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Short communication

Synthesis of crystalline zeolite-13X from waste porcelain using alkali fusion

Takaaki Wajima [a,*], Yasuyuki Ikegami [b]

[a] Faculty of Engineering and Resource Science, Akita University, 1-1, Tegata-gakuen-cho, Akita 010-8502, Japan
[b] Institute of Ocean Energy, Saga University, 1-48, Kubara, Yamashiro-cho, Imari, Saga 849-4256, Japan

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Abstract

We attempted to convert waste porcelain into crystalline zeolite-13X using the alkali fusion method. Waste porcelain is mainly composed of amorphous glass phase and crystalline phases such as quartz and mullite. Most of the amorphous and crystalline phases were converted into soluble phases by alkali fusion, and could be transformed into single zeolite-13X crystals with a high specific surface area (412 m^2/g) and unique micropore diameter (13 Å).

Keywords: A. Sol–gel processes; B. X-ray methods; D. Clays; E. Waste porcelain; Zeolites

1. Introduction

Zeolites are a group of more than 40 crystalline hydrated aluminosilicate minerals. Their structure is based on a three-dimensional network of an aluminum and silicon tetrahedral linked by shared oxygen atoms. Due to specific pore sizes and large surface areas, zeolites can be used in various applications, e.g., molecular sieves, adsorbents, catalysts [1]. Several researchers reported the synthesis of zeolites from a wide variety of starting materials containing high amounts of Si and Al, e.g., kaolin, high-silica bauxite, halloysite, interstratified illite-smectite, montmorillonite, bentonite, incinerated ash [2–9].

Unsold fired products from the ceramic industry are discharged as waste ceramics. Some are used as artificial aggregates, for cement production, or for other minor applications [10]. The remaining waste ceramics are deposited in landfill sites, and the limited capacity of landfill sites causes social and environmental problems.

In our previous study, we converted waste porcelain into zeolitic materials using a two-step alkali conversion at a low temperature (80 °C). Zeolitic material with high cation exchange capacity (ca. 170 cmol/kg) could be synthesized from waste porcelain using an alkali reaction as the first step. The waste solution with a high content of Si could be converted into pure zeolite crystals (e.g., zeolite-A, zeolite-X, and zeolite-P) by addition of aluminate solution in the second step. Only the amorphous glass phase is used to synthesize the zeolite phases, and almost all Si and Al content in the crystalline phases remains in the product and is not used in zeolite synthesis. The two-step process is complex. We now proposed effective and simple method.

We aimed to convert waste porcelain into crystalline zeolite-13X using a one-step process with the alkali fusion method. The amorphous and crystalline phases in the waste were first converted into soluble phases by alkali fusion, and were then used to synthesize single zeolite-13X crystals.

2. Experimental

2.1. Materials

Waste porcelain was ground with a mill. Particles of size <1 mm were sorted and washed with distilled water. Porcelain comprised SiO_2 and Al_2O_3, corresponding to 69.8 wt.% and 18.5 wt.%, respectively, with rest amount of Na_2O, K_2O, MgO, CaO, Fe_2O_3, and ZnO. This is the same material as was used by Wajima and Ikegami [11].

* Corresponding author. Tel.: +81 18 889 2755; fax: +81 18 889 2755.
E-mail address: wajima@gipc.akita-u.ac.jp (T. Wajima).

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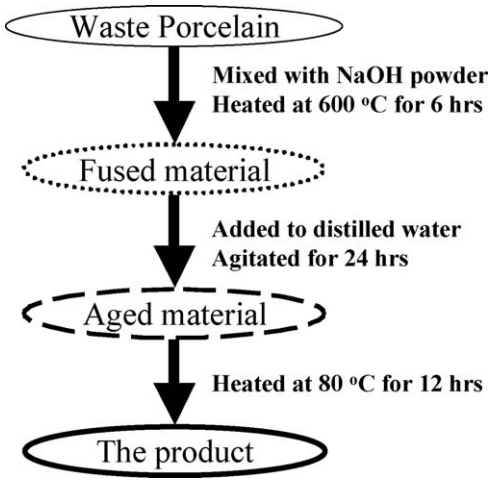

Fig. 1. Zeolite synthesis (schematic).

2.2. Zeolite synthesis

Zeolite synthesis was carried out as shown in Fig. 1. Ten grams of powdered waste porcelain was mixed with 12 g of NaOH powder. It was ground to obtain a homogeneous mixture. This mixture was heated in a nickel crucible in air at 600 °C for 6 h. The resultant material was cooled to room temperature and

