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Effect of ultrasound energy on the zeolitization of chemical extracts from fused coal fly ash

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A B S T R A C T

This paper investigates the effects of ultrasound (UTS) energy at different temperatures on the zeolitization of aluminosilicate constituents of coal fly ash. UTS energy irradiated directly into the reaction mixture utilizing a probe immersed into the reaction mixture, unlike previously reported works that have used UTS baths. Controlled synthesis was also conducted at constant stirring and at the same temperatures using conventional heating. The precursor reaction solution was obtained by first fusing the coal fly ash with sodium hydroxide at 550 °C followed by dissolution in water and filtration. The synthesized samples were characterized by XRF, XRD, SEM and TGA. The crystallinity of crystals produced with UTS assisted conversion compared to conventional conversion at 85 °C was twice as high. UTS energy also reduced the induction time from 60 min to 40 min and from 80 min to 60 min for reaction temperatures of 95 °C and 85 °C, respectively. Prolonging the UTS irradiation at 95 °C resulted in the conversion of zeolite-A crystals to hydroxysodalite, which is a more stable zeolitic phase. It was found that at 85 °C coupled with ultrasound energy produced the best crystalline structure with a pure single phase of zeolite-A. It has been shown that crystallization using UTS energy can produce zeolitic crystals at lower temperatures and within 1 h, dramatically cutting the synthesis time of zeolite.

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1. Introduction

Ultrasound (UTS) energy has been utilized in many chemical syntheses ranging from synthesis of metal and semiconductor particles, polymers, organic compounds, cleaning of industrial equipment, leather processing, drug delivery, inter-particle collisions and coupled with electrochemical reactions [1]. The reason for its extensive use is because UTS energy can initiate reactions more easily; furthermore UTS can accelerate chemical reactions. There are two types of sonochemical reactions, homogenous sonochemistry that results from the formation of radicals or radical intermediates, and heterogeneous sonochemistry that is influenced primarily through the mechanical effects of cavitation, such as surface cleaning, particle size reduction, and improved mass transfer [2]. The sonochemical effects do not come from a direct interaction between sound field and molecular species, but due to acoustic cavitation [3]. The cavitation is produced when gas nuclei that are present in the liquid go through oscillations expanding and compressing during the expansion of the ultrasonic field, creating a vacuum into which gas in the liquid diffuses. During the

compression half of the cycle, the gas within the bubbles diffuses back into the host liquid, however, due to the smaller surface area, not all the gas that diffused into the bubble diffuses out. After multiple expansion and compression, micro-bubbles reach a critical size resulting in bubble collapse during one compression cycle. Collapse of these bubbles results in adiabatic heating of gas and vapor inside the bubble. These cavitations produce radicals inducing sonochemical reactions. The hot spots produced due to these cavitations can reach a temperature of 5000 °C, the local pressure can go as high as 20 MPa with high cooling rates of 10^7 °C/s these cavitations result in particle collisions at high velocities [4–6]. There have been many reported works where zeolites have been synthesized utilizing UTS energy [7–14].

Musyoka et al. have converted aluminate and silicate extracts from coal fly ash fused with NaOH at elevated temperatures into zeolites. The progression of these reactions was observed utilizing UTS attenuation technique [15,16]. However, the UTS impulses used in their experiments were 2 MHz so there was no energy input and thus no effect on the zeolitization was expected [17]. It is hypothesized that dissipation of UTS energy in the reaction mixture obtained from fused CFA extracts would shorten the reaction time as observed in experiments conducted using pure chemical precursors [7]. All the previous experiments have investigated the effects of UTS energy on zeolitization from either pure

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chemical precursors [7–9,13,14] or CFA precursors [10,11]. The brief descriptions of the experimental procedures reported in literature are summarized in Table 1.

To the best of our knowledge, there has been no work reported on the zeolitization process utilizing a UTS probe irradiating energy directly into the reaction solution. It is observed that irradiated UTS energy directly into the reaction solution can dramatically decrease the zeolitization time and form pure single phase crystals at lower temperatures.

2. Materials and methods

2.1. Material

Coal fly ash was procured from a coal fired power plant (OPG, Nanticoke) located in Ontario, Canada, and was stored in seal container before use. Sodium hydroxide (Alphachem, Canada), sodium aluminate anhydrous (Sigma–Aldrich, USA) and sodium metasilicate, (Sigma–Aldrich, USA) were of analytical grade and used as received. Deionized (DI) water was used for the preparation of the solutions.

