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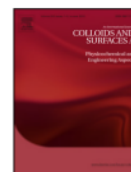
Synthesis of mesoporous silica with controlled pore structure from bagasse ash as a silica source

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HIGHLIGHTS

- A novel and cheap approach for producing mesoporous silica is proposed.
- The mesoporous silicas have very high surface area which can reach >600 $m^2\,g^{-1}$.
- The pore structure of mesoporous silicas can be tuned easily.
- Bagasse ash, a solid waste of sugar mills, is a viable material to produce mesoporous silicas.

GRAPHICAL ABSTRACT
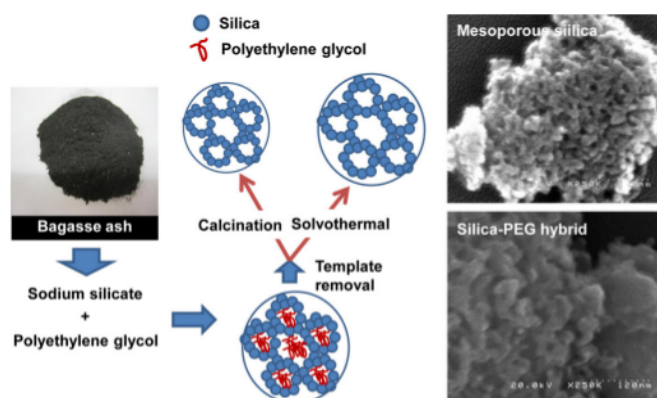
ARTICLE INFO

ABSTRACT

Mesoporous silica with controlled pore structure was prepared from bagasse ash as a silica source. The silica in the bagasse ash was dissolved by NaOH solution to produce sodium silicate precursor for the mesoporous silica, with or without polyethylene glycol (PEG) template. Without the PEG template, the pore structure was greatly influenced by the pH and the presence of Na^+ ions. The porous silica produced in the presence of Na^+ possessed higher surface area and pore diameter than those produced in the absence of Na^+. The surface area and pore diameter reached approximately 525 $m^2\,g^{-1}$ and 18 nm, respectively, when the gelation pH was 3. When the gelation pH was increased, the surface area decreased while the pore diameter increased. The use of PEG template increased significantly the surface area, which reached approximately 656 $m^2\,g^{-1}$ when the template was removed by solvothermal extraction. Calcination at high temperature caused a densification of pore structure resulting a smaller surface area, pore diameter and pore volume. The pore diameter for all cases was greater than 4 nm, indicating that the silicas were mesoporous.

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1. Introduction

Bagasse ash is a solid waste of sugar industry and has disposal problems. Bagasse ash is produced when bagasse, a cellulose fiber

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remaining after extraction of the sugar-bearing juice from sugar-cane, is burned to generate energy to operate plants. With a silica content of greater than 50%, bagasse ash may be a valuable feed-stock for the production of mesoporous silica useful for applications such as separation, adsorption, catalysis, thermal insulation and biomedical [1–5]. For such purposes, the surface area and pore size of the mesoporous silica are of importance. The large surface area allows for binding at a great number of active sites distributed within the framework of the porous materials. The large pores can overcome the pore-diffusion limitation and provide high-speed pathways for gas molecules [6].

Various biomass ashes, including rice hull ash and bagasse ash, have been used as the silica sources to prepare mesoporous silica. The conversion of biomass ashes into mesoporous silica was commonly carried out by an alkali extraction followed by a sol–gel process [7,8]. High-purity mesoporous silica could be produced from bagasse ash by this method [1]. However, the surface area was relatively low ($\sim$160 m^2 g^{-1}). The silanol groups on the silica surface cause the gel to collapse via irreversible condensation during drying. When the silanol groups on the silica surface were exchanged with alkyl groups, the condensation and shrinkage of the gel structure during drying could be prevented and silica aerogels with very high surface area (>1000 m^2 g^{-1}) could be produced [2].

Mesoporous silica with controlled pore structure can be prepared either without or with the addition of template. For the method without the addition of template, the pore structure is tuned by changing the processing parameters such as precursor concentration and pH [9,10]. The silica particles prepared using this method can be tuned to have the average pore size up to $\sim$20 nm and the total pore volume ranging from 0.8 to 1.5 cm^3 g^{-1}. For the method with the addition of template, the pore structure is tuned by using a template, typically surfactant or polymer, to form nanocomposite and after being removed forming silica pore structure. The method greatly relies on the capability of silica to be associated with organic to form organic/silica hybrid materials. The reaction of silicic acid with organic polymers is very complicated. The phase separations are very sensitive for relatively small changes in reaction conditions [11–15]. Although there is difficulty to associate silica with organic materials due to the inherent difference of chemical and physical properties between organic and inorganic materials, mesoporous silica with tunable pore size has been successfully fabricated from silicate precursor using organic materials, e.g., gelatin [14], polyethylene glycol (PEG) [12,16,17] and chitosan [18], as template.

