Fuel 191 (2017) 198–203

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Improved sodium adsorption by modified kaolinite at high temperature using intercalation-exfoliation method

Xiuju Zhang [a,b], Huan Liu [a,b,*], Haoxuan Xing [a], Haiyan Li [a], Hongyun Hu [a], Aijun Li [a], Hong Yao [a,b,*]

[a] State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Department of New Energy Science and Engineering, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

HIGHLIGHTS

- Intercalation-exfoliation method is applied to modify kaolin in this study.
- Kaolin modified with KAc served the best one to capture NaCl at high temperature.
- The pore structure of kaolin was significantly developed during modification process.
- Modification provides additional adsorption sites on kaolin for sodium fixation.
- Nepheline is proved to form when the sodium is chemically fixed by modified kaolin.

ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form 10 November 2016
Accepted 21 November 2016

Keywords:
Kaolin
Intercalation-exfoliation
Sodium capture

ABSTRACT

Kaolin is one of the most widely used additives to alleviate fouling and slagging problems, which often occurred on the boilers burning coal with high sodium content. In order to improve the adsorption capacity in this condition, the intercalation-exfoliation method in material field was applied to modify kaolin. Six representative intercalation agents were selected to prepare samples, including hydrazine, urea, potassium acetate, formamide, methylformamide and dimethyl sulfoxide. Experimental results showed that both of pore volume and pore diameter were expanded through modification, which is beneficial to adsorption in physical aspect. On the other hand, the reduction of mass loss rate (from 10.6% to 6.8%), i.e. the loss of hydroxyl groups during modification process was verified, which contributed to sodium-capturing through providing more available adsorption sites. There was little difference between raw kaolin and modified kaolin with regard to XRD patterns, suggesting that the main crystal structure of kaolin remained after modification. Sodium reacted with modified kaolinite to form nepheline during adsorption process, realizing its chemical fixation. It is concluded that intercalation-exfoliation method is capable of improving the sodium-capturing capacity of kaolin at high temperature. Kaolin intercalated with potassium acetate has the most significant sodium-capturing capacity, which increased from 77 mg/g to 100 mg/g, with the adsorption efficiency reaching 100%.

1. Introduction

Zhundong coalfield, located in the east of Junggar Basin, is a promising fuel resource in China for its large reserves up to 164 Gt [1]. However, the severe fouling and slagging often occurred on the boilers burning Zhundong coal, which hindered its widespread application. [2,3]. According to the literature [4], the content of sodium in Zhundong coal ash generally exceeds 5%, far more than the recommended limit of 1% for power coals. The released sodium vapor has been proven to be a precursor of condensates such as sodium sulfate, which adhered to the heating surfaces resulting in fouling, slagging or corrosion [5–7]. It is regarded that the sodium release is one of main causes of poor boiler efficiency, hence the capture of sodium attracted the concern of many researchers.

Kaolin is often the top choice among additives to capture alkali metals at high temperature [8]. Linjewile et al. [9] investigated that clay additive rich in kaolinite was effective to control agglomeration and defluidisation during combustion of two coals from South

* Corresponding authors at: State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

E-mail addresses: huanliu@mail.hust.edu.cn (H. Liu), hyao@mail.hust.edu.cn (H. Yao).

http://dx.doi.org/10.1016/j.fuel.2016.11.067
0016-2361/

Australia. Vuthaluru [10] discovered that kaolin with a blending ratio of 2–3 wt.% effectively alleviated ash fusion problems of Victorian brown coal, which arises from high content of alkali metals. As mentioned above, Zhundong coal contained much more Na than traditional power coals. Thus in this case, either blending ratio or sodium-capturing efficiency needs to be enhanced. Unfortunately, Wei et al. [11] found that sodium content of residual ash derived from 1 g raw Zhundong coal decreased when blending ratio increased from 3% to 9%. In other words, increasing the blending ratio of kaolin and coal is not an effective method. Besides, higher blending proportion will increase transportation cost as well as the difficulty of the coal ash utilization. It is essential to improve the sodium-capturing efficiency of kaolin.

Undoubtedly, the adsorption mechanism of sodium on kaolin should be clarified before attempting to strengthen the efficiency. Kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), main component of kaolin, is a 1:1 layer aluminosilicate. Each unit layer consists of a silica tetrahedral sheet and an alumina octahedral sheet, with hydrogen bonds connecting adjacent layers [12]. In the thermal conversion process, unstable metakaolinite is formed through dehydroxylation, during which alumina octahedral coordination gradually turns into unstable tetrahedral coordination [13,14]. Subsequently, sodium reacted with metakaolinite to form sodium aluminosilicates, realizing its chemical fixation [8,13]. Above all, the formation of unstable metakaolinite is important for sodium capture process by kaolinite. Therefore, promoting the dehydroxylation reaction to generate more adsorption sites might be a promising way to improve the sodium-capturing efficiency of kaolinite.

