Windshield-waste-driven synthesis of hydroxy sodalite

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We demonstrated the synthesis of hydroxy sodalite (HS) via a simple hydrothermal process using windshield waste as the source material. Acid-treated waste glass was directly used as the silicate precursor. The syntheses were conducted under various NaOH-precursor contents for 1, 12, and 24 h. The crystal structure and morphology of the HS were identified by X-ray diffraction and field-emission scanning electron microscopy. As per the results of the analyses, the HS and zeolite-A phases formed with low NaOH content, but HS was successfully synthesized in a single phase with a Na2O:SiO2:Al2O3 molar ratio of 2.2:1:1 over the course of 24 h. For uniform and high-purity HS crystals, the sizes of the particles of windshield waste were reduced via a high-energy milling process, and then we conducted the hydrothermal procedure under same conditions. Finally, uniformly sized HS crystals were produced with an average diameter of 3 μm. These optimized conditions were not only scientifically valuable to understand the formation process, but this process should also accelerate windshield-waste recycling.

Key-words : Hydroxy sodalite, Hydrothermal reaction, Waste glass, Windshield waste

1. Introduction

Synthetic zeolites are useful in various applications because of their many distinctive advantages, including their molecular-sieving properties, high thermal resistance, chemical inertness, high mechanical strength, and uniform pore sizes.3–5 Given the diversity of zeolites, several novel, industrial fields could benefit from suitable zeolites to meet their specific requirements.3,4 Hydroxy sodalite (HS) is an aluminosilicate-based, microporous-structured material. Tetrahedral SiO4 and AlO4 units are linked in six-membered chains, and they create molecular-pore sizes of 2.8 Å. HS and zeolite A have similar microporous structures, which are composed of three-dimensional channels and cages.5 However, HS has smaller pore sizes than does the eight-membered ring structure of zeolite A (4 Å). This feature provides many advantages, particularly exceptional gas-separation properties for such compounds as helium (2.6 Å) and water (2.7 Å) molecules.6–8

Synthetic HS can be produced by various methods, such as the hydrothermal method, sol–gel microwave techniques, and dry-gel-conversion method.9–11 Among them, the hydrothermal method is the most common route for the synthesis of zeolites due to the high reactivities of the reactants, low heating temperature (i.e., economical energy consumption), and relatively simple process. Hydrothermal methods can utilize a diversity of aluminosilicate-based reagents as source materials, even industrial waste such as coal-tar ash, waste glass, and blast-furnace slag.12–16

Waste glass, which is mainly composed of SiO2, is a suitable material for the synthesis of zeolites. Among the many kinds of waste glass, a huge amount of waste automotive glass is recovered every year from end-of-life vehicles. Particularly, the development of recycling technology for windshield waste is urgently needed due to the current, expensive recycling process with high reactivities of the reactants, low heating temperature (i.e., economical energy consumption), and relatively simple process. Hydrothermal methods can utilize a diversity of aluminosilicate-based reagents as source materials, even industrial waste such as coal-tar ash, waste glass, and blast-furnace slag.12–16

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In this study, we fabricated synthetic HS via a simple hydrothermal process using windshield waste. In order to use it as a raw material for the formation of HS, waste glass requires optimized synthetic conditions due to the different elemental compositions of each manufacturer. Therefore, the microstructures and elemental components of the windshield waste were evaluated first via field-emission scanning electron microscopy (FESEM) and X-ray fluorescence (XRF). To better understand the formation process of HS, we optimized the ratio of the NaOH precursor and the hydrothermal reaction time. Through the results of morphological and crystal-structure analyses, we understood the formation process and explored the synthesis of HS using windshield waste. Finally, uniform and high-purity HS crystals were produced via high-energy-milled windshield waste.

2. Experimental procedures

2.1 Synthesis of HS

HS was synthesized via a simple hydrothermal process using acid-treated windshield waste as the source material. Seoul Glass Industry (Umsong, South Korea) provided the crushed and separated windshield waste. First, the as-received windshield waste was ground in a mortar and screened using a sieve. [Hereafter, this processed waste will be referred to as waste glass (WG) powder.] Then, 10 g of WG powder were treated in aqueous 5 M HNO3 solution under stirring at 70°C for 96 h. Acid-treated WG (a-WG) powder was washed using deionized water several times. The a-WG powder was directly used as the silicate source material. NaAlO2 (anhydrous; Sigma-Aldrich, St. Louis, MO) and 1.24 g of a-WG powder were mixed in 20 mL water. The NaAlO2 requirements were calculated to maintain a constant molar ratio of Na2O:SiO2:Al2O3 (1:1:1) using the elemental composition of the a-WG powder (based on the XRF results).