The removal of the organic substance from the organic/silica hybrid is a crucial step in the preparation of porous silica. This step must be able to preserve the structure of the templated silica phase and to remove the template as completely as possible. Several methods have been commonly used to remove the template including calcination [19] and solvothermal extraction [14,20]. Calcination requires high temperature that tends to cause sintering, a densification of pore structure and a loss of mesostructure. Solvothermal extraction requires less energy and simpler equipment because it is operated at atmospheric pressure in an open system and at a temperature no higher than the boiling point of the solvent.

All works described above used sodium silicate commercially available as the silica source. In this work, a process for preparing mesoporous silica from bagasse ash as the silica source was investigated. Although the physical and chemical phenomena of silica gels produced from sodium silicate have been extensively investigated, there is relatively little study on using bagasse ash and on integrating process conditions to provide insight into product characteristics. Sodium silicate as a precursor for mesoporous silica was prepared from bagasse ash using a method developed in our laboratory [1]. PEG was used as the template for the porous

silica preparation. The effects of various parameters including the pH and the amount of PEG added in the sol–gel reaction system on the specific surface area, pore volume and pore size distribution were investigated. The effect of template removal method, namely calcination and solvothermal extraction, was also investigated systematically. The properties of the porous silica prepared using template were compared to those of silica prepared without template. This route appears to be beneficial for effectively utilizing a renewable resource or a waste for an economically value-added product using an environmentally friendly process.

2. Materials and method

2.1. Materials

The bagasse ash was obtained from a cane sugar mill, PG. Kebon Agung, Malang, Indonesia. All chemicals used to prepare mesoporous silica from bagasse ash were reagent grade and used without further purification. The sodium hydroxide (NaOH), polyethylene glycol (PEG 1000), hydrochloric acid (HCl), dimethyl sulfoxide (DMSO), ammonium hydroxide (NH$_4$OH) and cation resin were supplied by Merck. The silica content of the bagasse ash was 50.36 wt.%, and the main impurities were K$_2$O (19.34 wt.%), Fe$_2$O$_3$ (18.78 wt.%) and CaO (8.81 wt.%). Demineralized water was used during all synthesis and treatment processes.

2.2. Silica extraction

The silica in bagasse ash was extracted using an alkali extraction method. The extraction procedure has been described in detail elsewhere [1]. Briefly, 10 g bagasse ash was dispersed in 60 ml of 2 N NaOH and the mixture was boiled for 1 h with constant stirring. The slurry was allowed to cool to room temperature and filtered through the Whatman no. 41 ashless filter paper. The filtrate was the sodium silicate solution used to prepare the mesoporous silica.

2.3. Preparation of mesoporous silica

The sodium silicate prepared above was used to prepare the porous silica. Three different methods were employed to induce gel formation: adding HCl solution (Method I), mixing with acidic ion exchange resin (Method II), and adding acidic PEG solution (Method III). For the latter case, there were two methods to remove PEG from the silica-PEG hybrid to form porous silica: calcination (Method IIIa) and solvothermal extraction (Method IIIb).

In Method I, the sodium silicate was titrated with 1 N HCl solution under constant stirring until a pre-determined pH, which was varied from 3 to 7, to induce gel formation. The hydrogel was aged for 18 h. Then, it was gently broken by adding 100 ml demineralized water to make slurry. The slurry was filtered, the filtrate was discarded and the washing step was repeated. The gel was dried in an oven at 100 °C for 24 h.

In Method II, the sodium silicate was mixed with an acidic ion exchange resin in a 1:2 volumetric ratio. The slurry was then stirred by magnetic stirrer for 1 h and filtered to produce silicic acid (pH $\sim$ 2). The silicic acid was titrated with 1 N NH$_4$OH solution to induce gel formation. The hydrogel was aged for 18 h to strengthen the gel network. The aging pH was varied from 3 to 7. Afterward, the gel was dried in an oven at 100 °C for 24 h.

