Short Communication

Preparation of ultra-stable foams stabilized by large-size platelet particles via direct foaming method

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Abstract

Stable colloidal foams that are usually stabilized by 0.02 – 5 μm particles have attracted increasing interests due to their outstanding stability. However, there were no studies on stable foams stabilized by large platelet particles so far. In this paper, we reported the study and successful preparation of ultra-stable foams using platelet particles with large particle size of dozens of microns for the first time, which subverts the conventional wisdom about particle-stabilized foams. Herein, intact platelet diatomite particles with diameter in the range of 10 – 50 μm was employed as starting material to prepare foams via mechanical frothing. The ultra-stability of foamed diatomite suspension was established by the well-ordered arrangement of whole lamellate diatomite particles at bubble interfaces in a very wide pH range of 4.0 – 12.0, using cetyltrimethyl ammonium bromide (CTAB) as surfactant. The obtained diatomite ceramic foams exhibited light weight and uniform macropores, and possessed four kinds of multilevel pores, which have potential applications in the fields of removal of fine particulate matter and treatment of waste gas and waste water.

Keywords: Stable foams, intact diatomite, platelet particles, particle size, multilevel pores

I. Introduction

Ceramic foams are a kind of porous inorganic materials constituted by three-dimensional network of ceramic struts, which have been commonly used as carriers for catalysts, filters, bioreactors and bone substitutes, thermal insulations and lightweight structured components, depending on their pore structure ¹–³. Among methods for fabrication of ceramic foams, direct foaming method is widely applied due to its straight and simple processing route, which involves introducing gas into suspension to generate pore structure, and thus to endow ceramic lightweight, to save raw materials and improve thermal and other performances simultaneously ⁴,⁵. In the past ten years, particle-stabilized foams recognized as a promising, cost-effective and eco-friendly method has become an important approach for the fabrication of ceramic foams with relatively high porosity, small and uniform closed pores, which attracted more and more researchers’ attention ⁶–¹¹.

In particle-stabilized foams, partial hydrophobic particles modified by surfactant assemble in a jammed armor-coat on bubble surface to strive toward a closely packed layer of particles at the liquid/air interfaces, thus creating a mechanical resistance to unstable factors ¹²,¹³. In most cases, commercial powders such as alumina particles, zirconia particles, silica particles has been used commonly to prepare particle-stabilized foams. In fact, natural powder can also be used as raw materials for the fabrication of particle-stabilized foams. One such material is diatomite, which is a kind of mineral powder with mesoporous pores, abundant reserves and low cost, and therefore can be applied as filter, sorbents, catalyst carriers and thermal-insulating materials ¹⁴,¹⁵. A challenge among applications of diatomite is how to consolidate them as bulk structure that retains their inherent pores ¹⁶. Song I. H. et al. ¹⁶ has performed excellent work firstly, who has prepared particle-stabilized diatomite foams with bimodal pore structure by ball-milling diatomite for 24 h.

Generally, partially hydrophobic particles for preparation of particle-stabilized foams reported in the literatures have particle size in range of 20 nm-5 μm ⁵,¹⁷, and stable foams prepared with particle sized above 10 μm is seldom reported so far. In addition, Song’s research also demonstrates the difficulty in preparing stable foams using large particles ¹⁶. They found diatomite foams were not stable when using large raw diatomite particles without ball-milling, and only the foams stabilized by ground particles with ball-milling time more than 4 h were stable. Therefore, it can be concluded that particle size is a non-ignorable factor that rules the foam stability. It is of significance to figure out if large particles can be used to prepare stable foams.

Considering the lack research in particle-stabilized foams by using large particles with size of dozens of microns, the preparation of large particle stabilized foams is focused.
The aim of this work is to demonstrate it is achievable to make stable foams even using very large particles. Herein, ultra-stable foams were successfully prepared using whole platelet diatomite particles (with particle size of 10–50 μm) for the first time. The stable foams were further sintered to prepare diatomite ceramic foams with hierarchical pore structure.

