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Synthesis of large-sized mesoporous silica spheres by pseudomorphic transformation of commercial silica spheres

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ABSTRACT

Large-sized spherical mesoporous silica (LMS > 3 mm) has been synthesized through a pseudomorphic transformation method. For this, cetyltrimethylammonium bromide (CTAB) was selected as a templating agent and commercial silica spheres were used as the parent silica material. The effects of synthesis parameters, such as NaOH:SiO_2 molar ratio, reaction time, and ethanol:H_2O volume ratio, have been quantitatively investigated. The structure and morphology of the spheres have been investigated by N_2 sorption–desorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses. The pore structure of LMS obtained from a molar ratio of 140H_2O:0.1NaOH:0.27CTAB after 48 h was examined with the addition of ethanol, and the optimal volume ratio of ethanol:H_2O was identified as 0.252. Under the optimum conditions, high-quality mesoporous silica spheres were synthesized with a high specific surface area (about 1078.19 m^2/g) after post-hydrothermal treatment. The ordered pore structure was maintained over four cycles in recyclability experiments on the reaction solution. The large-sized particles showed improved capacity for Pb^{2+} removal, suggesting that they might be applied as a basic material for heavy metal adsorption in treating industrial or natural waste water.

1. Introduction

Mesoporous materials have been extensively studied because of their controllable pore size and narrow pore size distributions, coupled with high thermal and hydrothermal stabilities [1–4]. Significant efforts have been undertaken to synthesize various kinds of mesoporous silica materials. At the same time, mesoporous silica materials with different functions have been widely used for many promising applications in diverse fields, such as adsorption, catalysis, biochemistry, and electrochemistry [5–8]. However, with small particle size (0.2–1 μm) [9] and strong fluid resistance, mesoporous silica obtained by traditional methods is difficult to apply to adsorption, catalysis, and so on for industry [10,11].

Galarneau et al. [12] tried to overcome these problems by pseudomorphic transformation of a purified silica particle precursor. In the past decade, many scholars have studied pseudomorphic transformations in different silica resources, and the results showed good promise for low-cost syntheses [13–15]. In this process, the key point in maintaining the morphology of the silica spheres is to find appropriate synthetic conditions under which the rate of silica precipitation is equal to that of silica dissolution [10,12,16].

Large-size silica sphere, especially>1 mm, can be utilized to industrial catalyzer, adsorbent and ion exchanger. Limited by the industrial production process, the BET surface area of silica sphere is just 200–300 m^2/g. As a result, pseudomorphic transformation is a better way to synthesize large-size mesoporous spheres than traditional way which needs more energy and time to create macroscopic morphology.

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At present, however, the process of pseudomorphic transformation is more easily controlled in small particles (<100 μm) and at low concentrations of sodium hydroxide. With a high molar ratio of sodium hydroxide, the rate of silica precipitation and the phenomenon of fragmentation are difficult to control in attempting to synthesize large-sized (>1 mm) mesoporous silica spheres by pseudomorphic transformation [10,17]. Consequently, it is still a great challenge to obtain large-size mesoporous materials (>1 mm) for industrial applications.

An effective way to control the rate of silica precipitation is to change the composition of reaction solution, such as adding more water or decreasing the NaOH concentration [10,18–20]. While in these methods, more water and surfactant were needed to maintain the reaction condition, leading to concentration of NaOH and silicate decreased rapidly. Among the many organic additives tested, ethanol has been proved to have a great influence in the process of mesoporous material synthesis [18,21]. The diffusion rate and concentration of ethanol can influence the formation of micelle. Ethanol, as a co-surfactant, could change the reaction parameter such as g value, surface curvatures, critical micelle concentration (CMC) [22]. Therefore, it is very important to study the influence of ethanol on solution systems for pseudomorphic transformation.

One of the most important considerations in using mesoporous silica as an industrial sorbent is its high cost. Reusing from the reaction solution is an efficient approach for controlling the cost. Under traditional synthesis conditions, the CMC is the key parameter to form pores with different structures, such as hexagonal [23]. Nevertheless, in many experiments, it has been found that the CMC value in the traditional method is not always critical and that hexagonal pores could sometimes be formed at a lower concentration. The probable reason is that the CMC value in solution is related to the solvent and template concentration [24]. Hence, to devise a lower cost method, the solution composition and the recyclability of the pseudomorphic transformation need to be studied.