In Method III, different amounts of PEG (0.5–2.5 g/100 ml) were dissolved in a solution of 0.5 M HCl. Silica-PEG hybrid precursor sol was prepared by slowly adding the acidic PEG solution to 35 ml of the sodium silicate from bagasse ash under vigorous stirring. The adding rate was kept constant at 1 ml min^{-1} using a syringe pump. The final pH of the mixture was varied from 3 to 7, which required the acidic PEG solution from 135 to 145 ml. The final concentration

of PEG in the mixture ranged from approximately 4 to 20 g l^{-1}. The gels formed were aged for 18 h. Demineralized water was added to gel and the gel was then broken to make slurry. The slurry was filtered, the filtrate was discarded and the washing step was repeated. The gel was dried in an oven at 100 °C for 24 h to produce SiO$_2$-PEG hybrid. In Method IIIa, the SiO$_2$-PEG hybrids were calcined in air in a furnace at 550 °C for 4 h. In Method IIIb, the SiO$_2$-PEG hybrids were extracted with 5 wt.% aqueous DMSO solution in a Soxhlet apparatus for 24 h to ensure that the PEG was completely extracted. The PEG-free silica was then dried in an oven at 100 °C for 12 h.

2.4. Characterization

The nitrogen adsorption-desorption isotherms were determined at its boiling point (77 K) using a gas adsorption-desorption instrument (Nova 1200, Quantachrome). Prior to the measurements, the samples were degassed under flowing of nitrogen gas at 300 °C for 3 h. The specific surface area of the materials was calculated using the multi-point Brunauer-Emmett-Teller (BET) method at $P/P_0 < 0.3$. The total pore volume was evaluated from the adsorption-desorption profiles. The average pore diameter and pore size distribution were estimated from the desorption branch using the Barrett-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 infrared spectra were recorded using a Fourier transform infrared (FTIR) spectrophotometer (FTIR 8400s, Shimadzu). The X-ray diffraction (XRD) patterns of the samples were obtained with an X-ray diffractometer (X'Pert, Philips). The weight loss of the porous silica was studied using thermo gravimetric and differential thermal analysis (TG-DTA, Shimadzu) in air from room temperature to 1000 °C.

3. Results and discussion

3.1. Effect of pH and Na$^+$ ions

In the preparation of silica gels, gelation pH and the presence of counterions have a pronounced effect on the microstructure of the gelified networks [10,21,22]. Fig. 1 shows the typical N$_2$ adsorption–desorption isotherms at 77 K of the porous silica obtained using Method I and Method II. The samples were
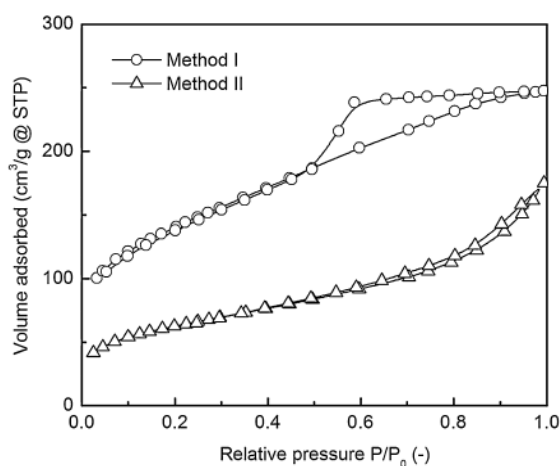

Fig. 1. Typical N$_2$ adsorption–desorption isotherms at 77 K of the porous silicas obtained using Method I and Method II. The samples were prepared at pH 4.

prepared at pH 4. The porous silica obtained by Method I showed a typical Type IV isotherm according to the IUPAC classification. This type is characterized by the disappearance of saturation limit with a hysteresis, which indicates an indefinite multilayer formation after completion of the monolayer and that the obtained materials are mesoporous. The hysteresis can be classified as an H2 type of hysteresis that involves a vapor-percolation threshold of the boundary curve occurring at P/P_0 of approximately 0.42. This reflects an abrupt release of almost all of condensed phase to the bulk vapor surrounding the sample. The adsorption–desorption isotherms of porous silica obtained by Method II indicated linear and step-shaped uptakes at relative pressures between 0.2 and 0.7. At higher relative pressures, the adsorption capacities scarcely increased, implying that less secondary mesoporosity and external surface area is present in the samples.

Fig. 2(a) shows the effect of pH on the specific surface area of silica gels prepared in the presence of Na$^+$ (Method I) and in the absence of Na$^+$ (Method II). In the presence of Na$^+$, the surface area of silica gels tended to decrease with the increase in pH. On the other hand, in the absence of Na$^+$, it tended to increase when increasing pH, peaking at approximately 5 and decreasing afterward. The surface area of silica gels prepared in the presence of Na$^+$ was larger than that of prepared in the absence of Na$^+$ at pH ≤ 4 and was lower at pH > 4. For the silica gels prepared in the presence of Na$^+$, the surface area ranged from approximately 204 to 525 m^2 g^{-1}. It ranged from approximately 380 to 430 m^2 g^{-1} when prepared in the absence of Na$^+$.

