Successful preparation of self-setting particle-stabilized zeolite 13X foams

Jang-Hoon HA,1 Da-Woon JUNG, Rizwan AHMAD and In-Hyuck SONG

Powder and Ceramics Division, Korea Institute of Materials Science, 797 Changwondaero, Seongsan-gu, Changwon, Gyeongnam 642–831, Republic of Korea

Zeolites are commonly used as adsorbents for a wide range of industrial applications. Recently, to alleviate the pressure drop and mass-transfer problems when zeolites are used as pellets in a packed bed system, the need for a self-standing zeolite foam has grown. Therefore, in this study, a zeolite 13X wet foam was stabilized by zeolite 13X particles that were rendered partially hydrophobic by propyl gallate, mixed with a commercial calcium aluminate cement, and then self-set. A self-setting particle-stabilized zeolite 13X foam contains primary macropores with a size range of approximately 200 to 400 μm formed by zeolite 13X particles that are irreversibly adsorbed at liquid–gas interfaces as well as secondary inherent micropores. In addition, we investigated the pore characteristics of the self-setting particle-stabilized zeolite 13X foams by scanning electron microscopy, mercury porosimetry, physisorption analysis, and capillary flow porosimetry.

Key-words : Self-setting, Particle-stabilized foams, Permeability, Zeolite 13X

1. Introduction

Zeolites are microporous and aluminosilicate minerals commonly used as adsorbents for industrial applications. Zeolites are conventionally used in the form of beads, extruded pellets, or granules in a packed bed system. The inherent drawbacks of a packed bed system, such as limited heat and mass transfers, high pressure drops, and unevenly distributed flows, hinder efficient operations in industrial applications.1–4 Accordingly, a challenging area in the applications of zeolite is how to consolidate these minerals as a self-standing zeolite foam that retains its unique and inherent micropores, while having an appropriate permeability and rigidity.

To fabricate a self-standing zeolite foam, in this study, a particle-stabilized direct foaming method is newly adopted to zeolite. Unlike a conventional zeolite coating on a separate support, a particle-stabilized zeolite foam consists of strut walls of thin zeolite layers; gas or liquid can freely move inside the zeolite foam through highly inter-connected macropores.

Although numerous studies of particle-stabilized direct foaming methods have been reported,5–12 the previous works have focused on particle-stabilized ceramic foams prepared by conventional sintering processes. However, because the micropores of zeolite cannot withstand conventional sintering temperatures,13 it is not possible to simply adopt a conventional sintering process to a particle-stabilized zeolite foam to obtain a self-standing zeolite foam. Accordingly, a particle-stabilized zeolite foam needs to be self-set. As far as we know, no group has studied a self-setting particle-stabilized zeolite foam, though several recent reports show the possibility of a self-setting particle-stabilized direct foaming method using calcium aluminate cement.14–16

In this study, we used a commercial calcium aluminate cement as a reactive phase to consolidate a particle-stabilized zeolite wet foam to eliminate the need for a sintering process. Incidentally, we did not consider adding zeolite to an autoclaved aerated concrete (AAC) foam. Instead, we added calcium aluminate cement to a particle-stabilized zeolite foam because a conventional AAC foam shows negligible permeability due to the concrete’s closed pore structure17 and the necessity of a high-pressure autoclave process.

A self-setting particle-stabilized zeolite foam would potentially contain primary macropores formed by zeolite particles that are irreversibly adsorbed at liquid–gas interfaces as well as secondary pores induced by the material’s inherent micropores. Furthermore, foaming by a particle-stabilized method and self-setting by calcium aluminate cement would provide an easy, inexpensive, and fast approach to fabricate highly porous zeolite foam with a bimodal pore structure. Because drying and sintering processes are usually accompanied by shrinkage that might cause cracks and defects, a self-setting particle-stabilized direct foaming method can avoid shrinkage, bypass delicate and costly drying and sintering processes, and widen the application range.

The aim of this paper is to clarify whether zeolite (in this study, zeolite 13X was used as a model zeolite material) with a bimodal pore structure can be foamed by a particle-stabilized method and can be set with the aid of a calcium aluminate cement to a self-standing foam without a conventional sintering process. To find out whether the micropores of zeolite were filled and covered with commercial calcium aluminate cement powder during hydration process, the pore diameter and the BET surface area were measured. Additionally, for comparison with self-setting particle-stabilized zeolite foams, conventionally sintered particle-stabilized zirconia foams were also prepared.

