Recycling of typical difficult-to-treat e-waste: Synthesize zeolites from waste cathode-ray-tube funnel glass

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HIGHLIGHTS

- An open-loop recycling method for CRT funnel glass was developed.
- The influence of various factors on the resulting products were investigated.
- Successive transformation among NaA, NaP1, Faujasite and hydroxysodalite was confirmed.

ARTICLE INFO

ABSTRACT

The disposal of waste cathode ray-tubes (CRTs) from old televisions and discarded computer monitors has become a major environmental concern worldwide. In this work, an open-loop recycling method was developed to synthesize zeolites using CRT funnel glass as the raw material. The effects of hydrothermal temperatures and pressure, $n(SiO_2/Al_2O_3)$ molar ratios and hydrothermal time on the resulting products were investigated. The results indicated that hydrothermal temperatures and pressure played critical roles in zeolite synthesis. Amorphous phases were detected at lower temperatures (80–100 °C) and pressure (0.47–1.01 bar) with $n(SiO_2/Al_2O_3) = 2.0$. At the temperature of 110 °C (pressure 1.43 bar), NaA formed with a mixture of NaP1 and Faujasite. With further increase in the temperature and pressure, the unstable NaA and Faujasite disappeared, and Hydroxysodalite developed. The influence of $n(SiO_2/Al_2O_3)$ ratios on resulting products revealed a single phase of NaA was formed at the ratio of 1.5 and a mixture of NaA and Faujasite at the ratio of 2.0. Prolonging hydrothermal time, however, could promote zeolite crystallization, and NaA gradually developed with an increase in the time from 2 to 6 h at $n(SiO_2/Al_2O_3) = 1.5$. By comparison, crystallization phases were observed only when the time was longer than 8 h at $n(SiO_2/Al_2O_3) = 2.0$.

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1. Introduction

With the rapid innovations in electronic display technology during the last decade or so, conventional cathode ray-tubes (CRTs) have been gradually replaced by advanced display products, such as liquid-crystal displays (LCDs), plasma display panels (PDPs) and organic light-emitting diode (OLEDs) displays, resulting in a large number of waste CRTs that need to be disposed of. According to the waste electrical and electronic equipment (WEEE) collection and pretreatment market, approximately 50,000–150,000 tons/a of end-of-life CRTs are currently collected in Europe, and this volume is not expected to decrease any time in the next few years [1].

The recycling and dismantling amounts of waste electrical appliances in China came to 56 million units in 2010, of which 80% were CRT monitors [2]. CRTs are generally made of four different types of glass—panel, funnel, neck and frit junction—with varying chemical compositions and properties [3]. Among these glass types, funnel glass has been confirmed as having hazardous characteristics, because of its high level of lead content [4–7]. However, most discarded CRTs currently end up concentrated in landfills or e-waste recycling centers, and only a small portion of them are recycled. A long-range plan is needed, to find improved recycling methods for this waste.

Generally, there are two principal ways of recycling CRT glass: closed-loop and open-loop recycling [8–10]. In closed-loop recycling, waste CRT glass is commonly used as raw material to manufacture new CRTs. This approach has the advantage of economic benefit and a high resource utilization rate. However, most

CRT manufacturers (e.g. Ancai Hi-tech Co., Ltd., and IRICO Group Electronics Co., Ltd., in China) have gradually ceased or restructured the funnel manufacturing facilities of their CRT operations, since the demand for new CRT monitors is rapidly shrinking. Consequently, attention has shifted to open-loop recycling. A number of projects have been undertaken to use CRT glass as raw material for the production of foam glass [11,12], glass ceramic [13,14], ceramic glazes [15], stoneware tile [16,17] and cement mortar [18,19]. Nevertheless, these approaches are problematic from the point of view of environmental and human safety, because the regenerated products still contain toxic heavy metals. Therefore, many attempts have been made to recover lead from leaded glass. Saterlay et al. [20] used ultrasound to facilitate lead leaching from CRT glass, achieving a removal rate of over 90% of the leachable lead. Yuan et al. [21] applied mechanical activation to pretreat CRT funnel glass, followed by diluted nitric acid leaching, and a high yield of 92.5% of the lead was achieved. Lu et al. [22] recovered lead from CRT funnel glass by thermal reduction with metallic iron, and 58 wt.% lead extraction was achieved. Xing and Zhang [23] extracted nano-lead particles by retrofitting the pyro-vacuum process; the leaded glass was thus converted into harmless glass. Erzat and Zhang [24] also used chloride volatilization to recover lead from CRT funnel glass. From the above literatures, it can be seen that lead can be effectively removed from leaded glass using recent advanced technologies. However, little attention has been paid to the comprehensive utilization of other fractions (e.g. silicon and aluminum) in the leaded glass. Hu et al. [25] prepared sodium silicate frit by melting leaded glass with sodium carbonate and then dissolving it and precipitating lead to obtain a sodium-silicate-rich solution. Okada and coauthors [26–29] treated funnel glass by a process combining reduction melting to recover lead from glass. The oxide phase generated by the thermal treatment was subjected to water and acid leaching for SiO_2 purification. In this work, we attempted to prepare zeolites using CRT funnel glass as the raw material. The effects of hydrothermal temperatures and pressure, $n(SiO_2/Al_2O_3)$ molar ratios and hydrothermal time on zeolite synthesis were investigated. The aim was to develop an innovative technology for CRT funnel glass recycling and thus solve the significant environmental problems associated with leaded glass.