Figs. 2(b) and (c) show the effect of pH on, respectively, the pore size and the pore volume of silica gels in the presence of Na$^+$ (Method I) and in the absence of Na$^+$ (Method II). The pore size increased when increasing the pH both for silica gels prepared by Method I and Method II. However, the pore size of silica gels prepared by Method I was larger than that of Method II. It ranged from approximately 8 to 18 nm for Method I and from 3 to 9 nm for Method II. The typical pore size distributions of silica gel prepared by the two methods are shown in Fig. 3. The distribution is narrow indicating that the pore size is nearly uniform. The pore volume of silica gels exhibited a similar trend for the effect of pH, increasing when increasing the pH. The effect of Na$^+$ on the pore volume was in contradictory with that of the pore size. The pore volume of silica gels prepared by Method I was smaller than that of Method II. It ranged from approximately 0.3 to 0.6 cm^3 g^{-1} for Method I and from 0.3 to 0.9 cm^3 g^{-1} for Method II.

These findings may be explained using the general theory of silica polymerization. The condensation polymerization of silica in aqueous solution involves an ionic mechanism, which is mainly influenced by pH and the presence of counterions. In the presence of Na$^+$ ions, silica particles bear very little ionic charge at a pH around the isoelectric point (pH 2) that causes the particles to aggregate first into chains before forming three-dimensional gel network [10]. This way the gels produced contains many microporosity with high surface area. The rate of condensation reaction to form three-dimensional porous silica cluster aggregate is faster when pH increases. The faster aggregation causes the primary particles grow before the gel is formed and the primary particles are less branched and platey. Consequently, the gels have lower surface area with larger pore size and smaller pore volume after drying.

When the sodium silicate is pretreated with an acidic cation exchanger to exchange Na$^+$ with H$^+$ ions, gelation is accelerated when pH decreases [23]. The faster gelation causes the gels formed contain less branched and platey primary particles. Consequently, the gels at low pH have lower surface area with larger pore size and smaller pore volume. The slower gelation at high pH without the presence of Na$^+$ ions causes the primary particles in the gel grow larger and repel each other [10]. This causes the gel weakens and suffers more from the capillary forces with drying due to the
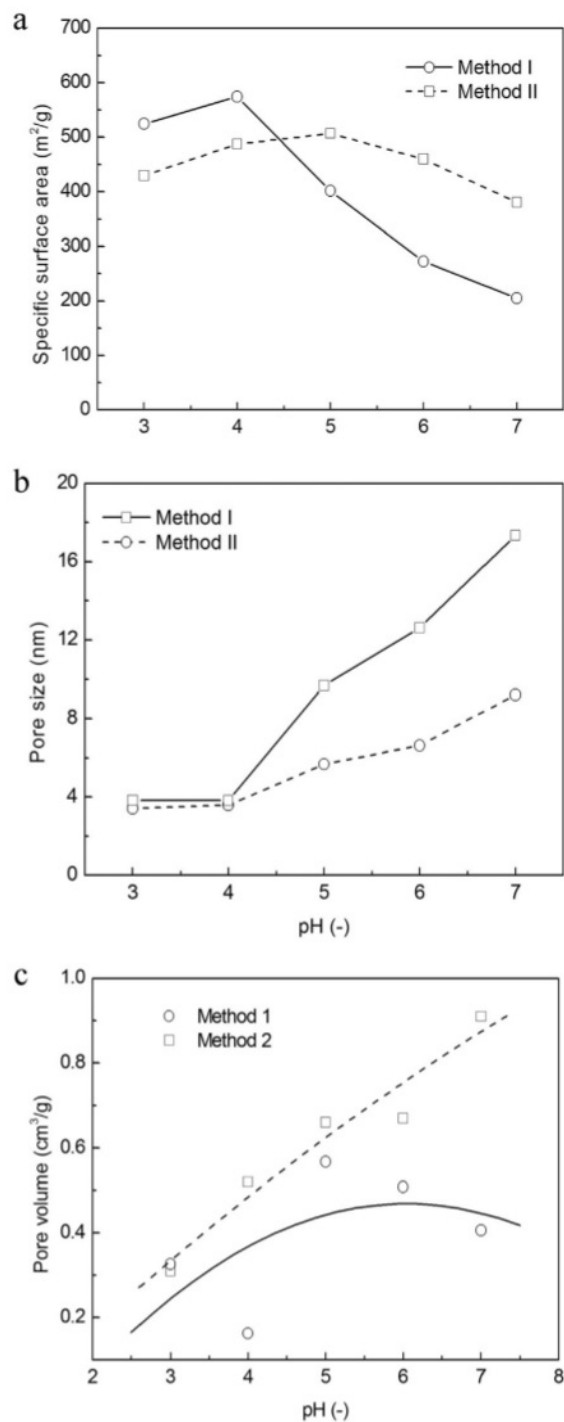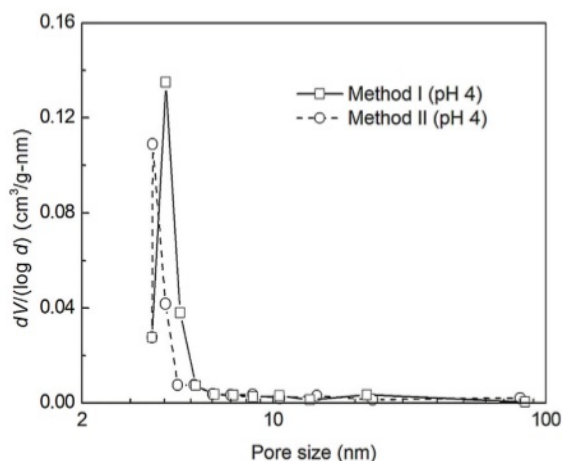
Fig. 3. Typical pore size distributions of porous silica prepared by Method I and Method II. The porous silicas were prepared at pH 4.