II. Experimental procedure

Natural platelet diatomite with mostly unbroken lamellate diatomite particles (supplied by Linjiang Beifeng Diatomite Co., Ltd., China) was employed here. Cetyltrimethyl ammonium bromide (CTAB) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. 1 mol/L HCl and NaOH solutions were used to tailor the pH value of diatomite suspension. Firstly, deionized water was added to a plastic beaker, followed by adding diatomite powder and simultaneously waggling the plastic beaker. Then, CTAB (CTAB concentration here is based on the total quantity of final aqueous suspension) was added to the suspension, after which the pH value of the suspension was adjusted to set value. In order to avoid the sedimentation, the breaker was subjected to ceaseless waggle before frothing. At last, the obtained suspensions with solid loading of 20 wt% were agitated using a digital mechanical stirrer with stirring speed increased gradually from 500 rpm to 1500 rpm. After that, the foamed diatomite suspensions were dried at room temperature to obtain dry body, followed by sintered at 1100 °C and 1200 °C with heating rate of 3 K/min and holding time of 2 h in a furnace.

The diameter distribution of raw diatomite particles was evaluated using a particle size analyzer (MasterSize Analyzer 2000, Malvern, Worcestershire, UK). The element composition of diatomite was measured by the X-ray fluorescence spectrograph (XRF-1800, Shimadzu, Kyoto, Japan). The zeta potential of diatomite was measured by a Zeta Potential Analyzer (CD-7020, Colloidal Dynamics Co., Ltd., Ponte Vedra Beach, FL, USA). The geometric density of diatomite foams was calculated by the mass to volume ratio. The microstructure of diatomite particles and foams was observed by a scanning electron microscope (MERLIN VP Compact, Carl Zeiss, Jena, Germany). The specific surface area and nitrogen adsorption-desorption measurement of diatomite foams were conducted on Gemini VII 2390 (Mike, USA).

III. Results and discussions

The raw diatomite powder is mainly composed of complete disk diatomite particles with diameter in the range of 10–50 μm (see Fig. 1a and c) and thickness in the range of 1.5–4.5 μm. The main composition of diatomite is silica as shown in Table 1. Zeta potential of diatomite free of modification of surfactant exhibits strong negative charge at the pH above 3.0, as shown in Fig. 1d. Therefore, it is possible to render diatomite’s surface by adsorbing positive charged surfactant to endow it partially hydrophobicity. One such surfactant is CTAB, which has been proved to be able to prepare ultra-stable diatomite stabilized foams with addition amount above 0.10 wt% in the present work. After the modification by CTAB, zeta potential of diatomite exhibits significant increase (namely decrease of absolute value of zeta potential) in the pH range of 3.0–11.0, comparing with that of diatomite free of surfactant, which indicates there is strong interaction between the anchoring group of CTAB and the particle surface of diatomite.
As a result of efficient modification of CTAB, partially hydrophobic diatomite can generate ultra-stable diatomite particle stabilized foams in a very wide pH range of 4.0 – 12.0, as demonstrated in Fig. 2a, which is consistent with Fig. 1d illustrating that CTAB has strong adsorption ability on diatomite’s surface in such a wide pH range. Song I. H. et al 16 has found that stable foam could not be prepared using as-received diatomite or using diatomite particles with ball-milling time less than 4 h. Moreover, the fact that there is few report on ultra-stable foams with particle size above 20 μm proves it is still full of challenge. Now, our present work demonstrates that it is feasible to obtain ultra-stable foams just using complete diatomite particles with diameter of dozens of micron range, as confirmed by Fig. 2a-c.

It is believed that large particles tend to deposit under the influence of gravity, which could lead to the instability of foams. However it is fascinating to find that the wet foams obtained here are ultra-stable with excellent foamability, in spite of the presence of large diatomite particle with diameter size of 20 – 50 μm, which is attributed to the effective hydrophobization-modification and strong foaming capacity as long-chain surfactant. The demolded wet foams exhibit excellent shape retention during drying without distortion (see Fig. 2b and c). The platelet diatomite particles arrange parallelly to the air/liquid interfaces (as shown in Fig. 2e), which is further confirmed by the microstructure of pore wall shown in Fig. 3c). The adsorbed diatomite at the air/liquid interfaces form rigid network that can inhibit drainage, coalescence and disproportionation between adjacent bubbles as illustrated in Fig. 2d and e.

