Morphology and adsorption capacity of sodium silicate-based hierarchical porous silica templated on natural rubber: Influence of washing–drying methods

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ABSTRACT

The effects of washing–drying methods on morphology and pores of hierarchical porous silica produced via calcination of the silica–natural rubber composite are reported. The composite, prepared by a sol–gel method involving sodium silicate and natural rubber, was subjected to different washing–drying protocols: suction filtration followed by drying the composite in paste form (Method **A**); liquid decantation followed by drying a pile of composite beads (Method **B**); and liquid decantation followed by drying the composite beads forming a single layer on the bottom of a container (Method **C**). The different washing–drying methods produced hierarchical porous silica with different morphologies and pore properties. Compared with the other samples, Method **C** yielded the porous silica with the highest total pore volume and the best pore interconnectivity, as well as the highest equilibrium adsorption capacity for methylene blue. Method **A**, however, produced the porous silica with the poorest properties.

1. Introduction

A network of interconnected pores of different sizes distinguishes hierarchical porous silica (HPS) from porous silica with a uniform pore size distribution. HPS provides a high specific surface area, a high total pore volume, and low intraparticle mass transfer resistance [1]. Thus, HPS is of substantial interest in applications such as adsorption and separation [2,3]. Typically, the macropores in HPS are formed by thermally degrading a polymer template. The micro/mesopores result from the decomposition of surfactant template and from the interspaces between secondary silica particles deposited on the template [4,5].

As a means of broadening the applications of natural rubber (NR) produced in Thailand, this work used the NR particles as a template to make HPS. The NR particles recovered by centrifuging the fresh NR latex are round and have a narrow size distribution (50–300 nm). As both the NR template and sodium silicate are negatively charged, salt is added to screen the repulsion to

produce the silica–natural rubber composite (SNC). The effect of different washing–drying treatments [6,7] of freshly made SNC on the HPS morphology and pores is reported. The equilibrium adsorption capacity of the HPS prepared by different washing–drying protocols is compared for the positively charged methylene blue (MB) dye. The dye adsorption studies provide a practical perspective on the effects of washing–drying protocols on adsorbent preparation.

Table 1
Pore properties of HPS prepared via different washing–drying protocols.

Washing–drying method	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)[a]		
			V_{micro}	$V_{Meso-macro}$	V_t
A	611.8	11.98	0.01	1.23	1.23
B	663.5	11.65	0.01	1.34	1.35
C	633.1	22.88	0.01	2.47	2.48

[a] The meso- and macropore volume ($V_{Meso-macro}$) is determined by subtracting the micropore volume (V_{micro}), calculated using the t-plot method, from the total pore volume (V_t).

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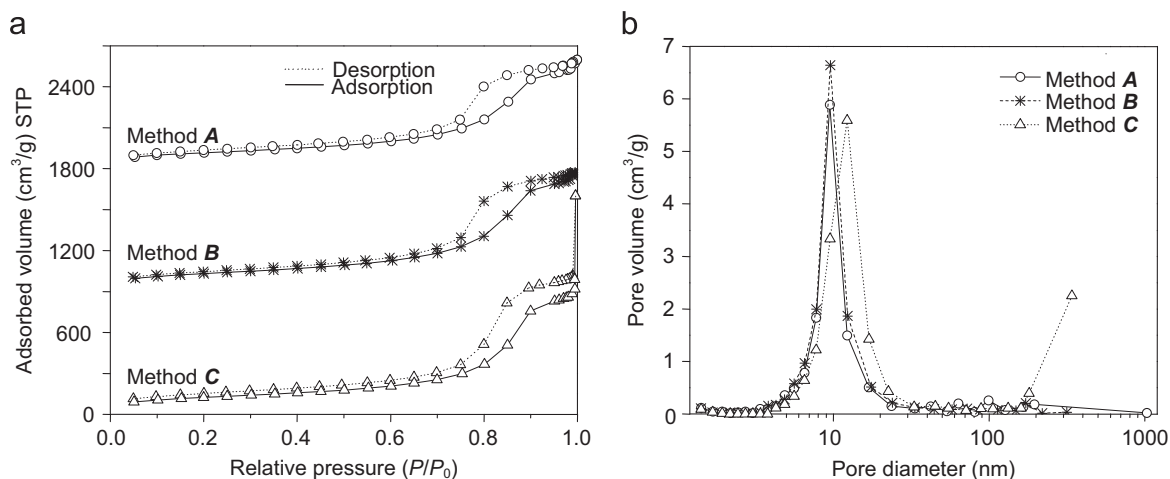E-mail address: fengnyh@ku.ac.th (N. Hansupalak).

Fig. 1. N$_2$ sorption isotherms (a) and pore size distributions (b) of HPS undergoing different washing–drying treatments.

