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Supercritical hydrothermal synthesis of zeolites from coal fly ash for mercury removal from coal derived gas

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ABSTRACT

The supercritical hydrothermal method was proposed as a new approach to synthesize zeolite from Coal fly ashes (CFAs). Eight kinds of CFAs from different power plants were used as raw material. The effects of the types of CFAs, the concentration of NaOH, liquid-solid volume ratio, reaction time and SCW temperature on the formation of zeolites and their properties were investigated. All the CFAs can form zeolite in supercritical conditions in 5 min at 400 °C, especially for the coal fly ash with medium mass ratio of SiO_2/Al_2O_3 and low content of Fe_2O_3 and CaO. The different type of zeolites (cancrinite and sodalite) could be formed by changing the solution concentration of NaOH. The best crystallinity can be obtained under the conditions of the SCW temperature of 400 °C, liquid-solid volume ratio of 15:1 and NaOH concentration of 1 mol/L. The potential application of the products synthesized from CFAs was studied and the results suggested that CFA zeolites had a good activity for Hg removal from the simulation coal gas.

1. Introduction

Coal fly ash (CFA) is a by-product of coal-fired power plants. Coal fly ash is generally stored at power plants or placed in landfills [1,2]. Generally, 1 ton of CFA will be produced in power plant through consuming 4 tons of coal (*2010 China Fly Ash Survey*). These CFAs take up a lot of land and it is detrimental to health in sufficient quantities because it contains trace concentrations of heavy metals and other substances. Therefore, the effective utilization of CFA has been a worldwide issue. Usually, CFA can be used as building and road materials such as fly ash brick, panel wall and concrete additive. But the problem needed to deal with is that in some area, the transportation cost is much higher than the price of CFA, so a mass of CFA is left without any management. It should be more realistically significant to develop high value-added utilization methods of CFA.

CFA contains plentiful Si and Al, which is a readily available source for zeolite synthesis [3–6]. The fly ash zeolite has a high value added and it has been used for a wide range of purposes, including agricultural, environmental, and industrial applications [7–9]. Some synthetic methods of fly ash zeolite have been reported, such as hydrothermal process [10–12], salt-thermal [13], alkali fusion method [14,15], microwave-assisted synthesis [16,17], and two-step process method [7,18]. In nature, the formation of zeolite is a complicated geologic process, usually accompanying with high temperature and high pressure reaction. The supercritical hydrothermal synthesis has the similar characteristics. Moreover, in recent years, supercritical water (SCW) synthesis has received a great deal of attention as a generalized crystallization method for the production of metal oxide particles [19,20], supported adsorbent [21,22], and nanocrystal compound [23]. At the supercritical region, a fast reaction rate and low metal oxide solubility will lead to an extremely high nucleation, and greatly reduce the preparation time compared to the traditional method of material synthesis [24].

Zeolite has favorable adsorption properties, which can be used for gas purification and separation. X. Querol [5] and A. Srinivasan et al. [25] used fly ash zeolite effectively eliminated the SO_2 in the simulated flue gas. Hg is another main pollutant in coal derived fuel gas. It may be a potential approach to remove Hg from coal-based gases by zeolite with proper adsorption capacity.

Based on the description above, a novel and fast synthesis method of CFA zeolite for removing Hg from coal derived flue gases is introduced in this study. The eight kinds of CFAs from different power plant in China were used as raw material and conducted on zeolitization at the region of the supercritical water. The effect of NaOH solution

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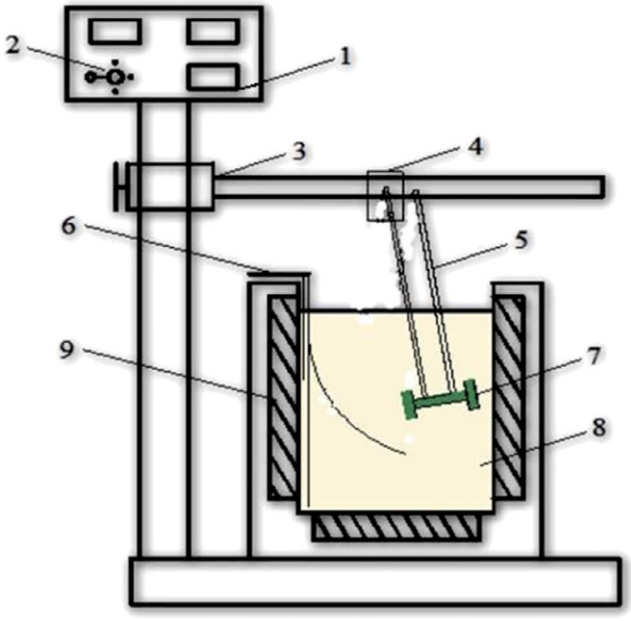

Fig. 1. Schematic diagram of experimental apparatus. (1) temperature-controlling instrument, (2) speed controller, (3) cantilever, (4) motor, (5) crank, (6) thermocouple, (7) tube reactor, (8) KNO_3–$NaNO_3$ salt, (9) heater.

concentration, reaction time, SCW temperature, and the liquid–solid volume ratio on the formation of zeolite and its properties was investigated. The synthesis products were characterized by XRD, SEM, EDS, XPS and N_2 adsorption techniques. The focus is to establish the proposed supercritical hydrothermal synthesis method as a new zeolitization technique and achieve its optimization.