This is the first time to achieve stable foams using large particles as stabilizer, which develops particle-stabilized foams theory. The results demonstrate that foam stability is feasible even using large platelet particles with large diameter, which can bring new insights into the preparation of stable foams when involving particle size and shape. Owing to the outstanding stability of wet foams, there is no need for the addition of organic or inorganic binders to cure the foams during drying. The dried foams can be further sintered to fabricate porous ceramic (see Fig. 3a) that consist of three-dimensional platelet particle assembled foams with macropore size around 100 μm, which is (see Fig. 3b). The present work demonstrates a novel method to fabricate diatomite particle stabilized foams starting from complete diatomite, which offers several advantages, such as simple and straight processing route, avoiding the processing of grinding, preserving original morphology and inherent pore structure of diatomite. The obtained diatomite ceramic foams exhibit light weight, attributing to the uniform and thin strut wall constituted by well-ordered platelet particles. The samples sintered at 1100 °C and 1200 °C have bulk density of 0.207±0.009 cm3/g and 0.225±0.011 cm3/g, respectively.

Table 1: Compositions of raw diatomite powder employed in the present work.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>Na2O</th>
<th>K2O</th>
<th>CaO</th>
<th>MgO</th>
<th>Ti2O</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>96.31</td>
<td>1.63</td>
<td>0.55</td>
<td>0.52</td>
<td>0.32</td>
<td>0.22</td>
<td>0.17</td>
<td>0.09</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**Fig. 2:** a) Photo of ultra-stable foams stabilized by complete diatomite particles prepared at different pH values taken a week after frothing, b) photo of wet foams prepared at pH of 9.5 taken instantly just after demoulding, c) dried diatomite foam bodies prepared at different pH values (0.2 wt% CTAB), d) and e) show the schematic diagram of foams stabilized by intact diatomite particles.
The obtained diatomite ceramic foams exhibit four kinds of multilevel pores as can be seen from Fig. 3b-d. The first level pores are macropores with size around 100 μm evolved from the bubbles of wet foams. The second level pores are interval between disk-like diatomite particles with size of several micrometers. The third level pores are inherent straight pores of diatomite in submicron scale, which are perpendicular to the diatomite plain. The fourth level pores are mesoporous pores also derived from the diatomite itself, which is confirmed by the hysteresis loop in the adsorption-desorption isotherm shown in Fig. 4a. The foams sintered at 1200 °C possess surface area of 5.20 m²/g, and average pore size of 2.4 nm (Fig. 4b). Generally, particle-stabilized ceramic foams from near sphere shape powder feature mostly closed pores and inferior permeability due to the compact self-assembly of particles at the bubble interfaces 8–11, 20, 21. In contrast, this approach endows ceramic foams relatively high permeability due to the interparticle pores and the inherent pores of diatomite fossilized skeleton, which may have potential application in the fields of filtration of fine particulate matter and adsorption of dye molecules.

IV. Conclusions

Intact platelet diatomite particles with particle diameter of 10–50 μm were used to study the foam stability via direct foaming method. 0.2 wt% CTAB was employed to modify diatomite particle surface in a wide pH range of 4.0–12.0. The platelet diatomite particles adsorbed paral-
lelly to the air/liquid interfaces and form stable network throughout the foams, thus endowing the ultra-stability of foamed diatomite suspension. It was demonstrated for the first time that it was feasible to prepare stable foams using large particles with diameter of dozens of microns as stabilizer, which bring new insights into the preparation of stable foams when involving particle size and shape. Based on the stable foams, light weight and hierarchical diatomite ceramic foams with uniform macropores and multilevel pores were further prepared, which exhibit bulk density of 0.225 cm$^3$/g and surface area of 5.20 m$^2$/g. This new fabrication approach offer some advantages, such as straight and eco-friendly processing route, free of ball milling for smashing, no need for the addition of organic or inorganic binders due to the excellent foam stability.

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References