2. Material and methods

Zeolite 13X (Molecular sieve 13X, Sigma-Aldrich, U.S.A.) was used as a model zeolite material for the preparation of particle-stabilized zeolite wet foams. In 20 g of the zeolite 13X batch, 40 mL of distilled water, 0.6 g of propyl gallate [3,4,5-(HO)C₆H₅CO₂CH₂CH₂CH₃, 98% pure, Sigma-Aldrich, U.S.A.], and 20 g of commercial calcium aluminate cement (KS L 5201

1) Corresponding author: J.-H. Ha; E-mail: hjhoon@kims.re.kr

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standard, Tongyang cement, Korea) were added. Optionally, 1 g of lithium carbonate (99% pure, Sigma-Aldrich, U.S.A.) was added. Foaming was performed out by using a direct driven motor at a speed of 1000 rpm, and the slurry was poured into a Perspex mold for 168 h at room temperature for self-setting.

For comparison, conventionally sintered particle-stabilized zirconia foams were prepared. ZrO_2 powder (3 mol.% Yttria stabilized ZrO_2, Heshan Huawang Zirconium Materials Co. Ltd., China) was used. Valeric acid (C_5H_10O_2, 99% pure, Sigma-Aldrich, U.S.A.) was used as an amphiphile and distilled water was used as a solvent. The particle-stabilized zirconia foams were sintered at 1500°C for 2 h. More detailed experimental procedures were described in our previous report.18)

The pore characteristics of the particle-stabilized zeolite 13X and zirconia foams were investigated by scanning electron micrography (JSM-5800, JEOL, Japan), mercury porosimetry (Autopore IV 9510, Micromeritics, U.S.A.), and capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., U.S.A.). The compressive strengths were measured by a uni-axial mechanical tester (Instron 4206, Instron, U.S.A.) with 10 mm × 10 mm × 10 mm specimen dimensions, and a crosshead speed of 0.5 mm/s.

3. Results and discussion

A self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate after 168 h of self-setting time, and the Perspex mold that was used are shown side by side in Fig. 1. Although we used a 5-cm diameter Perspex mold, the shape and size of the specimen has no limitation due to its self-setting ability. Note that only the outermost surfaces of the specimen have irregular and mm-size pores due to the contact of the Perspex mold during the self-setting process.

Typical scanning electron microscope (SEM) images of the self-setting particle-stabilized zeolite 13X foam with no added lithium carbonate after 168 h of self-setting time are shown in Figs. 2(a)–2(c). It was found that the self-setting particle-stabilized zeolite 13X foam contained primary macropores with a size range of approximately 200 to 400 μm formed by the zeolite 13X particles that were irreversibly adsorbed at liquid–gas interfaces. The macropores were highly inter-connected with neighbor macropores through voids within strut walls, as shown in Fig. 2(a). Additionally, a needle-like ettringite phase is formed as a result of the reaction of calcium aluminate with calcium sulfate that commonly present in the microstructure of hardened calcium alumina cement as seen in Figs. 2(b) and 2(c). As it is shown in Figs. 2(a)–2(c), the macropores are highly inter-connected with neighbor macropores through voids within strut walls. The morphology of the self-setting particle-stabilized zeolite 13X foam with no added lithium carbonate after 168 h of self-setting time is shown in Figs. 2(a)–2(c). The macropores are highly inter-connected with neighbor macropores through voids within strut walls, as shown in Fig. 2(a). Additionally, a needle-like ettringite phase is formed as a result of the reaction of calcium aluminate with calcium sulfate that commonly present in the microstructure of hardened calcium alumina cement as seen in Figs. 2(b) and 2(c). As it is shown in Figs. 2(a)–2(c), the macropores are highly inter-connected with neighbor macropores through voids within strut walls. The morphology of the self-setting particle-stabilized zeolite 13X foam with no added lithium carbonate after 168 h of self-setting time is shown in Figs. 2(a)–2(c).
well known that ettringite does not contribute to strength\textsuperscript{19} and noting the detrimental effect of voids within strut walls to strength, the particle-stabilized zeolite 13X foam with no added lithium carbonate was not expected to have an appropriate compressive strength. Therefore, to accelerate the hydration process of the calcium aluminate cement, lithium carbonate was added.\textsuperscript{14} We expected that the crystallization of ettringite could be inhibited by accelerating the hydration process.

Typical SEM images of a self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate after 168 h of self-setting time are shown in Figs. 3(a)–3(c). With an addition of 5 wt.% of lithium carbonate, it was found that the self-setting particle-stabilized zeolite 13X foam contained primary macro-pores with a size of approximately 200 to 400 \( \mu \)m just as in the particle-stabilized zeolite 13X foam with no added lithium carbonate. However, the microstructure of the self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate shows few voids inside the strut walls and ettringite needles among the zeolite 13X particles. The generated ettringite phase may have been decomposed in hydration process was decomposed in the presence of lithium carbonate, similar to the case of barium carbonate.\textsuperscript{20} In addition, the microstructures of the
closed-pore structure of the conventionally sintered particle-stabilized zirconia foam were well described in our previous report.\textsuperscript{(16)}

