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Hollow silica nanospheres as thermal insulation materials for construction: Impact of their morphologies as a function of synthesis pathways and starting materials

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HIGHLIGHTS

- Hollow silica nanospheres (HSNS) are promising thermal insulators for construction.
- Structural features, e.g. sizes and shell structures influence thermal conductivity.
- Formation of thermally insulating HSNS in general favoured by alkaline reaction.
- Synthesis route with tetraethyl orthosilicate (TEOS) was more robust.
- Water glass is a greener precursor for HSNS production.

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ABSTRACT

Hollow silica nanospheres (HSNS) show a promising potential to become good thermal insulators with low thermal conductivity values for construction purposes. The thermal conductivity of HSNSs is dependent on their structural features such as sizes (inner diameter and shell thickness) and shell structures (porous or dense), which are affected by the synthetic methods and procedures including reaction medium, polystyrene template, and silica precursor. Formation of thermally insulating HSNS was favoured by alkaline reaction, whereby highly porous silica shells were formed, promoting less silica per volume of material, thus a lower solid state thermal conductivity. The Knudsen effect is in general reducing the gas thermal conductivity including the gas and pore wall interaction for materials with pore diameters in the nanometer range, which is also valid for our HSNS reported here. Further decreasing the pore sizes would invoke a higher impact from the Knudsen effect. The additional insulating effect of the inter-silica voids (median diameter $D_{50} \approx 15$ nm) within the shell coating contributed also to the insulating properties of HSNS. The synthesis route with tetraethyl orthosilicate (TEOS) was more robust and produced more porous silica shells than the one with water glass (Na_2SiO_3, WG), although the latter might represent a greener synthetic method.

1. Introduction

According to the EU commission, heating and hot water alone account for 79% of total final energy use (192.5 Mtoe). While cooling is a fairly small share of total final energy use, demands from households and businesses such as food industry rise during the summer months. Therefore, in order to fulfil the EU's climate and energy goals of more than 20% energy savings by 2050, the heating and cooling sector must sharply reduce its energy consumption.

High-performance thermal insulation materials for buildings is one of the most direct methods to meet the demand of improved energy efficiency. Studies [1] have demonstrated that energy efficiency measures such as thermal insulation retrofit are the most cost-effective with respect to CO_2 emissions, whereas other measures e.g. solar photovoltaics and wind energy are far less cost-effective. Today, efforts are being put into moving from the common thermal insulation materials [2] to develop new materials with as low thermal conductivity as possible [3–9]. While this is the best solution for construction purposes, the current state-of-the-art thermal insulation materials are still in their infancy. Further work is needed before proper incorporation into the building industry could be achieved at an affordable cost.

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Both macro and micro scale developments have been conducted. The latest trend is to develop nanostructured thermal insulation materials, which can function and thermally insulate from the nano scale. A promising class of nanostructured thermal insulation materials are the nano-hybrid composite consisting of organic/inorganic particles and inorganic hollow particles. These materials have been investigated extensively in the context of chemistry and materials science. Principally, composite organic/inorganic particles can be classified as organic core with an inorganic shell or vice versa. Both polymer encapsulation of inorganic particles and coating of polymer particles with minerals can modify the properties of the precursor particles and lead to nanocomposite particles with tailored structures and morphologies [10,11]. Considerable research has been devoted to the preparation of mineral-coated polymer particles, and there are three main approaches: sol-gel nano-coating [12–16], hetero-coagulation [17] and layer-by-layer self-assembly [18]. By far, sol-gel synthesis is the most attractive for forming core-shell particles due to its ease of operation. Hollow nanospheres can be produced from hybrid nanoparticles, by extraction of the polymeric core through methods such as calcination, solvation, etc.

Among the different elements, silica is the most abundant chemical compound in the earth crust, most commonly found in nature as quartz and as the major constituent of sand. Its abundancy makes it a logical starting point material on the path to create nano insulation materials (NIM) for the future [19–21]. In parallel, our laboratory has been working on the development of new composite materials involving silica aerogel-concrete hybrids for both structural and thermal insulation properties so as to minimize the thickness of the material during construction [22–25]. Hollow silica nanospheres (HSNS) could potentially be a replacement material for silica aerogels. HSNS could also potentially be a replacement for thermal insulation materials such as expanded polystyrene (EPS) and extruded polystyrene (XPS), materials that may suffer from challenges related to fire, apart from their relatively large thermal conductivity values compared to silica aerogel [7].

This investigation thus aims to analyze the creation of thermally insulating hollow silica nanospheres (HSNS) for construction purposes. The current investigation is a follow-up on our investigations on the formation of HSNS based on a sacrificial polystyrene template and a silica precursor of tetraethyl orthosilicate (TEOS) [19–21]. We have previously shown that through such synthesis methods, thermally insulating materials with low thermal conductivity values of about 20–40 mW/(mK) can be produced [20,26], although the overall carbon footprint may be relatively high due to the use of organic silica precursor. It was then suggested that water glass (Na_2SiO_3, WG) can be an alternative for lowering the carbon footprint. The current investigation will thus explore the alternative synthesis route using water glass as the silica precursor. The synthesis of spherical polystyrene templates and formation of HSNS with TEOS will first be described to form the basis for a water glass based HSNS synthesis. Thereafter, a comparison of the differences in morphological formation of the silica network by applying TEOS and water glass as precursors will be discussed in relation to their thermal conductivity. The parameters affecting the formation, mode of formation and final product will be highlighted.

