PEG-templated mesoporous silicas using silicate precursor and their applications in desiccant dehumidification cooling systems

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ABSTRACT

Polyethylene glycol (PEG) was employed as a templating agent for the preparation of mesoporous silica materials starting from sodium silicate solutions using a sol–gel method. We show that PEG can serve as a structure-directing agent resulting in silica structures with pores spanning a range of 3.3–3.9 nm depending on the PEG concentration and the PEG removal method. The use of a PEG template increased significantly the surface area from 252 $m^2\,g^{-1}$ without PEG to >340 $m^2\,g^{-1}$ and >634 $m^2\,g^{-1}$ when the PEG was removed by, respectively, calcination and solvothermal extraction. It appears that calcination at high temperature caused a densification of the pore structure resulting in a smaller surface area and pore diameter. The impregnation of mesoporous silica with $CaCl_2$ significantly increased the adsorption capacity of water. At high humidity, the composite adsorbents containing approximately 42 wt.% $CaCl_2$ yield a maximum adsorption capacity of 1.6 times their own weight and 4.4 times that of bare silica. The adsorption is physical in nature as viewed from the adsorption energy calculated by the Dubinin –Radushkevich (D–R) equation.

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1. Introduction

Mesoporous silicas with controlled pore structures have been widely investigated due to their wide potential applications in catalysis [1,2], separations [3,4], microelectronics [5], drug-delivery systems and biomedical devices [6,7]. This is because these materials have very high surface areas that allow for binding to a great number of active sites distributed within the framework of porous materials. Moreover, they also have large pores that can overcome the pore-diffusion limitation and, in turn, provide high-speed pathways for adsorbate molecules. Therefore, in a system, such as desiccant dehumidification or cooling system, the dehumidifying performance of a desiccant strongly depends on the capacity and selectivity of the adsorbent [8]. Adsorbents with a high adsorption capacity and selectivity exhibit better performance [9–11].

The use of a silicate precursor as a substitute for alkoxide compounds that are commonly used for the synthesis of mesoporous silicas has recently attracted more attention. This is motivated by the fact that these materials are cheap and non-toxic [12].

Mesoporous silicas with a controlled pore structure are typically prepared using an organic template, typically a polymer or surfactant, although they can also be prepared by changing the processing parameters [13–16]. When using a template, mesoporous silica with a controlled pore structure is obtained after removing the template from the organic–inorganic composites. Several polymers have been successfully used to prepare mesoporous silica, including gelatin [12], polyethylene glycol (PEG) [17–19] and chitosan [20].

The template removal is a crucial step in the preparation of mesoporous silica. During this step, the template must be removed as completely as possible while preserving the templated silica structure. To date, compared to the other template removal methods, calcination [15,18,21] and solvothermal extraction [12,22] are the most favored because of their simplicity and low costs. Calcination at a high temperature tends to cause sintering, a densification of pore structures and a loss of mesostructure. Conversely, solvothermal extraction tends to preserve the structure of the templated silica phase because it is performed at a low temperature no higher than the boiling point of the solvent. However, solvothermal extraction requires a longer time.

In this paper, PEG was used as a template to prepare mesoporous silica starting from a sodium silicate solution. The effect of

the amount of PEG added into the sol—gel reaction system on the specific surface area, pore volume and pore size was investigated. In addition, the effect of the template removal method, namely, calcination and solvothermal extraction, was also investigated systematically. The mesoporous silicas produced were then impregnated with $CaCl_2$ to enhance their adsorption capacity and selectivity of water. This composite may be used as an adsorbent in a solid sorption refrigeration system utilizing low-temperature energy resources, such as waste heat and solar energy. The refrigeration system can be an alternative to environmentally friendly refrigerating devices [9,23].

2. Experimental

2.1. Materials

Industrial-grade sodium silicate solution was used as the silica source (water glass; 28% SiO_2, SiO_2:Na_2O = 3.3, provided by PT. PQ Silica Indonesia). All of the chemicals used to prepare mesoporous silica were reagent grade and used without further purification. The sodium hydroxide (NaOH), polyethylene glycol (PEG 1000), hydrochloric acid (HCl), dimethyl sulfoxide (DMSO) and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) were supplied by Merck. Distilled water was used during all synthesis and treatment processes.

2.2. Preparation of mesoporous silica

A silica—PEG hybrid was prepared following the reported procedure [15,18] with some modifications. Sodium silicate was diluted with distilled water in a 1:2.5 volumetric ratio to obtain a final silica concentration of approximately 8.0%. Then, 30 mL of the diluted sodium silicate was added to 75 mL of acidic PEG solution drop by drop under stirring. The acidic PEG solution was prepared by mixing 30 mL of aqueous PEG solution and 45 mL of HCl (1 M). The amount of PEG added was varied from 1 to 3 g. Then, the pH was adjusted to 4 by adding NaOH solution. The mixture was aged at room temperature for 1 h and subsequently at 80 °C for 2 h to form a gel. The gel was dried in an oven at 90 °C for 16 h to produce the silica—PEG hybrid. Then, it was washed with distilled water to remove the NaCl.