Here, we had investigated the influence of the solvent used in syntheses of LMS. In particular, we have tested the influencing factors on re-precipitation in the silica spheres ($NaOH:SiO_2$ molar ratio, reaction time, and ethanol:H_2O volume ratio). By characterizing the morphology and texture of mesoporous products obtained after pseudomorphic transformations, we have also investigated the difference in LMS before and after post-hydrothermal treatment. Furthermore, we performed five cycles, designated as rounds 1 to 5, to investigate the recyclability of the reaction solution in the synthesis of LMS to save cost. Finally, we have studied the capacity for Pb^{2+} adsorption on columns of the silica spheres. The results suggested that with a proper condition, pseudomorphic transformation can be used for synthesis large-size mesoporous material applied in adsorption, catalysis, and so on for industry.

2. Experimental procedures

2.1. Materials

As precursor material, commercial silica spheres were purchased from a silicon factory in Qing Dao. The main productive processes are grinding, mixing, shaping, drying and calcination et al. The SEM figure for primary particle and the substance content for parent silica sphere after calcination were shown in Fig. S1 and Table 1, respectively. Cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), ethanol, and other chemicals were of analytical grade and were used as received.

Table 1
Compositions (%) of the parent silica spheres before and after purification with 0.1 M HCl.

Sample	SiO_2	Al_2O_3	CaO	Na_2O	Fe_2O_3	TiO_2	ZrO_2	CuO
Before purification	98.88	0.15	0.23	0.26	0.08	0.04	0.005	0.03
After purification	99.44	0.10	0.09	0.07	0.06	0.035	0.006	0.006

2.2. Synthesis of LMS

LMS was synthesized by pseudomorphic transformation using commercial silica spheres as the precursor material and CTAB as a template. Typically, 7.5 g CTAB and different amount of NaOH($0.05 < x < 0.1$) were dissolved in 151 ml deionized water or the mixture solution of ethanol and water ($0 < y < 0.658$), and the mixture was vigorously stirred at 313 K for 30 min. After cooling to the stated temperature 25 °C, calculated amounts of silica spheres (4.5 g) were added to aliquots of this solution, and the mixtures were stirred for 30 min. The molar ratios of $NaOH:SiO_2:CTAB:H_2O$ were x:1.0:0.27:140, where x ($0.05 \leq x \leq 0.1$) denotes the proportion of NaOH. In this study, ethanol was also used as an organic additive in the synthesis system to control the rates of dissolution and polymerization. The ethanol:H_2O volume ratio is denoted as y, and was varied from 0 to 0.658. The final samples are denoted as $LMS_{x,\ y,\ time}$.

We transferred the aforementioned mixtures to a hydrothermal reactor for pseudomorphic transformation at 383 K for 24–48 h. The silica spheres were recovered by filtration and extensively washed with deionized water. After drying at 353 K for 12 h, the samples were subjected to post-synthesis hydrothermal treatment at the same temperature and for the same time as in the hydrothermal reaction to improve their hydrothermal stability and the uniformity of their pore structures. After extensive washing with deionized water and drying at 373 K for 12 h, the samples were calcined in a flow of air at 823 K for 5 h to obtain LMS.

2.3. Solution reusing experiments

To investigate the recyclability of the reaction solution in the process of pseudomorphic transformation, the solution after the reaction was collected in a beaker for reusing. After adding the same quantity of parent silica spheres and NaOH to the system, the solution was run for five cycles (round 1 to round 5) under the optimal conditions for pseudomorphic transformation. The final samples are designated as round (1–5).

2.4. Pb^{2+} adsorption experiments

Column study of LMS and parent silica spheres for Pb^{2+} removal were used to investigate the ability of Pb^{2+} adsorption. In this study, 30 g LMS was filled in the column. The initial concentration of Pb^{2+} was 100 mg/L, and the flow rate was 5 ml/min. Otherwise, as contrast, 60 g parent silica spheres was filled in the column and the initial concentration of Pb^{2+} was 40 mg/L, and the flow rate was also 5 ml/min. Both experiments had a same pH value at 4. Total adsorbed Pb^{2+}, qt(mg), in the column for a specific flow rate and initial concentration can be calculated from following equation [25]:

$$qt = \frac{Q}{1000}\int_0^t Cdt$$

where Q is the flow rate (mL/min), where C is the concentration of metal ions removal, (C=C_0–Ce, mg/L) versus time (min), t is the