decreasing amount of interparticle bonds. This may be the reason why the surface area decreases with an increase in pH after pH > 5.

3.2. Effect of PEG and template removal method

Porous silica can be produced using PEG template after removing the template from silica-PEG hybrid, either by calcination or solvothermal extraction. FTIR and thermo gravimetric studies of the porous silica produced by the two different methods of template removal were conducted to verify the successful of the PEG removal. Fig. 4 shows the typical FTIR spectra of porous silica prepared without PEG templating, silica-PEG hybrid and PEG-free silica after PEG removal. The FTIR spectra of the bared silica and PEG-free silica are similar. Two typical bands of silica are apparent at 1100 and 802 cm^{-1} that corresponds to the Si–O–Si bonds. The band at 954 cm^{-1} can be attributed to the stretching of non-bridging oxygen atoms such as Si–O–(H. . .H$_2$O) [9]. In addition to the bands corresponding to silica, two other bands are apparent in the FTIR spectra of the silica-PEG hybrid. The band at 1695 cm^{-1} can be attributed to urethane carbonyl group and the band at 2929 cm^{-1}
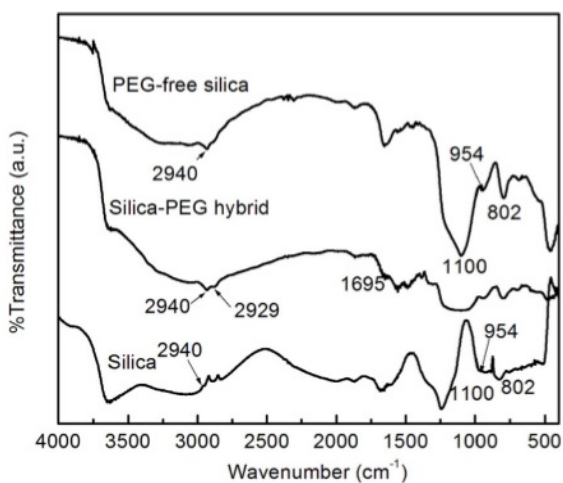

Fig. 4. Typical FTIR spectra of porous silica prepared without PEG templating, silica-PEG hybrid and PEG-free silica after PEG removal.

Fig. 2. Effect of pH on the surface area (a), pore size (b) and pore volume (c) of porous silica prepared by Method I and Method II.
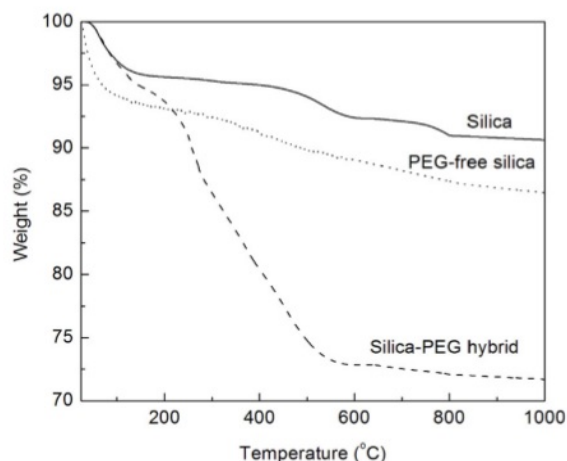
Fig. 5. Thermo gravimetric analysis of porous silicas from bagasse ash prepared without PEG templating, PEG-silica hybrid and PEG-free silica.

corresponds to alkyl group ($-CH_2-$) [24]. The signals indicate the formation of PEG into silica particles. The band at 2929 cm^{-1} disappeared after the PEG was removed.