2. Materials and methods

2.1. Materials

Reagent grade styrene (St), polyvinvylpyrrolidone (PVP; Mw ≈ 40 k Da), potassium sulfate (KPS), ammonium hydroxide (NH_4OH, 28–30 wt%), tetraethyl orthosilicate (TEOS), ethanol (96%), water glass (sodium silicate solution, Na_2SiO_3, WG) and 1 M hydrochloric acid (HCl) were supplied by Sigma Aldrich.

2.2. Synthesis of polystyrene templates

Polystyrene (PS) templates based on varying PVP/St ratios were synthesized via emulsion polymerisation. In a typical synthesis, 10 g of styrene and required amount of PVP were homogenized in 90 g of distilled water at room temperature (RT) for 15 min in a 250 mL Erlenmeyer flask. The following eleven PVP/St ratios were employed: 0.0050, 0.0075, 0.0100, 0.0500, 0.1000, 0.1500, 0.2000, 0.2500, 0.3000, 0.4000 and 0.5000. 0.10 g of KPS dissolved in 10 g of distilled water was then added to the mixture maintained at a constant temperature of 70 ± 1 °C in an oil bath under stirring conditions of 300 rpm for 24 h before quenching by cooling in air at RT. The PS solutions are denoted as PS-ratio, e.g. PS-0.0050.

2.3. Coating PS templates with silica

2.3.1. TEOS as silica precursor

6 g of PS-0.1000 was dispersed in 95 g of 96% ethanol at 500 rpm for 15 min. 1.5 mL of NH_4OH was added (pH was about 13). The mixture was stirred for 15 min. 5 mL of TEOS in 5 mL of ethanol was added to the reacting pot in three manners: (1) TEOS-1: all at once, (2) TEOS-2: 1/5 of the TEOS/ethanol added at hourly interval over a period of 5 h and (3) TEOS-3: 1/100 of TEOS/ethanol added at 3 min interval over 5 h. The final mix was stirred at 500 rpm overnight at RT.

2.3.2. WG as silica precursor

20 g of PS-0.1500 (or PS-0.3000) were mixed with 3 g of WG in 240 g of distilled water. When further PS with lower PVP/St ratios were employed, no stable colloid could be formed at the original PS concentration. For synthesis purposes, an optimized diluted system was employed. To PS-0.0050 and PS-0.0075 samples, 5 g of PS was added to 1 g of WG in 50 g of distilled water. 1 M HCl was added to all samples until a pH of 2.0 was reached. The solutions were left stirring at 400 rpm overnight at RT.

All coated PS-silica samples were subjected to centrifugation at 8000 rpm for 10 min, air dried overnight and calcined at 500 °C for 5 h (heating rate = 5 °C/min) to remove the PS core.

2.4. Characterization

Microstructures of the obtained materials were analyzed by using a Hitachi S-5500 scanning transmission electron microscope (STEM). Analysis with secondary electrons employed an acceleration voltage of 10 kV and current of 7 μA while 30 kV was used in bright field transmission mode.

The thermal conductivity of unmodified PS-silica samples were determined by employing a Hotdisk Thermal Constants Analyzer (TPS 2500S). A transient plane source technique was applied [27,28] and the PS-silica were measured using the Kapton sensor with radius of 3.189 mm. The sensor is sandwiched between two well packed powder samples of PS-silica. The sensor acts both as a heat source, as well as to register the temperature increase in the samples. The temperature increase over time is recorded and used to calculate the thermal conductivity of the samples. The heating power and heating time can be varied independently to obtain the most appropriate testing conditions for each sample. The conductivity measurements were performed with a heating power ranging from 100 to 700 mW and a heating time of 320 s. All unmodified PS-silica samples were measured only after cooling to ensure equilibrium of the thermal conductivity. Repacking of the samples for measurements were employed and the final reported data are given as the arithmetic mean of 3–5 individual results, depending on the repeatability of the measurements.

3. Results and discussion

3.1. Size determination of PS templates

A nano insulation material (NIM) is a homogeneous, nanostructured material with closed or open nano-sized pores (Fig. 1). The overall thermal conductivity (λ_{tot}) of NIM can be attributed in a simplified form to the proximity of gases to solid interfaces, molecular collisions and the inherent materials properties for heat transfer within a specific area or volume as governed by the following expression:

$$\lambda_{tot} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coupling} \quad (1)$$

where λ_{tot} is the total overall thermal conductivity, λ_{solid} is the solid state thermal conductivity, λ_{gas} is the gas thermal conductivity, λ_{rad} is the radiation thermal conductivity, λ_{conv} is the convection thermal conductivity, commonly termed as part of the gas thermal conductivity and $\lambda_{coupling}$ is the thermal conductivity term accounting for second order effects between the various thermal conductivities