To remove PEG from the silica—PEG hybrids, two methods were used: calcination and solvothermal extraction. In the first method, the silica—PEG hybrids were calcined in air in a furnace at 550 °C for 4 h. In the second method, the silica—PEG hybrids were extracted with a 5 wt.% aqueous DMSO solution in a Soxhlet apparatus for 24 h. The PEG-extracted silica was then dried in an oven at 100 °C for 12 h.

Silica—$CaCl_2$ composites were prepared by diffusion impregnation of $CaCl_2$ into the host mesoporous silica. This was performed by immersing the host mesoporous silica in aqueous $CaCl_2$ solution containing 10—50 wt.% $CaCl_2$ to obtain composites with different $CaCl_2$ loadings. The mesoporous silicas were kept in the solution for 12 h to allow the liquid solution to fill the silica pores. The samples were then dried at 80 °C until a constant weight was obtained. The contents of $CaCl_2$ in the anhydrous samples were calculated and designated in terms of percentages with respect to the total weight of the host silica and the $CaCl_2$ used.

2.3. Characterization

The porosity of the prepared silicas was studied using nitrogen adsorption—desorption isotherms at the boiling point of nitrogen (77 K) using a Nova 1200e apparatus (Quantachrome). Prior to the measurements, the samples were degassed under flowing nitrogen at 300 °C for 3 h. The pore-size distributions of the materials were calculated based on their desorption branches using the Barret—Joyner—Halenda (BJH) method. The BJH method is the most widely used method for the calculation of pore-size distribution over the mesopore range. The specific surface area was calculated using the multiple-point Brunauer—Emmett—Teller (BET) method at $P/P_0 < 0.3$, and the total pore volume was evaluated as P/P_0 approached unity. The oil absorption test was performed using a spatula rub-out method. One gram of silica sample was placed upon a glass plate, and ethylene glycol was added gradually, drop by drop, by means of a syringe. After the addition of each drop, the oil was thoroughly incorporate by rubbing with the spatula until a very stiff, putty-like paste that did not break was produced. The equilibrium water adsorption capacity was measured at various relative humidities by gravimetry in a flow column [24]. The morphologies of the prepared silicas were observed by scanning electron microscopy (SEM; FE-SEM S-5000, Hitachi Ltd.).

3. Results and discussion

3.1. Mesoporous silica

The addition of the acidic silicate solution to the PEG solution leads to the precipitation of a white solid, as indicated by the immediate turbidity of the mixture. This suggests that some interactions exist between silicate and PEG that induce precipitation. After the pH was adjusted to 4 by adding NaOH solution, the mixture changed into a gel. After the gel was aged and dried, a silica—PEG hybrid was obtained. When the PEG was removed from the hybrid, either by calcination or solvothermal extraction, porous silica was produced. Fig. 1 shows the SEM images showing the morphology of the silica—PEG hybrid (a) and porous silica after the PEG was removed (b). PEG is an organic polymer known to have an ability to decrease the dielectric constant of the solvent. Hence, PEG tends to induce particle aggregation, leading to the formation of an aggregated platelet structure (Fig. 1(a)) due to a relaxation of the internal tension in the silica network [18,25]. When PEG was removed from the hybrid material, well-defined spherical and smooth silica particles with sizes between 0.5 and 2 μm were obtained (Fig. 1(b)). The microstructures of the porous silica particles were examined using nitrogen adsorption—desorption.

The crucial step in the preparation of porous silica using a template is to remove the template as completely as possible. An FTIR study of the porous silica was performed to verify the successfulness of the PEG removal from silica—PEG hybrid, either by calcination or solvothermal extraction. Fig. 2 shows the typical FTIR spectra of a silica—PEG hybrid (a), bare porous silica (b) and porous silica particles after PEG removal, either by calcination (c) or solvothermal extraction (d). Bare porous silica was prepared using the same conditions used to prepare PEG-templated porous silicas except without the addition of the PEG template. In the four samples, two typical bands of silica are apparent at 1084 and 799 cm^{-1} that correspond to the Si—O—Si bonds [26]. In addition, the band at 956 cm^{-1} can be attributed to the stretching of non-bridging oxygen atoms such as Si—O—(H…H_2O) [13]. In the FTIR spectrum of the silica—PEG hybrid, two other bands at 1685 and 2934 cm^{-1} are apparent in addition to the bands corresponding to silica. The band at 1685 cm^{-1} can be attributed to the urethane carbonyl group, and the band at 2934 cm^{-1} corresponds to an alkyl group (—CH_2—) [27]. The absence of these two bands in the FTIR spectra of porous silica particles after PEG removal, either by calcination or solvothermal extraction, indicates that PEG has been successfully removed from the silica—PEG hybrid.

Fig. 3 shows the typical nitrogen adsorption—desorption isotherms at 77 K of the porous silicas obtained with and without a PEG template. The adsorption—desorption isotherms of porous