2. Experimental

Sample preparation using the sol–gel method [6]: The NR latex (24 wt% dry rubber, 5 wt% NH$_3$) was mixed with sodium silicate (Na$_2$SiO$_3$: 9.4 wt% NaO$_2$, 29 wt% SiO$_2$) and deionized water in a ratio of the dry rubber:SiO$_2$ (from Na$_2$SiO$_3$):water = 1:2:120. The mixture pH was immediately lowered to pH 6 by adding 1 M HCl. NaCl was added to the slurry to attain a NaCl concentration of 0.5 M, yielding opaque spherical SNC beads (diameter ∼ 1 mm). The suspension was hydro-thermally aged at 80 °C for 24 h. The resulting beads were washed by repeated rinsing/decanting with deionized water. Each wash volume was equal to the initial slurry volume. The final washed solids were subjected to three washing–drying treatments: Method **A**: suction filtration (Büchner funnel) using a Welch 1405 DuoSeal vacuum pump, producing SNC paste (the beads lost their individuality) that was dried in an oven at 50 °C until a constant weight was obtained; Method **B**: sedimentation followed by water decantation to leave behind a pile of SNC (the beads remained distinct) that was dried the same way as in Method **A**; Method **C**: letting the slurry spread as a single layer of the SNC beads at the bottom of a container before drying the same way as in Method **A**. Finally, all dried samples were identically calcined at 550 °C for 6 h. This yielded HPS materials.

Characterization: HPS samples were characterized by an N$_2$ sorption method (Quantachrome Autosorb-1C instrument), a scanning electron microscope (SEM; FEI Quanta-450) and by a 200 kV transmission electron microscope (TEM; JEOL JEM-2010).

Dye adsorption: The HPS sample (20 mg) was agitated at 180 rpm with 20 mL of a 0.5 mM solution of MB in a water bath at 40 °C for 6 h. The MB concentration in the supernatant was determined by a GENESYS 10S UV–vis spectrophotometer at 664 nm. The equilibrium adsorption capacity, Q_e (mmol/g), of each sample is calculated from

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 and C_e are the initial and the equilibrium dye concentrations (mmol/L), respectively. V is the initial volume of the dye solution (L) and m is the mass of the dry adsorbent (g).

3. Results and discussion

Table 1 shows the pore properties of HPS samples of identical compositions prepared under identical conditions, but using different washing–drying treatments. Irrespective of the method used, the pore volume of all HPS samples was primarily associated with meso- and macropores (Table 1). The sorption isotherms (Fig. 1a) of the HPS samples were combinations of types II and IV with H2 hysteresis loops, indicating the existence of meso- and macropores forming complex porous networks [8,9]. However, only the isotherm of the Method **C** sample displayed the second capillary condensation above P/P_0 of 0.9 (Fig. 1a), implying the presence of macropores connected through channels of smaller size [10]. The corresponding pore analysis confirmed the presence of the macropores with diameters > 100 nm (Fig. 1b) with the highest values of the total pore volume (V_t) and the average pore size (Table 1, Method **C**).

TEM images (Fig. 2) show that all the HPS samples have disordered pore structure. Furthermore, in relation to the other washing–drying methods, Method **A** gave the thickest silica walls and the most dense silica framework in HPS samples as shown by the SEM and TEM images (Fig. 2a), respectively. These results were attributed to the use of the vacuum pump during recovery of the soft and wet SNC paste comprising numerous secondary silica particles, NR particles, and interstitial water. The suction force led to the beads packing tightly in three dimensions (3D). The extreme closeness of the beads enhanced the degree of bridging among the secondary silica particles via the formation of siloxane links during drying [11]. This greatly reduced the interspaces between the secondary silica particles. Also, the suction force tended to break the soft silica framework formed on the template particles during filtration. This broken silica layer readily slid off the template particles as it was held to the template by long-range electrostatic interactions. This contributed to the occurrence of many large regions of a dense structure (Fig. 2a, TEM). A combination of these factors may have prevented the nitrogen molecules from passing into pores, explaining the lowest values of the specific surface area (S_{BET}) and V_t for the Method **A** sample.

In the absence of suction filtration, the 2D SEM and TEM images of the samples from Methods **B** and **C** were similar (Fig. 2b and c). However, Method **B** led to 3D close packing of the wet SNC beads, whereas Method **C** resulted only in 2D packing. Consequently, Method **B** led to the generation of a large number of siloxane bonds between secondary silica particles during drying [11]. As the degree of bridging resulting from Method **B** was much less than that associated with Method **A**, additional pores were created in 3D in the particles subjected to Method **B**. This gave rise to the higher S_{BET} value for the Method **B** sample, relative to the Method **C** sample (Table 1) [12]. However, the reduced V_t value resulting from the Method **B** in comparison with the Method **C** (Table 1) suggests that a greater number of the macropores of the former sample were inaccessible to the gas molecules [12]. This probably resulted from a