In the field of materials science, intercalation-exfoliation is a common method to modify kaolin in polymer composites [15,16], catalyst and molecular sieve application [17,18]. Recently more attention is paid to structural improvement of kaolinite through this modification process. Cheng et al. [19] prepared kaolinite-potassium acetate complexes using solution synthesis method, and the basal spacing of kaolinite was expanded from 0.71 to 1.42 nm. M. Valášková et al. [20] investigated the effect of exfoliation on kaolinite, then the specific surface area increased with little structural degradation. The method of intercalation with organic molecule was often applied to enhance the adsorption capacity of kaolinite for heavy metals in water [21]. It demonstrates that intercalation-exfoliation method is able to improve the adsorption property of many substances at room temperature by changing the interlayer structure of kaolinite. However, there is little literature with regard to modified kaolinite adsorbing Na at high temperature.

To address this, the sodium-capturing performance of modified kaolin was firstly accessed in this study. And the adsorption mechanism was investigated by exploring porosity structure, thermogravimetric behavior, the amount of adsorption sites and the crystallographic characteristics of samples. Then a new insight into the application of kaolin additives to capture alkali metals was tried to provide through this research.

2. Experimental section

2.1. Preparation of samples

The starting material used in this study is a low ordered, high-defect kaolinite marked as Kaolin, which is directly used as additives in a power plant located in Xinjiang province. The main elemental components of Kaolin are SiO_2 and Al_2O_3, as listed in Table 1. However, problems originating from sodium, such as fouling and slagging were not effectively resolved upon using raw Kaolin. So the intercalation-exfoliation method was proposed to improve the adsorption efficiency of Kaolin. Although the impurity of Kaolin (quartz) contributes little during the modification process, owing to its very stable structure. It can be assumed that the enhancement of high-purity kaolin is possibly more significant, if this modification is effective in boosting the adsorption performance of Kaolin. Six representative intercalation agents including hydrazine, urea, potassium acetate, formamide, methylformamide and dimethyl sulfoxide were chosen in the sample preparation procedure [22–27]. The corresponding modified kaolin samples are labeled as K-N_2H_4, K-Urea, K-KAc, K-MF, K-NMF and K-DMSO, respectively.

The modification method can be briefly classified into two parts, namely, intercalation process and exfoliation process as depicted in Fig. 1. Specifically, the intercalation process varied with the state of intercalation agents, while the exfoliation for total six modified samples was realized by ultrasonic wave treatment at 50 °C for 30 min. For intercalation agents in solid state (e.g. urea and potassium acetate), a 20-g mixture of agent and kaolin (mass ratio of 1:1) was grounded in a planetary ball mill (400 rpm) for 1 h, and was subsequently placed at room temperature for 48 h, thus ensuring the complete reaction of agents and kaolin. Then the intercalation process ended with the centrifugation (three times) and drying. For the remaining agents in liquid state, intercalation process was achieved by treating the mixture of agents and kaolin in a shaker and subsequent centrifugal machine.

2.2. Adsorption experiments

In view of the fact that sodium in Zhundong coals mainly exists in water-soluble state [28], besides, NaCl was proved to be the primary sodium species in the flue gas [29], the alkali source was specified as sodium chloride during the adsorption process. The adsorption experiments were conducted by treating the mixture of kaolin samples and NaCl (molar ratio of 1:1) at 1000 °C for 2 h. Then the capture capacity of seven kaolin samples (six modified kaolin and raw kaolin) was evaluated by quantitatively comparing the sodium content of adsorbed products. Through sulfuric acid washing (with 0.5 M H_2SO_4) and microwave digestion, the soluble and insoluble sodium of adsorbed products was sequentially extracted and the precise concentration was tested by microwave plasma atomic emission spectrometer (MP-AES, Agilent 4200).

2.3. Characterization of samples

A series of characterization methods were adopted to investigate the effect of modification on kaolin samples, including porosity structure, thermogravimetric behavior, the functional groups as well as the mineralogical characteristics. According to above tests and analysis, a possible adsorption mechanism of sodium on modified kaolin may be proposed.

The nitrogen adsorption/desorption measurements were conducted by ASAP2020 (Micromeritics Instrument) to find out the effects of modification on porosity structure. The thermogravimet-

Table 1
Element composition of Kaolin.

Composition	SiO_2	Al_2O_3	SO_3	K_2O	TiO_2	Fe_2O_3	CaO
Wt.%	68.7	18.6	4.1	2.5	2.3	2.1	1.3