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Ceramics International 38 (2012) 2153–2157

CERAMICS INTERNATIONAL

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Preparation of porous material from waste bottle glass by hydrothermal treatment

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Received 18 August 2011; received in revised form 20 October 2011; accepted 21 October 2011
Available online 25 October 2011

Abstract

Porous materials were prepared from colored waste glass by hydrothermal treatment with Na_2CO_3 aqueous solution. The resultant specific surface area was approximately 140 m^2/g at maximum. Specific surface area increased at first, reached a maximum, and decreased gradually to be constant at approximately 60 m^2/g depending on the period of hydrothermal treatment, irrespective of the concentration of Na_2CO_3 aqueous solution. However, the period at which the specific surface area reached maximum shortened with an increase in Na_2CO_3 concentration. On the other hand, the mass of the sample decreased and eventually saturated at approximately 30 mass% of the initial weight during the hydrothermal treatment. Both the dissolution of the mother glass and the formation of crystalline deposits, which were identified as calcite, zeolite-P and analcime, affected the porous structure of the treated samples.

Keywords: B. Porosity; B. Composites; D. Glass; E. Functional applications; Hydrothermal treatment

1. Introduction

Colored waste glass, especially that from bottles used for alcohol, such as wine, brandy and whiskey, are available in large quantity. This glass is difficult to reuse because of its many colors, for instance, brown, green, red, and blue, and thus is mixed as crushed waste glass. Such mixed colored glass cannot be remelted or reshaped for use in new bottles because the colors cannot be separated. Part of the crushed waste glass has been applied as a filler of asphalt cement for scattering decoration [1,2]. However, the limit of substitution in asphalt cement is approximately 10% to cause no problems because the fractured surface of glass is inactive for coalescence with asphalt. Another application of waste glass is as an agent for liquid sintering and ceramic glazing [3,4].

Foamed porous glass is a great candidate for the reutilization of colored waste glass. Actually, foamed porous glass is already available on the market. Foamed porous glass is prepared by mixing glass with foaming agents, e.g., $CaCO_3$, AlN, SiC, cellulose, and H_2O, and heating the mixture at 700–1000 °C [5–9]. Foamed porous glass is a very useful material because of its large porosity and permeability. However, its specific surface area is small owing to the large bubbles. In addition, its cost of production is relatively high because a high temperature is necessary for foaming. Another candidate is porous glass prepared by selective leaching [10–12]. Generally, a glassy phase shows metastable or stable immiscible phenomena. Raw materials and complemental components for the control of chemical composition are mixed and then heated at arbitrary temperature to generate a phase separation texture. Then, an unwanted phase is leached to form pores. This technique can be used to control pore size; however, the heat treatment at a high temperature poses a high cost in the preparation.

We focus on hydrothermal treatment, which is very useful as a low-energy process because of its use of an aquatic solvent and a low temperature. Silicate glass including bottle waste glass may be corroded by alkali salt aqueous solutions. Chen et al. reported that an alkali salt aqueous solution dissolves

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.057

$Na_2O{\cdot}CaO{\cdot}nSiO_2$ glass at 150 °C [13]. We therefore examine the formation of porous glass with a high surface area by the hydrothermal treatment of waste glass in this study.

2. Experimental

Crushed waste glass was first sieved through a 125 μm steel mesh. The sieved glass 125 μm in size was used as the starting material. An arbitrary mass (0.6 g) of the starting waste glass was placed in 60 mL of sodium carbonate aqueous solution with a concentration of 0.1, 0.2, 0.5, 1.0 or 2.0 mol/L in a Teflon-lined thermally durable vessel. The sample was hydrothermally treated for 6 to 504 h at 150 °C. Then, the products were filtered and washed with distilled water, and dried at 50 °C. The samples before and after hydrothermal treatment were weighed. The waste aqueous solution must not contain colorants (generally Ti, Cr, Mn, Co, Cu, etc.) because general colorants are stable in the basic solution used. The waste solutions in this study were treated as inorganic aqueous solutions containing some transition-metal cations.

Crystalline or glassy phases in the products were identified using XRD patterns with monochromated CuKα radiation (RINT-2000, Rigaku). The porous properties of the products were calculated from N_2 gas adsorption isotherms measured using a microporosimeter at 77 K (Belsorp-mini, Nippon BEL). The products were observed by FE-SEM (JSM-6500F, JEOL) and the chemical composition of the products was determined by EDX analysis.