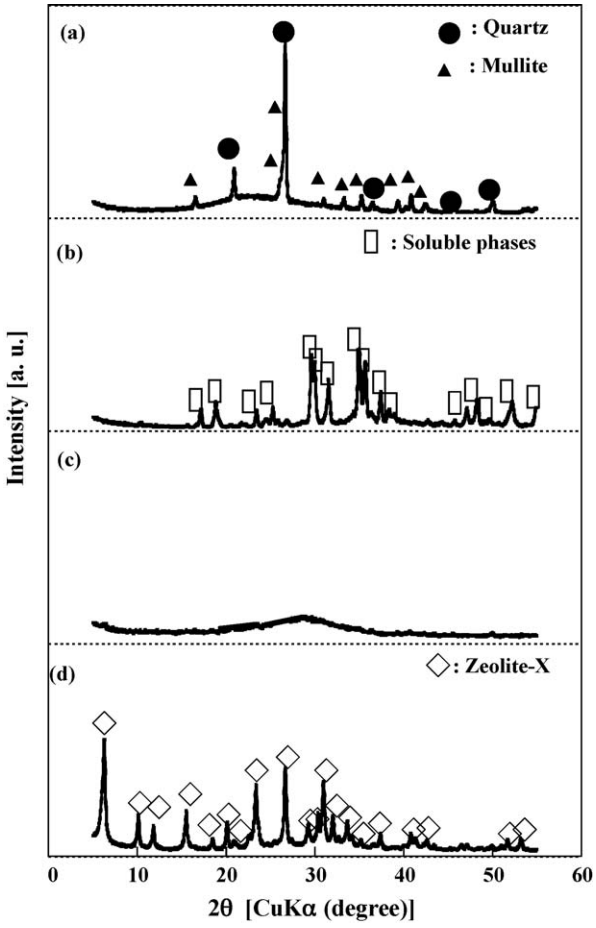

Fig. 2. X-ray diffraction patterns of (a) raw material, (b) fused material, (c) aged material, and (d) product.

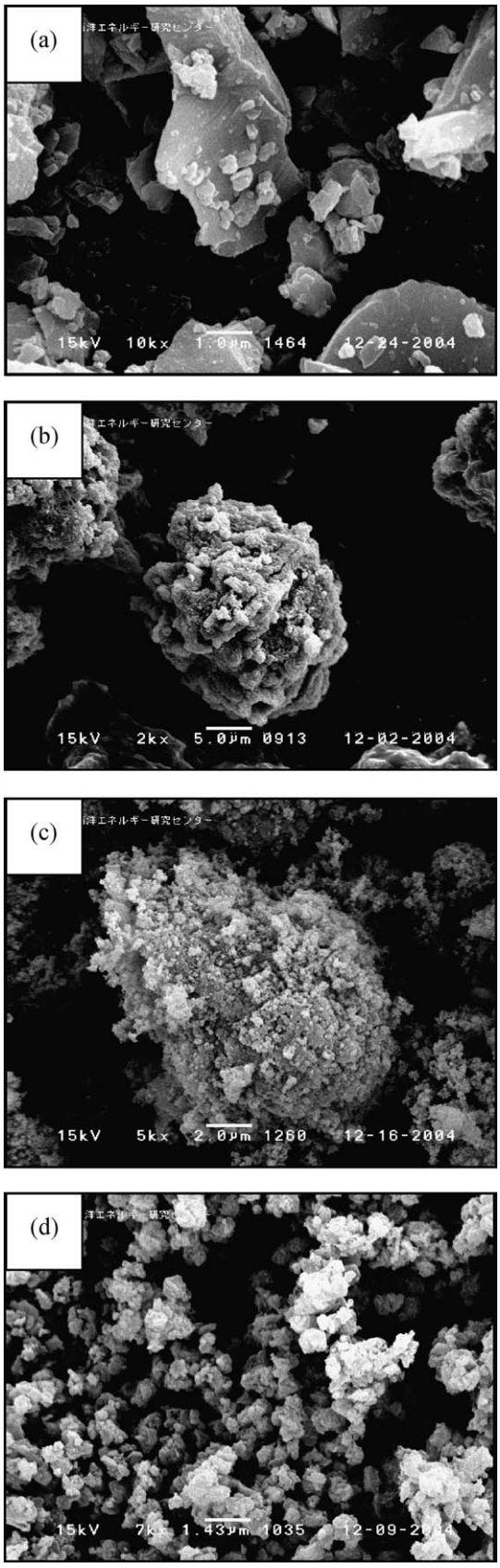

Fig. 3. Scanning electron microscopy images of (a) raw material, (b) fused material, (c) aged material, and (d) product.

Table 1
Specific surface areas of raw material, aged material and product.

Specific surface area [m^2/g]	
Raw material	0.6
Aged material	36.3
The product	412.0

ground again to obtain fused material. Fused material (0.5 g) was added to 2 mL of distilled water in a 10-mL tube made of polymethylpentene. This was followed by an aging process with vigorous agitation by a reciprocal shaker at room temperature to obtain aged material. After agitation for 24 h, the aged material was heated in a water bath at 80 °C for 12 h to obtain the product. The aged material and product were filtered, washed with distilled water, and dried in a drying oven at 60 °C overnight.

Characterization of raw material, fused material, aged material and product was by X-ray powder diffractometry (XRD) (XRD-DSC-XII, Rigaku, Japan) and scanning electron microscopy (SEM) (SM-200, Topcon, Japan). The specific surface area and distribution of pore sizes of raw material, aged material and product were measured by an nitrogen adsorption method (BET) using Sorpmatic (Thermoquest, USA) at 77 K.