Fig. 5 shows the results of thermo gravimetric analysis of porous silica from bagasse ash prepared without PEG templating, silica-PEG hybrid and PEG-free silica after PEG removal. For all samples, a weight loss is detected from room temperature to approximately 150 °C, indicating the loss of physically adsorbed water. In the temperature range from 150 °C to approximately 470 °C, the weight of silica prepared without PEG and PEG-free silica is relatively constant, and then decreases slowly. In contrast, the weight of PEG-silica hybrid remains relatively constant from 150 °C to approximately 200 °C and then decreases sharply by a further increase in the temperature. The weight loss may come from the decomposition of PEG. Thus, it was confirmed that PEG has been successfully removed from PEG-silica hybrid and the porous silica discussed in the following are relatively free from PEG.

Fig. 6 shows the SEM images of the silica-PEG hybrid (a) and the porous silica after PEG was extracted (b). It can be observed that the silica-PEG hybrid consisted of an aggregated platelet structure (Fig. 6(a)). When the PEG was removed from the hybrid material leaving only silica, the structure changed to spherical nanoparticles assembled in a porous network (Fig. 6(b)).

The typical N$_2$ adsorption–desorption isotherms at 77 K of the porous silica obtained after PEG removal by calcination and solvothermal extraction are presented in Fig. 7. The samples were prepared at pH 4 using PEG concentration of 8 g l^{-1}. The adsorption–desorption isotherms of porous silica obtained by calcination similar to that of obtained by Method II as discussed above. There was linear and step-shaped uptakes at relative pressures between 0.2 and 0.7 and at higher relative pressures, the adsorption capacities scarcely increased. The porous silica obtained by solvothermal extraction shows a typical Type IV isotherm with H2 type of hysteresis, similar to that of porous silica obtained by Method I, indicating that the obtained materials are mesoporous.

The effect of PEG concentration on the surface area and pore volume of silica prepared by solvothermal extraction is presented in Fig. 8. It appears that the surface area and pore volume increased by the increase of PEG concentration at low PEG concentration and then tended to be constant afterward. At low PEG concentration, there is a synergetic effect between PEG and silica, where the negatively charged silica induces the aggregation of PEG, forming a gel network that directs the growth of silica particles. Thus, PEG was
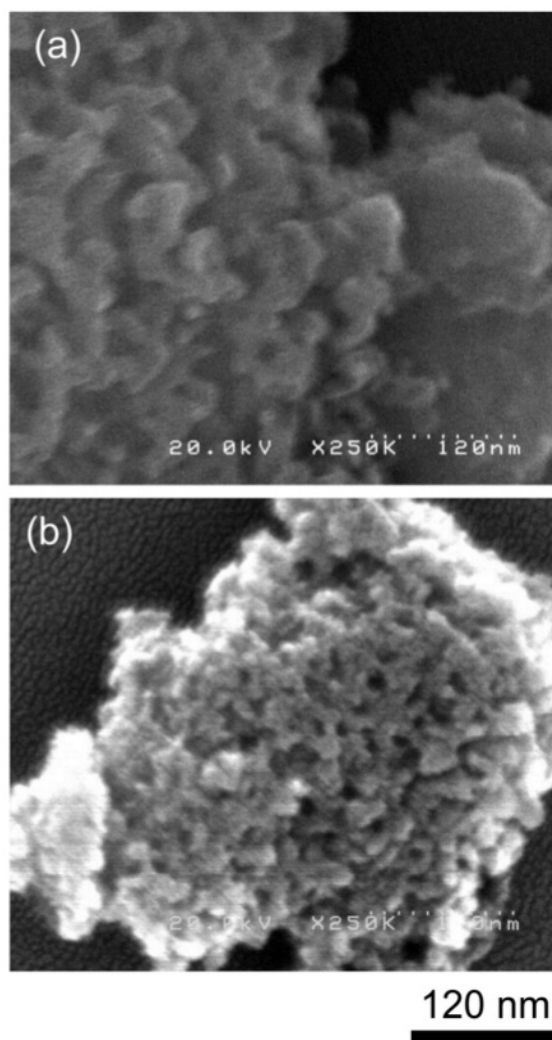

Fig. 6. SEM images of the silica-PEG hybrid (a) and the porous silica after PEG was extracted (b).

entrapped between silica networks and plays the role of a template, leaving pores after extraction. On the other hand, at high PEG concentration, upon silica addition, a PEG–silica precipitate was first formed, followed by the formation of gel embedded in the composite precipitate. Hence, increasing the PEG more had almost no effect on the surface area and pore volume. The discussions on the effect of pH and template removal method below are based on the PEG concentration of 8 g l^{-1}.