3. Results and discussion

3.1. Preparation of porous material from glass waste

To examine a suitable amount of waste glass for one batch, glass samples with different masses, i.e., 0.6, 1.2, 1.8, 2.4 and 3.0 g, were hydrothermally treated in 60 mL of 1.0 mol/L Na_2CO_3 aqueous solution. Fig. 1 shows the N_2 isotherms at 77 K of the untreated and hydrothermally treated waste glass. For the isotherm of the untreated waste glass, the adsorption volume of N_2 is quite low. On the other hand, for the treated waste glass, the adsorbed volume apparently diminished depending on the waste glass load. Such changes in the amount of the adsorbed N_2 apparently result from the formation of porous phase. The specific surface area calculated from the isotherms is maximum (approx. 96 m^2/g) at 0.6 g of waste glass load, and clearly decreases with an increase in waste glass load. Such a tendency probably indicates an incomplete reaction when a large amount of waste glass is present. The tendency will be investigated in detail in the next section.

Fig. 2 shows the dependence of specific surface area on the hydrothermal treatment period with different concentrations of Na_2CO_3 aqueous solution. From these plots, the maximum surface area reaches to approximately 140 m^2/g, decreases and eventually becomes approximately 60 m^2/g. The general trend is longer than the period at which surface area becomes maximum with a lower Na_2CO_3 concentration. Since the relationship between the concentration and the period seems to be reversely proportional, the mechanism of pore formation that will be considered in the next section does not change irrespective of the concentration of Na_2CO_3 aqueous solution. The reason for such a tendency is possibly the dependencies of dissolution rate and deposition time on Na_2CO_3 concentration. That is, a high Na_2CO_3 concentration results in a high dissolution rate. The decrease in specific surface area seems to be collateral evidence of deposition within pores. Fig. 3 shows the dependence of mass loss on hydrothermal period. All the samples show similar tendencies; mass loss steeply increases up to approximately 70 mass%. In other words, the fraction of 30 mass% in the initial mass remained in the samples. However, the rate of the mass reduction is faster with higher Na_2CO_3 concentration. The consequent mass loss of approximately 70 mass% was possibly determined by the balance between the deposits of other phases and the amount of partial leaching. Since the deposition seems to generate mainly within pores, as mentioned above, the dissolution can be stopped by

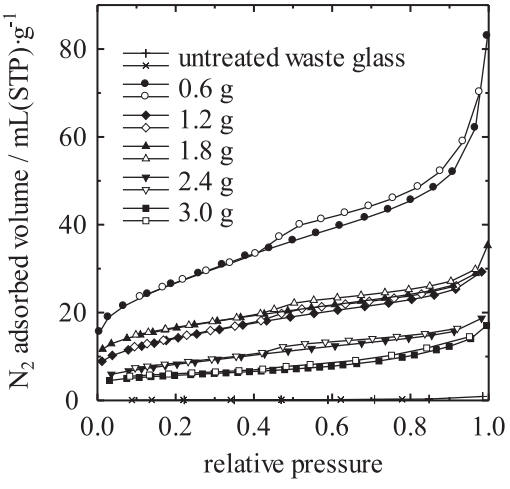

Fig. 1. N2 adsorption and desorption isotherms of hydrothermally treated waste glass with different loads, 0.6, 1.2, 1.8, 2.4 and 3.0 g.

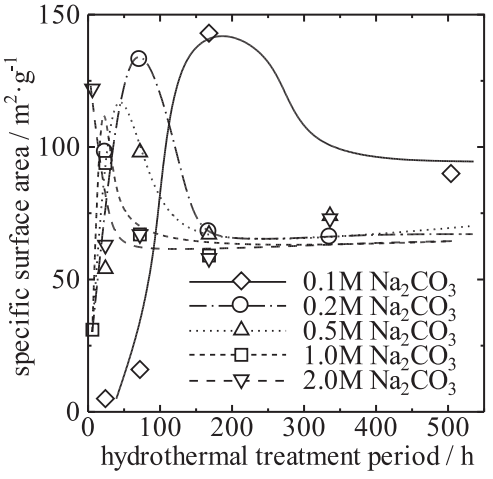

Fig. 2. Dependence of specific surface area of samples treated in Na_2CO_3 aqueous solution of different concentrations, 0.1, 0.2, 0.5, 1.0 and 2.0 mol/L, on hydrothermal treatment period.