Various excess amounts (0, 0.8, and 1.7 mol) of NaOH were added to the above precursor solution. The mixtures were stirred homogeneously for 10 min, transferred to a 25 mL Teflon-lined autoclave, and heated at 90°C for 1, 12, and 24 h. Final products were washed several time with deionized water and freeze-dried for 24 h. Hereafter, sample names are referred to as HS-nNa2O or

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HS-nh, based on the experimental conditions. To synthesize uniformly sized HS particles, WG powder was finely ground through a high-energy milling process. Then, uniform HS (u-HS) particles were synthesized using fine a-WG powder via the same hydrothermal procedure used to synthesize HS-24h.

2.2 Characterization
FE-SEM (JSM-4300, JEOL), X-ray diffraction (XRD, SmartLab, Rigaku), and XRF (ZSX Primus, Rigaku) were applied to analyze and elucidate the crystal structures, phases, microstructures, and elemental compositions of the various HS samples.

3. Results and discussion
The main chemical constituents (Na2O, SiO2, and Al2O3) in HS (Na4Al3Si3O12·OH) are identical to those of zeolite A (Na96Al96Si96O384·216H2O). Therefore, zeolite A was frequently detected as an impurity in the various HS syntheses. In much previous research focused on the synthesis of HS, either large or small amounts of zeolite A were found to contaminate these samples, depending on the experimental conditions.17),18) It is necessary to minimize this secondary phase to synthesize high-purity HS. The composition of Na2O, which is the biggest difference in the chemical formula of the two phases, is the important factor to determine the crystal phases between HS and zeolite A. We first treated the as-received windshield waste and evaluated the properties of the WG powder for accurate details about the source material. Then, we optimized the synthetic conditions by controlling both the ratio of Na2O and the hydrothermal-reaction time.

3.1 Properties of windshield waste and the effects of acid treatment
The as-received windshield waste was inappropriate for either synthesis or analysis, because it contained huge particle sizes of up to several millimeters in diameter. Before synthesizing and analyzing the WG, the windshield waste was first crushed using a mortar (i.e., creating WG powder). Then, the WG powder was treated with HNO3 solution to activate it and remove impurities on the surface of the WG (i.e., creating a-WG powder).

The morphologies of the WG and a-WG powders were investigated with FESEM images, as depicted in Figs. 1(a) and 1(b). As shown in Fig. 1(a), the particles of the WG powder had irregular shapes and a wide size distribution (~0.1–50 µm). The average diameter of the particles of the WG powder was 3 µm, as per the results of a particle-size analyzer. In the inset of Fig. 1(a), many small particles existed on the surface of the WG powder. However, many of these small particles were removed by the acid treatment, as per the results of the analysis of the SEM images of the a-WG powder [Fig. 1(b) and Fig. S1]. We did not observe the typical morphological change between the low-magnification FESEM images of the WG and the a-WG powders, but the sharp edges and rough surfaces became smooth and clean. The XRF results of the WG and a-WG powders are presented in Fig. 1. The majority of the elements present in the WG powder decreased after the acid treatment, except for SiO2, which seldom dissolves in HNO3 solution.19) The removal of minor impurities, especially on the surface of each particle, was also confirmed by the EDS analysis of a-WG after acid treatment (Fig. S2). The overall amount of SiO2 was maintained, but the percentage of SiO2 was increased from 66.1 to 69.4% due to the reduced portion of most of the other elements, such as Mg, Na, and Ca. The a-WG powder, including approximately 70% silicate, was suitable as a source material for the synthesis of HS. The nitric-acid process provided a silica-rich surface that have high activity with the precursor solution for the synthesis of zeolite as well as HS.19) These XRF results were also used to calculate the amount of the NaAlO2 precursor (SiO2/Al2O3 = 1).

3.2 Effects of the Na2O molar content
The effects of varying the Na2O molar contents were demonstrated by the changes in both the crystal structures and the

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**X-Ray Fluorescence (XRF) results of waste glass and acid-treated waste glass**

<table>
<thead>
<tr>
<th></th>
<th>SiO2</th>
<th>CaO</th>
<th>Fe2O3</th>
<th>Na2O</th>
<th>MgO</th>
<th>Bi2O3</th>
<th>Al2O3</th>
<th>K2O</th>
<th>TiO2</th>
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<tr>
<td>Waste glass</td>
<td>66.1</td>
<td>24.9</td>
<td>2.4</td>
<td>1.7</td>
<td>1.2</td>
<td>0.5</td>
<td>1.1</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Acid-treated glass</td>
<td>69.4</td>
<td>23.7</td>
<td>1.7</td>
<td>1.5</td>
<td>1.2</td>
<td>0.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.4</td>
</tr>
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</table>

