phase was performed. Naproxen was used as a model guest adsorbate.

2. Experimental part

2.1. Materials

Amberlite XAD7HP (Rhom & Haas), Naproxen (98%), tetraethoxysilane (TEOS) and CTAB hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. All materials were used without further purification. NH_4OH (25%), HCl (33–35%) and ethyl alcohol absolute were obtained from POCH (Poland). Di-sodium hydrogen phosphate and sodium dihydrogen phosphate were obtained from Chempur (Poland). All reagents were analytical grade. Amberlite XAD7HP prior the experiment was washed with deionized water and dried at 80 °C under vacuum.

2.2. Synthesis procedure

Polymer resins were wetted by TEOS until all the polymeric beads were swollen. The prepared sample was left for 2 days at room temperature for equilibration and to facilitate the homogeneous distribution of TEOS within resin particles. The reaction mixture was prepared by dissolving CTAB in deionized water at 40 °C while stirring for 30 min. Subsequently, NH_4OH (25%) was added, followed by slowly poured polymer beads saturated with TEOS prepared earlier. After about 40 s of stirring, the mother liquid rapidly became milky. The mixture was continuously heated to 40 °C and stirred for 30 min. Molar composition of the reacting mixture was 0.00495:0.048:0.558:6.67 for CTAB/TEOS/NH_4OH(25%)/H_2O, respectively. The prepared suspension was left for 72 h at room temperature. After that time, the two fractions of white precipitate were separated in wet state using Nylon sieve with 0.15 mm sieve openings. Both fractions were washed with deionized water during filtration and dried at 80 °C for 24 h. Small fractions of each product were calcined at 550 °C for 10 h. As a result, white pure silica products were obtained. Three other one-pot syntheses were conducted in the same way. Two of them were of higher molar content of CTAB in the synthesis described above: with the molar fraction of the surfactant 0.0066 and 0.00825 for the second and third synthesis, respectively. Sample (IV) was prepared in the same recipe as sample II but with use HCl solution instead of NH_4OH as catalyst. In all preparation procedures, the yield of MCM-41 material was a little higher than 1 g. Thus, the weight ratio of spherical silica and MCM-41 silica fraction after recalculations of mass in pure silica products (after calcination) is about 2:1.

The as-synthesized samples were denoted for composites: XADSi-I, XADSi-II, XADSi-III for different concentration of CTAB, after acid catalyst XADSi-IV. Silica samples after calcination of the composite were named by analogy SiO_2-I, SiO_2-II, SiO_2-III and SiO_2-IV respectively. Fine particles of silica of MCM-41 type (basic synthesis) or SBA-3 type (acidic synthesis) [26] were denoted as MCM-41-I, MCM-41-II, MCM-41-III and MCM-41-IV. It should be mentioned that the production of pure silica samples requires long heating at 550 °C in air. We observed that calcination for 10 h is sufficient for removing the organics completely.

2.3. Drug loading

In order to illustrate the potential application of received materials as drug carriers we loaded them with Naproxen (non steroidal anti-inflammatory drug, NSAID). Naproxen was chosen as a model adsorbate due to its small molecular size and high pharmacological activity. The drug was loaded into XADSi-II composite, pure SiO_2-II, MCM-41-II and commercial XAD7 polymer for comparison.

Naproxen (NXA) was loaded into the above mentioned adsorbent materials (0.3 g) by immersion with anhydrous ethanol solution of Naproxen (16 mg/ml) with small excess to form semiliquid paste. The samples were outgassed under vacuum and then, the mixture was left for night at normal conditions. Next the samples were dried for 12 h at 60 °C. The Naproxen-adsorbent conjugate samples were named as XAD7-NXA, XADSi-II–NXA, SiO_2-II-NXA and MCM41-II-NXA. The samples were loaded, depending on the total pore volume and the uptake of NXA solution, in the range of 8–15 w/w% NXA. Highest contamination of NXA was for both silica samples SiO2-II and MCM-41-II exhibiting highest total pore volume.

2.4. Drug release

The drug release measurements were performed by adding 200 mg of the received samples to a vessel containing 50 cm^3 phosphate buffer solution, pH 7.4, and placed in a shaking incubator. The temperature was fixed to 37 °C and the stirring rate to 250 rpm. At predetermined time intervals, 5 cm^3 of release fluid were taken out for analysis of the drug concentration with UV–Vis spectroscopy (Varian Carry 100 Bio) at a wavelength of 330 nm for NXA. The taken aliquot was replenished with fresh dissolution medium. The concentration of the drug was determined on the basis of the correlation of the obtained results with Naproxen calibration curves based on the absorption maximum of 330 nm.

2.5. Methods

2.5.1. Scanning electron microscopy SEM

The morphology of the composites and silica spheres were examined with the use of scanning electron microscope (FEI Quanta 3D FEG) working at 5 kV.

2.5.2. Transmission electron microscopy TEM

The transmission electron microscope (TEM) studies were conducted on a Titan3™ G2 60–300 microscope (FEI Company USA).