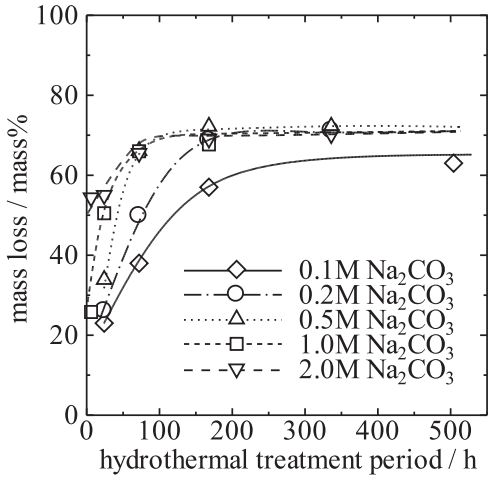

Fig. 3. Dependence of mass loss of samples treated in Na_2CO_3 aqueous solution of different concentrations, 0.1, 0.2, 0.5, 1.0 and 2.0 mol/L, on the hydrothermal treatment period.

the generation of deposits. Therefore, a decrease to approximately 70% irrespective of Na_2CO_3 concentration may be determined by stopping the dissolution by generating deposits. The period at which the surface area is maximum comes during the increase in mass loss; for example, surface area is maximized by hydrothermal treatment for 72 h, and mass loss becomes constant at a period of more than 168 h of hydrothermal treatment.

Fig. 4 shows the XRD patterns of the porous materials prepared from waste glass by hydrothermal treatment in 0.2 mol/L Na_2CO_3 aqueous solution. The XRD patterns confirm that $CaCO_3$ (calcite) and $Na_{3.6}Al_{3.6}Si_{12.4}O_{32}{\cdot}14H_2O$ (zeolite P) phases were formed by treatment for longer than 72 h. Such a formation phase indicates that the dissolved components are Ca and Si because the deposits formed by the

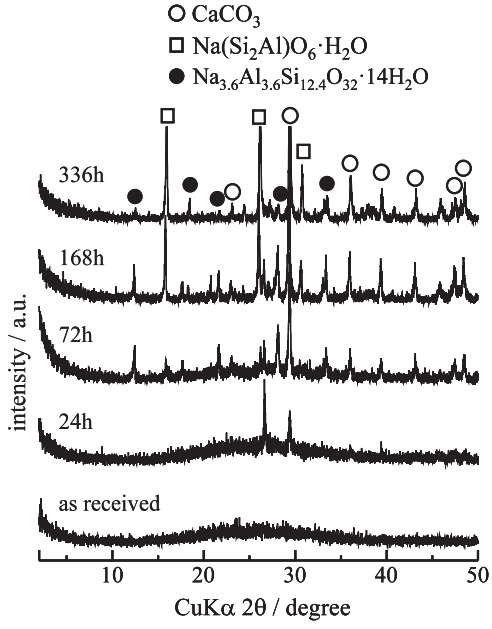

Fig. 4. XRD patterns of the samples treated for different periods, 24, 72, 168 and 336 h with 0.2 mol/L Na_2CO_3 aqueous solution.

dissolution of the glass and the reprecipitation of these phases. In addition, $NaSi_2AlO_3{\cdot}H_2O$ (analcime) crystallized at 168 h. Zeolite-P is generally formed as a precursor of the analcime phase [14]. The precipitated phases, i.e., zeolite P and analcime, are zeolite minerals; generally, zeolite has intrinsic pores in its crystalline structure. However, Intaraprasit and Kongkachuichay and Du et al. reported that the specific surface area of zeolite P and analcime are several tens m^2/g [15,16]. Actually, the crystal structures of zeolite P and analcime apparently have no pores several nanometers in radius. Thus, these phases contribute little to the surface area because intrinsic pores cannot be measured using N_2 molecules. These results imply that pores form by leaching in the glassy phase rather than in zeolitic structures in our samples.

Fig. 5 (a), (b) and (c) respectively show FE-SEM micrographs of the waste glass (a) and samples hydrothermally treated for 72 h with 0.2 mol/L Na_2CO_3 aqueous solution (b) and (c), where (c) shows an expanded image of the surface of the treated samples. For the waste glass, a very smooth surface is observed. In the photograph of the hydrothermally treated sample, some deposits are observed, which may be calcite, analcime or zeolite-P. In the expanded image (c), many pores are observed several nanometers in size on the surface of the sample. In the micrograph (c), the chemical composition was measured by EDX analysis. No significant change in the composition was observed. However, a very small compositional or density fluctuation, which cannot be detected clearly by EDX, may exist and a more undurable phase may dissolve possibly dissolved to form pore structures.