Fig. 1. The FESEM images of the (a) WG and (b) a-WG powders. XRF results of the WG and a-WG powders are presented in the table at the bottom of the figure. High-magnification FESEM images of the WG [inset of (a)] and a-WG [inset of (b)] powder surfaces are provided.
morphologies of the synthesized products, according to the different NaOH concentrations in the synthetic solutions. In our process, the a-WG powder included only negligible amounts of Al₂O₃ and Na₂O. The silicate to alumina ratio of 1:1 was maintained through the preservation of a constant amount of the NaAlO₂ precursor. NaOH was the only variable that changed the proportions of the Na₂O:SiO₂:Al₂O₃ ratio. Previously, the literature has reported that the excess addition of NaOH resulted in the formation of the HS phase and the prevention of the formation of other zeolitic phases. 20) It is possible to add additional NaOH, because unreacted Na⁺ and OH⁻ ions can be removed during the aqueous-washing process.

The effects of the Na₂O molar contents were observed through the change in the NaOH amount from 0 to 1.7 mol. The final ratios of the molar compositions of the various HS samples could be expressed as 1–2.2Na₂O:SiO₂:Al₂O₃ as per a calculation of the precursor components. 5),21) Figure 2 shows the XRD patterns of the HS-1Na₂O, HS-1.6Na₂O, and HS-2.2Na₂O samples. The XRD patterns of HS-1Na₂O indicated two types of crystal phases, HS and zeolite A. Synthetic conditions involving low Na₂O contents yielded little crystalline HS and the secondary phase of zeolite A, because there was not enough sodium to form HS. The crystallinity of the HS samples gradually increased with an increasing molar ratio of Na₂O. The XRD pattern of HS-2.2Na₂O was perfectly matched with that of cubic HS (JCPDS #11-0401). Ultimately, 1.7 mol NaOH provided enough sodium for the complete conversion of the precursor to HS.

The morphologies of the HS-1Na₂O, HS-1.6Na₂O, and HS-2.2Na₂O samples were analyzed with FESEM images. Figures 3(a) and 3(b) show the FESEM images of HS-1Na₂O; they depict the cubic shapes and aggregated-plate shapes of the sample. The cubic shape originated from the zeolite-A phase, and the plate shape was the typical shape of an HS crystal. The high- and low-magnification images of HS-1.6Na₂O revealed some intermediate, cubic, and plate shapes, which were all clearly distinguishable from one another [Figs. 3(a) and 3(b)]. Both HS and zeolite A were randomly observed on the surface of the waste glass particles (Fig. S3). Therefore, it is believed that the crystallization of both HS and zeolite A occurred simultaneously on the surface of each glass particle. The exact ratio of the zeolite A to HS could not be defined with only the FESEM images, but we could determine the aggregated-plate and mashed-cubic-shape increase in contrast to the cubic-shape decrease, corresponding to the XRD results in Fig. 2. In the case of HS-2.2Na₂O, there were only aggregated-plate shapes, as shown in Figs. 3(e) and 3(f). However, the HS particles agglomerated with each other, and these agglomerations grew quickly.

### 3.3 Effects of different reaction times

To further understand the formation process of HS, we controlled the hydrothermal-reaction time. The synthetic conditions, except for the reaction time, were maintained as per those of the HS-2.2Na₂O sample. HS samples were hydrothermally synthesized for 1, 12, and 24 h (HS-1 h, HS-12 h, and HS-24 h, respectively). To analyze the effects of the different reaction times, the crystal structures of the HS-nh samples were identified by their XRD patterns, as shown in Fig. 4. The XRD pattern of HS-1 h had a broad hump with weak peaks, corresponding to the cubic-zeolite-A phase (JCPDS #39-0222), as per the enlargement of the XRD pattern in the inset of Fig. 4. The unreacted a-WG
powder maintained an amorphous structure, and some zeolite A remained in the HS-1h sample. The small glass particles on the surface of the a-WG powder transformed into zeolite A, as 1 h was not enough to complete the formation of the HS crystals. A trace of the zeolite-A phase was also detected throughout the first 12 h of the reaction, but the HS phase primarily composed the XRD patterns of the HS-12 h and HS-24 h samples, which could clearly be indexed to the cubic HS phase.