3. Results and discussion

Fig. 2 shows the XRD patterns obtained for (a) raw material, (b) fused material, (c) aged material, and (d) product. The raw material (waste porcelain) comprised an amorphous glass phase, and crystalline phases such as quartz and mullite (Fig. 2(a)). After fusion, most of the phases in the raw material were initially converted into soluble sodium silicate and sodium aluminate (Fig. 2(b)) and then converted to amorphous material with the remaining crystalline phases through agitation for 24 h (Fig. 2(c)). Zeolite-13X phase was detected in the product (Fig. 2(d)).

Fig. 3 shows the SEM micrographs obtained for (a) raw material, (b) fused material, (c) aged material, and (d) product. The raw material was fragments of porcelain (Fig. 3(a)). The fused material was a large particle with a melting surface resulting from the formation of sodium silicate and aluminate by the alkali fusion method (Fig. 3(b)). After agitation, the aged material looked like a gel-like particle with an amorphous phase (Fig. 3(c)), whereas the final product was an octahedral crystallites (zeolite-X) (Fig. 3(d)).

Table 1 shows the specific surface area of raw material, aged material and product. Fig. 4 shows determination of the distribution of pore sizes for (a) raw material, (b) aged material and (c) product. The area of raw material was only 0.6 m^2/g because waste porcelain has little pore volume, but the area of aged material was 36.3 m^2/g due to the creation of an amorphous gel aggregate with a macropore. The final product had a high specific surface area (412 m^2/g), almost 700-times higher than that of raw material. The pore of the product had a diameter of 13 Å caused by zeolite-13X crystals.

It can be considered that waste porcelain was first converted into soluble material by alkali fusion, then transformed into an amorphous gel and finally zeolite-13X crystals can be synthesized from this gel.

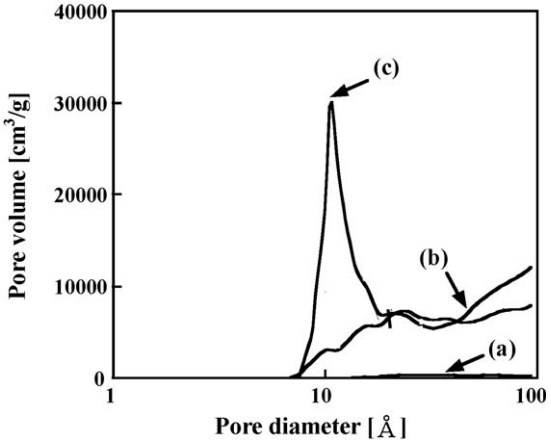

Fig. 4. Distribution of pore sizes for (a) raw material, (b) aged material, and (c) product.

4. Conclusions

We attempted to convert waste porcelain into crystalline zeolite-13X at 80 °C using alkali fusion. They had a unique pore size (13 Å) and high specific surface area (412 m^2/g). The synthesized product was a highly valued zeolite that could be used as a molecular sieve or adsorbent.

Acknowledgments

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References

[1] R.M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London, 1978.
[2] R.M. Barrer, R. Beaumont, C. Colella, Chemistry of soil minerals. Part XIV. Action of some basic solution on metakaolinite and kaolinite, Journal of the Chemical Society, Dalton Transaction (1974) 934–941.
[3] R. Ruiz, C. Banco, C. Pesquera, F. Gonzalez, I. Benito, J.L. Lopez, Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water, Applied Clay Science 12 (1997) 73–83.
[4] A. Baccouche, E. Srasra, M.E. Maaoui, Preparation of Na–P1 and sodalite octahydrate zeolites from interstratified illite-smectite, Applied Clay Science 13 (1998) 255–273.
[5] A.F. Gualtieri, Synthesis of sodium zeolites from a natural halloysite, Physics and Chemistry of Minerals 28 (2001) 719–728.
[6] D. Boukadir, N. Bettahar, Z. Derriche, Synthesis of zeolites 4A and HS from natural materials, Annual de Chimie Science des Materiaux 27 (2002) 1–13.
[7] X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, Synthesis of zeolites from coal fly ash: an overview, International Journal of Coal Geology 50 (2000) 413–423.
[8] G.C.C. Yang, T.-Y. Yang, Synthesis of zeolites from municipal incinerator fly ash, Journal of Hazardous Materials 62 (1998) 75–89.

[9] T. Wajima, K. Kuzawa, H. Ishimoto, O. Tamada, T. Nishiyama, The synthesis of zeolite-P, Linde type A, and hydroxysodalite zeolites from paper sludge ash at low temperature (80 °C): optimal ash-leaching condition for zeolite synthesis, American Mineralogist 89 (2004) 1694–1700.

[10] N. Ay, M. Űnal, The use of waste ceramic tile in cement production, Cement and Concrete Research 30 (2000) 497–499.

[11] T. Wajima, Y. Ikegami, Synthesis of zeolitic materials from waste porcelain at low temperature via two-step alkali conversion, Ceramics International 33 (2007) 1269–1274.