3.2. Mechanism of formation of porous structures in the waste glass

The mechanism of the formation of porous structures is investigated from the point of view of the mass and time dependencies to obtain information on the optimum size of waste glass and to determine the optimum treatment period and concentration of the solution. As mentioned in the previous section, calcite, zeolite-P and analcime do not contribute to the increase in the number of pores, although the leached part of waste glass can form pores.

We first investigate the mass-dependent mechanism underlying the formation of porous materials. Fig. 6 shows a schematic illustration of the two models changing with different masses. The left-hand side figure indicates the model for a constant volume of the porous phase. When the particle size of the waste glass is small, this mechanism is dominant. The right-hand side figure shows the model for a constant thickness of the porous layer. The large particles of the waste glass may result in a constant-thickness model. In this paper, we combine both mechanisms and then define the specific surface area as:

$$Sa = \frac{m_0 f \cdot S_{\max}}{(m - m_0) + m_0 f} k + S_{\max}(1 - k) \quad (1)$$

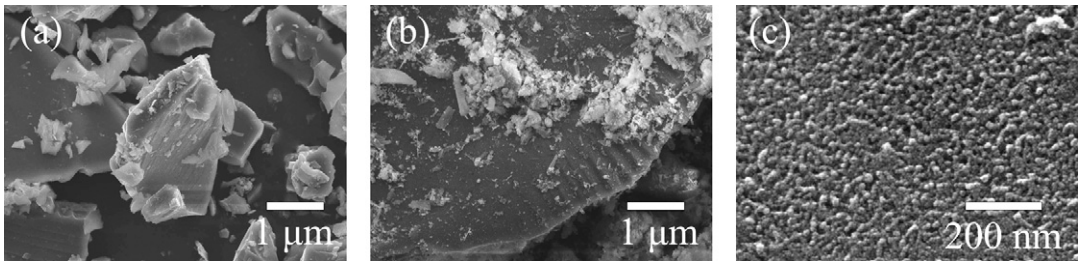

Fig. 5. FE-SEM micrographs of waste glass (a) and samples treated for 72 h in 0.2 mol/L Na_2CO_3 aqueous solution (b) and (c).

where m is mass of the sample, m_0 is the limit mass of the completion of reaction for pore formation in the constant-volume model, and f is the mass residue of the porous phase from the waste glass. S_{max} is the ideal maximum specific surface area when no deposition exists. The first and second terms on the right side of the equation are derived from constant-volume and constant-thickness mechanisms, respectively. Actually, the surface area does not depend on the mass of the waste glass in the constant-thickness mechanism, as shown by the second term. The k in the equation means the fraction of contribution for the constant-volume mechanism. In this study, S_{max} and f are fixed at 200 m^2/g and 0.20 by estimation based on the actual maximum surface area and eventual mass loss of approximately 140 m^2/g and 70 mass%, respectively. Fig. 7 shows the dependence of the specific surface area on the mass of waste glass loaded. The plots are experimental data and the five curves show the surface area calculated with different m_0 values using Eq. (1). The plots confirm that the line calculated with m_0 of 0.5 and k of 0.89 shows better suitability than at calculated with other data. From this consideration, a specific surface area larger than those of our results was obtained at a lower mass of waste glass. Since the specific surface area is very sensitive to the mass of waste glass, the constant-volume mechanism is predominant (approx. 90%) for the formation of the porous phase. This consideration indicates significant fact that waste glass 125 μm in particle size is small enough to be made porous by hydrothermal treatment at 150 °C at a glass concentration of less than 1 mass%.

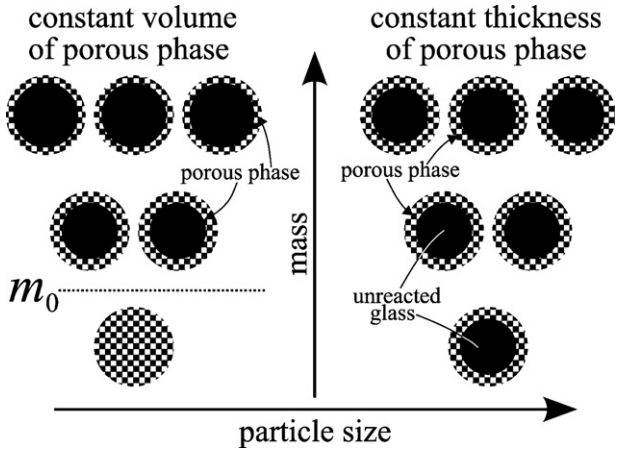

Fig. 6. Schematic illustration of two models changing with different masses. Left: constant volume of porous phase; right: constant thickness of porous phase.