Figure 5 shows the morphologies of the HS-1 h, HS-12 h, and HS-24 h samples. In Fig. 5(a), the particle sizes of HS-1 h did not change in comparison with those of the a-WG powder in Fig. (b). However, tiny cubic shapes were observed on the surface of the a-WG powder. This phenomenon originated from the better reactivity of the small-size particles and the silica-rich surface of the a-WG powder. During the short reaction time of 1 h, only zeolite A formed on the surface of the a-WG powder. This morphology reasonably explained the unreacted, amorphous a-WG powder and the few zeolite-A crystals in the XRD pattern of the HS-1h sample. Figures 5(c) and 5(d) present the middle stage of the synthesis of HS. Large a-WG particles were mostly broken and aggregated to the plate shape, and the cubic shapes of zeolite A were rarely observed, as shown in Fig. 5(c). These results also matched the XRD results of the HS-12 h sample.[Figs. 3(e) and 3(f) depict the images of the HS-24 h sample and have been described above.] The reaction time of 24 h was sufficient to convert the a-WG powder to HS. Although the single phase of HS was successfully synthesized using windshield waste as the source material, the morphological properties of HS did not meet our expectations due to the serious aggregation phenomenon. The HS-24 h sample would be difficult to apply to several novel and desired technologies, including chemical sensors, seeds for thin films, and so on.

3.4 Formation of uniformly sized HS particles
The particles of the HS-24 h sample had a broad size distribution with particle sizes reaching up to tens of micrometers. To apply to the desired variety of novel applications, the particles of the HS should be small in size and have a narrow size distribution. Fan et al. successfully synthesized uniform sodalite nanocrystals using a tiny silicate source.5) To form uniform HS crystals, a small-sized silicate precursor is necessary. The WG powder, our silicate source material, was crushed with a high-energy ball-milling procedure to decrease the particle size. Then, we fabricated uniformly sized HS particles (u-HS) using fine WG powder via the same hydrothermal process as that used for HS-24 h. As shown in Fig. 6(a), the morphology of the particles of u-HS had uniform sizes with an average diameter of approximately 3 μm. In the inset of Fig. 6(a), the thickness of the plates also decreased with the decrease in particle size. The XRD pattern of the u-HS indicated the presence of the cubic HS phase without any secondary phase of zeolite A. The peaks at 14.0, 24.5, 31.8, 35.0, 37.9, and 43.3° were indexed with the cubic HS (110), (211), (310), (222), and (411) planes, respectively. The decrease in size of the silicate materials did not affect the crystal structure. Additionally, the specific Brunauer-Emmett-Teller surface area of u-HS was 26 m² g⁻¹. Total pore volume and average pore diameter of u-HS were 0.0336 cm³ g⁻¹ and 24.6 nm, respectively (Fig. S4).

In summary, uniform HS crystals were successfully fabricated via optimized synthetic conditions using windshield waste as the silicate source material. Several factors played an important role during the HS formation process as follows. First, the Na₂O molar content had to be maintained at a minimum value of 2.2Na₂O:SiO₂:Al₂O₃ by supplying excess NaOH precursor. Otherwise, the zeolite-A phase, which required a smaller Na molar ratio than did HS, was generated together with the HS phase due to the lack of Na. Second, a sufficient reaction time was necessary for the formation of the HS. In the case of a short reaction time, unexpected formation processes occurred, and unreacted source material remained in an amorphous phase. Third, the size of the particles of waste glass used as the source material did not affect the crystal structure of the HS, but the size of the waste-glass

![Image](https://via.placeholder.com/150)

Fig. 5. Low- and high-magnification FESEM images of the (a) and (b) HS-1 h and (c) and (d) HS-12 h samples, respectively.

![Image](https://via.placeholder.com/150)

Fig. 6. (a) FESEM image of uniformly sized HS (u-HS), synthesized using high-energy-milled waste glass. (b) XRD pattern of the u-HS.)
particles needed to be small to facilitate the formation uniformly sized HS particles with a narrow size distribution.

4. Conclusions

We successfully synthesized HS via a hydrothermal process using windshield waste. Impurities such as Mg and Ca on the surface of the windshield waste were removed with an HNO₃ treatment. This process also provided a silicon-rich surface. To understand the effects of excess NaOH and the reaction time, HS samples were synthesized using diverse Na₂O molar contents (0, 0.8, and 1.6 mol) with the a-WG powder for 1, 12, and 24 h. The amount of excess NaOH should reach at least a 2.2Na₂O:SiO₂:Al₂O₃ ratio, and the complete formation of HS required a reaction time of over 24 h. Otherwise, the formation of secondary zeolite A occurred, and unreacted source material remained in the produced HS powder. For the production of uniform and high-purity HS crystals, the sizes of the particles of windshield waste were reduced via a high-energy milling process, and then we conducted the hydrothermal procedure. Finally, uniformly sized HS particles were produced with an average diameter of 3 μm. This study has provided desirable data for further research into the uses of industrial waste.

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References