Fig. 9 shows the effect of pH on the surface area of silica prepared from bagasse ash using PEG template by two different methods of template removal. It can be seen that for any values of pH, the surface area of silica obtained by solvothermal extraction exhibit greater values. The different in surface area is greater at low pH and becomes smaller when the pH is increased. At pH 3, the surface area of silica obtained by solvothermal extraction is approximately 656 m^2 g^{-1} and is smaller for calcination that takes the value of approximately 486 m^2 g^{-1}. It decreases by increasing the pH and takes the value of 205 and 155 m^2 g^{-1} for, respectively, solvothermal extraction and calcination.
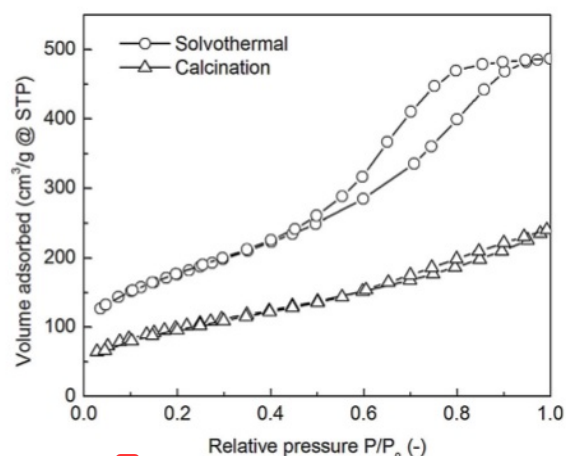
Fig. 7. Typical N$_2$ adsorption–desorption isotherms at 77 K of the porous silicas obtained after PEG removal by calcination and solvothermal extraction.
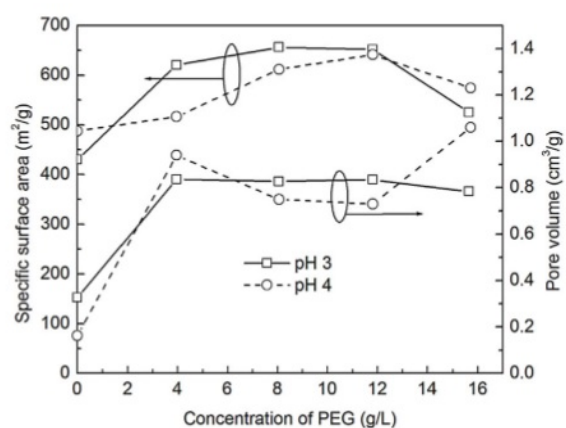

Fig. 8. Effect of PEG concentration on the surface area and pore volume of silicas prepared by solvothermal extraction.

The pore volume of silica is not significantly influenced by pH for both obtained by calcination and solvothermal extraction (Fig. 10). However, it is significantly influenced by the method of template removal. The pore volume of silica obtained by solvothermal extraction takes the value of approximately 0.8 cm^3 g^{-1} and those obtained by calcination is approximately 0.2 cm^3 g^{-1}. On the other hand, the pore diameter increases sharply by the increase of pH for solvothermal extraction and it is relatively constant for calcination. The pore diameter for calcination is approximately 4 nm and for solvothermal extraction ranges from 3 nm at pH 2 to 18 nm at pH 7.

Fig. 11 shows the pore size distribution of porous silica prepared by solvothermal extraction at various pH values. The distribution is narrow at low pH and becomes wider when the pH was increased. Compared with the porous silica prepared without PEG template (Fig. 3), the pore size distribution is wider and the average size is much larger. Thus, it is obvious that PEG can serve as a pore-directed agent to prepare porous silica.