Figure 4(a) shows the pore size distributions of the self-setting particle-stabilized zeolite 13X foam with/without lithium carbonate and of the sintered particle-stabilized zirconia foam. The self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate shows a peak at approximately 1–10μm and another peak at approximately 10–50μm. The former corresponds to inter-particle voids between the zeolite 13X particles, whereas the latter corresponds to the voids inside the strut walls, throats or entrance openings of spherical macropores, as mercury enters the macropores at a pressure determined by the entrance size rather than the actual spherical pore size.\textsuperscript{(21)} When lithium carbonate was added, the peak at approximately 10–50μm that was found in the self-setting particle-stabilized zeolite 13X foam disappeared, which is agreement with the SEM microstructure as previously shown in Fig. 3(a). To indirectly compare the conventional sintering process and the self-setting process, the particle-stabilized zirconia foam sintered at 1500°C for 2 h is also shown; this foam had a peak at approximately 0.1–1μm due to the size difference of starting powder between zirconia and zeolite 13X and the pore shrinkage induced by the high-temperature sintering process.

In general, the compressive strength and permeability have a trade-off relationship in porous ceramics, e.g., the addition of kaolin into a diatomite support.\textsuperscript{(22)} Therefore this process would not be acceptable for industrial applications, even though we could obtain a self-setting particle-stabilized zeolite 13X foam as a rigid monolith, if the permeability is severely degraded. Figure 4(b) shows the compressive strength and permeability of the self-setting particle-stabilized zeolite 13X foam with/without lithium carbonate and of the particle-stabilized zirconia foam. The compressive strength of self-setting particle-stabilized zeolite 13X foam significantly increased with the addition of lithium carbonate at the expense of slightly decreased permeability. In contrast to the negligible permeability of the particle-stabilized zirconia foam (0.46 liter/min/cm\(^2\) at 175 kPa), which has a closed-pore structure, the self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate which has an interconnected pore structure, has an appropriate permeability (9.08 liter/min/cm\(^2\) at 175 kPa) compared to the ceramic membranes for microfiltration such as the sintered diatomite membranes (1.45–2.80 liter/min/cm\(^2\) at 175 kPa),\textsuperscript{(23)} the sintered diatomite-kaolin composite membranes (1.13–2.87 liter/min/cm\(^2\) at 175 kPa),\textsuperscript{(24)} and the sintered particle-stabilized diatomite foam (3.70–7.29 liter/min/cm\(^2\) at 60 kPa).\textsuperscript{(25)}

As we added 50 wt.% of commercial calcium aluminate cement to the particle-stabilized zeolite 13X foam to give a self-setting ability, the micropores of self-setting particle-stabilized zeolite 13X foam could be partially filled or covered with hydration reaction products. Therefore, the pore volume of a self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate, as-received zeolite 13X powder and as-received calcium aluminate cement powder were measured. In Figs. 4(c) and 4(d), it was found that the micropores of the self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate in the range of 1–10 nm follow the rule of mixture of zeolite 13X and calcium aluminate cement with no further pore blocking of micropores by hydration reaction products.

In the literature, self-standing zeolite monoliths such as faujasite zeolite (63.31 m\(^2\)/g and 19.6 MPa),\textsuperscript{(26)} NaY (97.81 m\(^2\)/g and 57.00 MPa),\textsuperscript{(27)} and Zeolite A (30 m\(^2\)/g and 0.7 MPa)\textsuperscript{(28)} showed reduced BET surface areas, although the compressive strengths of these monoliths were significantly enhanced. Therefore, it is noteworthy that a self-setting particle stabilized zeolite 13X foam with 5 wt.% of lithium carbonate, which was prepared in this study, maintains its BET surface area (359.55 m\(^2\)/g), following the rule of mixture with calcium aluminate cement, and has an acceptable compressive strength under non-load-bearing conditions (1.80 MPa).

4. Conclusions

In summary, a self-setting particle-stabilized zeolite 13X foam with 5 wt.% of lithium carbonate would contain primary macropores formed by zeolite 13X particles that were irreversibly adsorbed at liquid–gas interfaces as well as secondary inherent micropores. In addition, the permeability was enhanced to the level of the typical ceramic membranes due to the highly interconnected primary macropores. Therefore, the combination of the particle-stabilized direct foaming method and the self-setting method by calcium aluminate cement and lithium carbonate would provide an easy, inexpensive, and fast approach to fabricate a highly porous zeolite foam with a bimodal pore structure. Furthermore a self-setting particle-stabilized zeolite 13X foam can be prepared without cracks and defects induced by a delicate and costly sintering process and can be free of shape and size limitations. These findings show the feasibility of using a self-setting particle-stabilized zeolite 13X foam in industrial applications.

Acknowledgments This study was supported financially by Fundamental Research Program of the Korean Institute of Materials Science (KIMS).

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