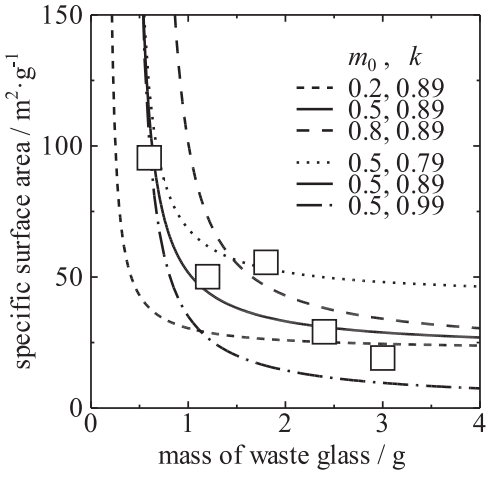

Fig. 7. Dependence of specific surface area on waste glass load. □: experimental data; five curves: calculated using Eq. (1).

The actual time dependence of the porous structure should be investigated using not only the pores formed by leaching but also deposits. Fig. 8 shows a schematic illustration of the time-dependent mechanism underlying the formation of porous structures. The process can be divided into three stages as follows: spans with an increase in, decrease in, and constant regions of a specific surface area for the initial, second and final

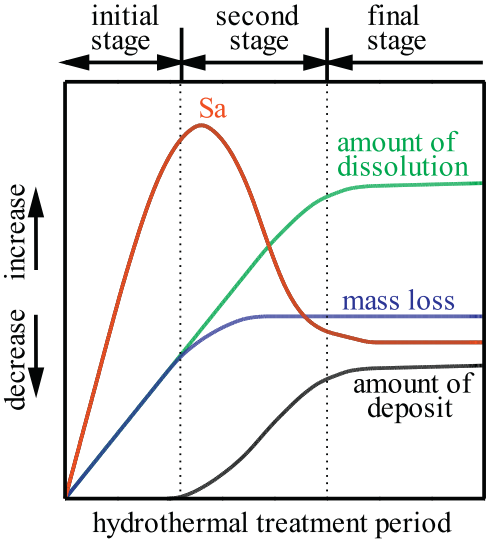

Fig. 8. Schematic illustration of the time dependence mechanism underlying the formation of porous structures.

stages, respectively. In the initial stage, the waste glass was partially leached to form pores. Specific surface area and mass loss increase within this stage. In this stage, the concentration of dissolved component increases. In the second stage, the dissolution of the glass increases continuously and then the supersaturated component deposits somewhere on the sample particles or perhaps within pores. In other words, the transformation of glass to some deposition phases occurs. The deposits reduce the surface area until the complete transformation of glass to the deposits. In the third stage, most of the glass phase may already be dissolved and only minor solution-precipitation possibly occurs.

4. Conclusions

Colored waste glass was hydrothermally treated in Na_2CO_3 aqueous solution of various concentrations. Colored waste glass under 125 μm in particle size was used for these experiments. The tendency of the specific surface area to change with the mass of the waste glass confirms that the particle size of the waste glass is small enough to consider the glass as a porous material. Specific surface area increased linearly depending on the treatment period in the initial period of hydrothermal treatment. Then, it became maximum at approximately 140 m^2/g, and gradually decreased with increasing treatment period. Eventually, it becomes constant at approximately 60 m^2/g. On the other hand, the mass of the sample decreased in the initial period, and consequently converged to approximately 30 mass% of the waste glass load. From these tendencies, the structure of waste glass seems to change in three stages. In the initial stage, glass is partially dissolved to generate pore structures. Specific surface area reaches maximum at the end of the initial stage. In the second stage, some crystalline phases deposit both within the pores and on the glass particles during the dissolution of the glassy phase. The XRD patterns obtained confirm that the deposits are calcite, zeolite-P and analcime phases. Specific surface area decreases in this stage. In the final stage, the deposition of the crystalline phase and dissolution of the glass are probably complete.

Acknowledgement

This work was financially supported by a Yamanashi Prefectural Grant for Monozukuri Industrials.

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