Fig. 10. Effect of pH on the pore volume and pore diameter of silicas prepared from bagasse ash using PEG template by two different methods of template removal: calcination and solvothermal extraction.
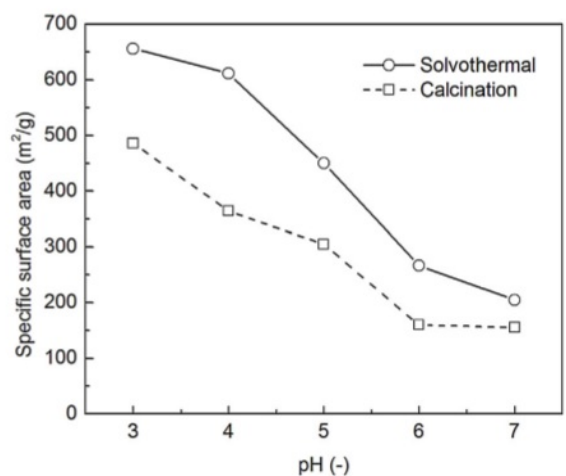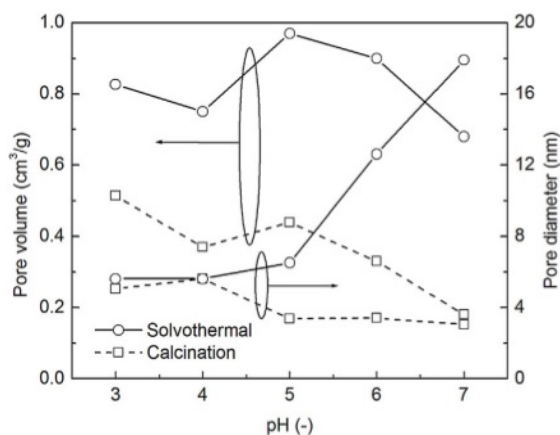
Fig. 9. Effect of pH on the surface area of silicas prepared from bagasse ash using PEG template by two different methods of template removal: calcination and solvothermal extraction.
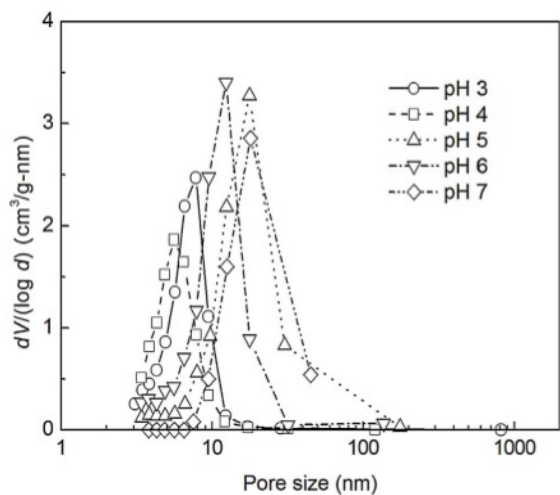
Fig. 11. Pore size distribution of porous silicas prepared by solvothermal extraction at various pH values.

4. Conclusions

Mesoporous silica with controllable porosity was prepared from bagasse ash as a silica source through, either with or without the addition of PEG template. The silica in the bagasse ash was extracted using a NaOH solution to form the sodium silicate precursor for the mesoporous silica. Without the addition of PEG template, the pore structure of the prepared mesoporous silica is greatly influenced by the pH and the presence of Na^+ ion. The surface area tends to increase with the increase of pH whereas the pore size and pore volume decrease. The surface area of silica prepared in the presence of Na^+ is larger than that prepared in the absence of Na^+ at pH ≤ 4 and is lower at pH > 4. The surface area ranged from 204 to 525 $m^2\,g^{-1}$ for the silicas prepared in the presence of Na^+ and from 380 to 430 $m^2\,g^{-1}$ when prepared in the absence of Na^+. The pore size is larger for the silicas prepared in the presence of Na^+ (ranging from 8 to 18 nm) than that prepared in the absence of Na^+ (ranging from 3 to 9 nm) whereas the pore volume is larger for silicas prepared in the absence of Na^+ (ranging from 0.3 to 0.9 $cm^3\,g^{-1}$) compared to that prepared in the absence of Na^+ (ranging from 0.3 to 0.6 $cm^3\,g^{-1}$).

The similar trend can be observed for the effect of pH on the surface area using PEG template. However, compared with the porous silica prepared with PEG template, the surface area, pore diameter and pore volume are much higher. The silicas prepared using the PEG template have the average pore size up to ~18 nm with higher surface area (ranging from 205 to 656 $m^2\,g^{-1}$) if the template is removed by solvothermal extraction. Calcination at high temperature causes a densification of pore structure resulting a smaller surface area, pore diameter and pore volume. Thus, it is obvious that PEG can serve as pore-directed agent to prepare mesoporous silica.

Acknowledgements

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