2. Experimental materials and methods

2.1. Materials

Raw CRT funnel glass was obtained from Henan Ancai Hi-tech Co., Ltd. The glass block was first crashed into small pieces, ground with a P-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany), and then sieved to achieve a particle size smaller than 200 μm. Its chemical composition was determined using X-ray fluorescence spectroscopy (SXF-1200, Shimadzu, Japan) and the resulting contents were (wt.%): SiO_2 53.90, PbO 23.10, K_2O 7.59, Na_2O 5.81, CaO 3.06, Al_2O_3 3.03, and others 3.51.

2.2. Zeolite synthesis

Zeolite synthesis includes three major procedures: leaching, purification and hydrothermal synthesis. 1) Before leaching, batch experiments were preliminarily carried out to determine the optimal conditions. Leaded glass powder and sodium hydroxide solution (6 mol/L), in a solid/liquid ratio of 1:8, were mixed and put into a 200-mL autoclave made of stainless steel. The reaction temperature and time were set as 220 °C and 8 h, respectively. After treatment, the solid-liquid separation was performed by vacuum filtration and a filtrate was obtained. 2) The lead and silicon concentrations in filtrate were measured and the leaching rate of them

were determined as 85.8 and 90.1%, respectively. Sodium sulfide was gradually added according to the molar ratio of Pb:S = 1.0:1.5 to remove the hazardous lead. The dark brown precipitate was separated through centrifugation and lead removal rate reached 99.4%. The silicon-rich and lead-free liquid was thus obtained. 3) Silicon and aluminum in the concentrated liquid were measured and their molar ratios of SiO_2 and Al_2O_3 adjusted, using sodium silicate and sodium aluminate. The precursors were aged at 60 °C in a water bath for 0.5 h and then put into the autoclave. The hydrothermal temperature and time were set as 80–210 °C and 2–12 h, respectively. At the end of the process, the solid was separated by vacuum filtration with a Büchner funnel, washed five times with distilled water and dried overnight at 100 °C. The dried products were then analyzed using X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR) and scanning electron microscopy (SEM).

2.3. Characterization and testing

The obtained products were characterized by various conventional methods. XRD analysis was employed to determine the crystalline phases present in the zeolitic products. A Rigaku D-Max/IIB X-ray power diffractometer was operated at 40 kV and 30 mA, with CuKα as the radiation source. The detector was scanned at a step scan of 0.02° and a scan speed of 4°/min. Scanning electron microscopy (SEM) investigations were conducted in an S-3400N scanning electron microscope (Hitachi, Japan) at an accelerating voltage of 15 kV to observe the microstructure of the samples. Transmission IR spectra were recorded with a Nicolet Nexus-670 Fourier transform infrared spectrometer with a resolution of 2 cm^{-1} using the KBr disc method. The concentrations of lead, aluminum and silicon in the liquid were measured with a Perkin Elmer Optima 8300 DV (Perkin Elmer, Shelton CT) ICP-OES.

3. Results and discussion

3.1. The influence of hydrothermal temperatures and pressure

The influence of varying hydrothermal temperatures and pressure on zeolite synthesis at $n(SiO_2/Al_2O_3) = 2.0$ is plotted in Fig. 1. It was clear that lower temperatures (80–100 °C) and pressure (0.47–1.01 bar) were not helpful for zeolite crystallization, and amorphous phases were detected. Increasing the temperature and pressure further resulted in the decrease of amorphous phases and promoted the growth of crystal zeolites, indicating the critical role of temperature and pressure in the zeolite crystallization [30,31]. At the temperature of 110 °C (pressure 1.43 bar), the major phase NaA (NaAlSiO₄·2.25H₂O, JPCDS card no. 39-0222) [32,33] developed with a mixture of NaP1 (Na$_{3.6}$Al$_{3.6}$Si$_{12.4}$O$_{32}$·14H₂O, JPCDS card no. 39-0219) [34,35] and Faujasite (Na₂Al₂Si$_{2.4}$O$_{8.8}$·6.7H₂O, JPCDS card no. 12-0246) [36,37]. Increasing the temperature still more, to 140 °C (pressure 3.61 bar), caused the diffraction peak intensity of the three zeolites to increase, especially for the Faujasite. Yet increasing the temperature from 140 to 160 °C (pressure 6.18 bar) resulted in even more development of zeolite NaP1, compared to Faujasite. When the temperature was increased to 180 °C (pressure 10.02 bar), the product was still confirmed by a mixture of the three zeolites. However, the intensity of NaP1 reflections increased at the expense of NaA and Faujasite. The two unstable phases completely disappeared at 190 °C (pressure 12.54 bar), accompanied by the formation of Hydroxysodalite (Na₆(AlSiO₄)₆·4H₂O, JPCDS card no. 42-0216) [38,39]. Further increasing the temperature to 210 °C (pressure 19.06 bar) caused the intensity of Hydroxysodalite reflections to increase at the expense of NaP1. This zeolite transformation coincided with Ostwald's rule of successive transformation [40,41]. With the rise in hydrothermal temperature and pressure,