2. Experimental

2.1. Synthesis of zeolite from CFA

Sodium hydroxide (NaOH, purity >98%) used as activation agent [11,26] was the purchased chemical reagent, deionized water used in preparation solution was made in the lab. The eight kinds of CFAs as raw material for synthesis of zeolite were collected from the representative coal-fired power plants in China and numbered as No. 1, No. 2, No. 3, No. 4, No. 5, No. 6, No. 7, and No. 8.

The synthesis of zeolite in supercritical water was conducted with a 21 ml stainless steel tube reactor shown in Fig. 1. The tube reactor was heated by a molten salt bath and the temperature of salt bath was measured by a K-type thermocouple. The reactor can swing up and down driven by a motor at a speed of 120 cycle/min. The pressure was calculated according to the temperature and the given density based on the NIST/ASME steam table. The 10 ml mixture of CFA and NaOH was fed into the stainless steel tube reactor. The reactor was immersed in the salt bath after reaching the desired reaction temperature. When the reaction time was arrived, the reactor was taken from the molten salt bath and rapidly quenched in a water bath to cool to room temperature. The solid products were obtained by filtration and then washed with deionized water, dried at 100 °C for 12 h.

2.2. Sample characterization

X-ray diffraction (XRD) was employed to investigate the crystal structures of the solid products. The instrument is a D/max2500 diffractometer (Rigaku, Japan), fitted with a nickel-filtered Cu Kα radiation source operating at a voltage of 40 kV and 100 mA. The scan rate was 8°/min in the range from 5 to 85°.

SEM images of the samples were obtained by JEOL Jsm-6700F with an accelerating voltage of 10 kV. The samples were sprayed with gold prior to measurements. The EDS analyzer (Quantax 400, Bruker, Germany) that was coupled to the SEM was used to identify the chemical composition of a specific area of a sample.

X-ray photoelectron spectroscopy (XPS) surface analysis was conducted for determining the surface concentration and binding energy of samples, using an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with an Al Kα source ($h\upsilon = 1486.6$ eV, 150 W). Energy correction was performed using the C1*s* peak at 284.6 eV. No smoothing routine of data was applied to analyze the results.

The pore structure properties of CFA and its products obtained under various NaOH concentrations were obtained using a JW-BK122W N_2 adsorption instrument (JWGB Sci. & Tech. Co., Ltd., Beijing) at −196 °C. The surface area and micropore volumes were obtained using the BET and the Dubinin–Astakhov equations, respectively.

2.3. The evaluation of Hg removal

The performance of removing Hg from simulated fuel gas over CFA-synthesized zeolites was investigated using a laboratory-scale fixed-bed reactor. The equipment and operation process were similar to the literature [27]. 0.50 g sorbents were placed in a quartz tube reactor (5.0 mm inner diameter and 64.2 cm length). The gas flow rate was 470 ml/min and it was controlled by a mass flow controller where the space velocity was $4.5 \times 10^4\ h^{-1}$. The simulated coal gas the reactive atmosphere 40 μg/m^3 Hg and 300 ppm H_2S, 10% H_2, 20% CO in N_2, 100 °C and $SV = 4.5 \times 10^4\ h^{-1}$.

Table 1
Major oxide contents of the CFAs from different power plants by XRF.

Plant code		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Power (MW)		200	600	600	330	600	600	360	240
Content of oxide (wt.%)	SiO_2	38.61	40.59	49.78	51.26	53.39	48.09	53.21	42.02
	Al_2O_3	27.30	33.10	32.59	29.27	36.30	23.32	33.64	27.88
	Fe_2O_3	3.65	2.85	7.09	7.58	4.50	10.61	5.48	3.43
	CaO	18.22	13.86	5.39	6.97	1.99	13.21	2.20	16.48
	MgO	1.44	1.40	0.98	0.96	0.53	0.79	0.64	1.16
	SO_3	8.11	4.11	0.52	0.30	0.14	0.96	0.54	5.18
	TiO_2	1.17	1.45	1.33	1.25	1.32	0.88	1.39	1.06
	K_2O	0.54	0.75	0.74	1.16	0.80	0.82	1.43	0.83
	Na_2O	0.17	0.22	0.36	0.47	0.30	0.34	0.39	0.26
	P_2O_5	0.10	0.19	0.23	0.18	0.16	0.13	0.24	0.14
	Other	0.69	1.48	0.99	0.60	0.57	0.85	0.84	1.56
Mass ratio of SiO_2/Al_2O_3		1.41	1.23	1.53	1.75	1.47	2.06	1.58	1.51
Content (Fe_2O_3 + CaO)		21.87	16.71	12.48	14.55	6.49	23.82	7.68	19.91