2.2. Method of conversion of CFA to Zeolite

The method used for converting CFA to zeolite was first introduced by Shigemoto et al. [18]. In this method a dry fusion step is introduced prior to hydrothermal treatment. The procedure outlined in the previous works was followed with few amendments [19]. CFA was fused with sodium hydroxide (granules) at a ratio of 1:1.2 by weight. The solid mixture was treated at 550 °C for 2 h. The fused substrate was milled to a greenish-yellow powder. The powder was mixed with DI water at a ratio of 1:5 by weight. The slurry mixture was stirred mechanically at 540 rpm for 2 h to extract the aluminosilicate components of CFA into the aqueous phase. The slurry was filtered and sodium aluminate solution (0.155 g/mL) was added to the filtrate at volumetric ratio of 3:17. The mixture was aged for 2 h at room temperature prior to crystallization.

The reaction mixture was crystallized at varied temperature of 75, 85 and 95 °C, and different reaction times of 20, 40, 60, 80, 100, 120 min utilizing UTS probe (Vibra Cell VCX-500, Sonics & Materials, USA) and with conventional heating. A Jacketed crystallizer with re-circulating water system was used to control the temperature during the reaction. Fig. 1 illustrates the reaction setup with UTS irradiation and without UTS irradiation.

Two identical crystallizers were used for UTS assisted synthesis and conventional synthesis. The experiments were run simultaneously under identical temperature and reaction time. The UTS conversion was conducted by immersing UTS probe into the reaction mixture while conventional conversion synthesis was conducted

by utilizing mechanical mixer. The temperature in both crystallizing vessel was by temperature controlled water circulator.

2.3. Characterization

Chemical composition of the CFA sample was determined by means of X-ray fluorescence spectroscopy (XRF) utilizing a PANalytical PW2400 Wavelength Dispersive System. A MiniFlex powder diffractometer (Rigaku, Woodlands, USA) was used to collect XRD data of the synthesized samples using CuK_α (λ for K_α = 1.54059 Å) over the range of $5° < 2\theta < 40°$ with step width of 0.02°. ICP-AES (Perkin Elmer Optima-3000 DV System) was utilized to analyze the metal elemental concentration in the reaction mixture. The net intensity was calculated through peak area integration minus the backgrounds. Crystal size distribution and morphology of zeolite were studied by scanning electron microscope (SEM) JSM 600F (Japan) operating at 10 keV of acceleration voltage. The thermal analyses were performed using a Mettler Toledo TGA/SDTA 851e model (Mettler-Toledo Inc., Schwerzenbach, Switzerland) with version 6.1 Stare software. The samples were heated from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen purge of 40 mL/min.

3. Results and discussion

3.1. X-ray analysis (XRF and XRD)

The chemical compositions of the raw CFA, the fused CFA after ageing and filtration and the produced zeolite were determined using X-ray fluorescence spectroscopy. The results are summarized in Table 2. The results show that the amount of sodium is considerably higher in the aged filtered CFA compared to raw CFA. The presence of sodium is the result of the addition of NaOH in the fusion step. However, the chemical composition of zeolite produced was dramatically different. The zeolite produced composed mostly of aluminum, silicon and sodium. Silicon to aluminum ratio of the zeolitic crystals produced was close to one and the zeolitic crystal charge was balanced by sodium present in the structure. The other elements present in the CFA samples, such as calcium and iron, were incorporated, however, in limited amount in the zeolitic crystals while magnesium, titanium and potassium were incorporated in the zeolitic composition but in lower amounts compared to the original CFA. The incorporation of titanium in the zeolite structure might be of interest as TiO_2 is extensively researched for its photocatalytic properties for detoxification of organic and inorganic compounds in the purification of polluted air and industrial wastewater [20].

ICP-AES was conducted to quantify the amount of metallic elements extracted from the CFA into the reaction mixture and the amount left in the supernatant after crystallization and

Table 1
Ultrasound assisted zeolite synthesis from literature.

Ultrasound				Conventional		Zeolite	Remarks	References
Frequency	Power	Treatment		Crystallization				
v (kHz)	P (W)	T (°C)	t (h)	T (°C)	t (h)			
47	n/a	60–70	4–6	n/a	n/a	Na-4A	Pretreated Kaolin at 800 °C for 3 h	Jin Park et al. [23]
35	n/a	50–60	2–15	n/a	n/a	Na-A	No treatment followed by UTS	Andaç et al. [7]
40	50	50	1	135–150	24–96	MCM-49	–	Wu et al. [14]
40	50	50	0.5–1	135–150	48–400	MCM-22	–	Wang et al. [13]
40	50	n/a	0.5	180	18–72	BZSM-5	–	Abrishamkar et al. [8]
40	50	25	0.5–1.5	160	48–72	ANA	–	Azizi and Yousefpour [9]
35	240	21–46	1	25–60	96	Na-X	CFA fused with NaOH prior to UTS	Belviso et al. [10]
35	240	21–46	1	25–60	96	Na-X	Fused CFA with NaOH, Sea Water	Belviso et al. [11]
n/a	100	30	0.67	800	3	Na-P1	Perlite precursor used	Azizi et al. [8]