Fuel 237 (2019) 170–177

Contents lists available at ScienceDirect

Fuel

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

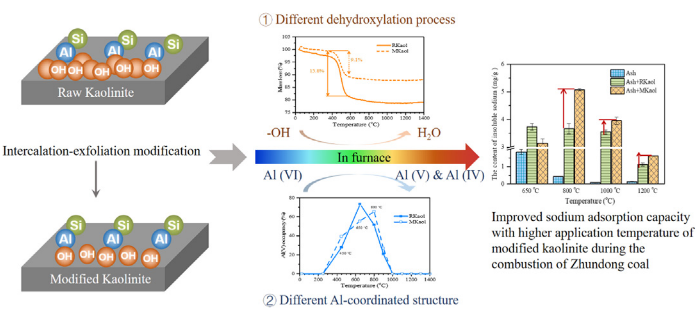
Full Length Article

Correlations between the sodium adsorption capacity and the thermal behavior of modified kaolinite during the combustion of Zhundong coal

Xiuju Zhang[a], Huan Liu[a,b,*], Haoxuan Xing[a], Geyi Wang[a], Hongping Deng[a], Hongyun Hu[a], Xian Li[a], Hong Yao[a]

[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

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Kaolinite
Modification
Sodium adsorption
Thermal behavior
Coal combustion

ABSTRACT

Kaolin is often utilized as an additive to relieve fouling and slagging problems in boilers. In a previous work of the authors it was successfully employed the modification of intercalation-exfoliation method to improve the adsorption capacity of kaolinite at 1000 °C, and this work aimed to investigate the best adsorption performance and corresponding application temperature of modified kaolinite at different temperatures. The adsorption experiment with Zhundong coal was conducted from 650 °C to 1200 °C. The thermal behavior of modified kaolinite was characterized over a wide temperature range to reveal the mechanism from the perspective of structural change. Results showed that modified kaolinite exhibited the best adsorption performance at 800 °C, with the adsorption capacity increasing by 39% after modification. The effect of modification on kaolin was also reflected in the thermal behavior. About 43% of the hydroxyl groups were removed via modification, the amount of mullite above 1100 °C approximately decreased by 38%, and the expulsion of crystalline SiO_2 was totally inhibited by modification, suggesting that modification affected the reconstruction of Si/Al-related compounds at high temperature. In addition, the enhanced yield of unsaturated Al (V) at 800 °C after modification was totally consistent with the improved adsorption capacity of modified kaolinite at 800 °C. It is concluded that kaolinite can be used at higher temperature with improved adsorption capacity through a modification of intercalation-exfoliation method, which was presumably related to the greater content of 5-coordinated Al in modified kaolinite. Moreover, this discovery indicated that Al (V) content might be a useful index for the selection of various aluminasilicates as efficient adsorbents in furnace.

* Corresponding author at: State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.
E-mail address: huanliu@mail.hust.edu.cn (H. Liu).

https://doi.org/10.1016/j.fuel.2018.09.121
Received 12 June 2018; Received in revised form 17 September 2018; Accepted 24 September 2018
0016-2361/

Table 1
Elemental composition of kaolin samples.

Samples	SiO_2	Al_2O_3	SO_3	K_2O	Fe_2O_3	P_2O_5	TiO_2	Others
Rkaol	52.2	43.1	2.6	0.6	0.5	0.4	0.2	0.4
Mkaol	51.9	42.8	2.7	1.3	0.5	0.4	0.3	0.1

Table 2
Proximate and ultimate analyses of Zhundong coal sample.

Proximate analysis (wt%, ad)				Ultimate analysis (wt%, daf)				
Moisture	Volatile	Ash	Fixed Carbon	C	H	N	S	O[a]
6.04	43.31	6.14	44.52	60.91	5.25	0.56	0.14	33.14

[a] Calculated by difference.

1. Introduction

Owing to the rapid consumption of conventional fossil fuels of high quality, there is an urgent demand for the clean and efficient utilization of relatively low-grade fuels. Zhundong coal has attracted much attention because of huge reserves and some good combustion characteristics [1,2]. However, it was also notorious for its high sodium content [3–6]. During the combustion process of Zhundong coal, fouling and slagging were common phenomenon that had adverse effects on boiler operation [7,8]. Many scholars investigated the related growth mechanism and proposed that the massive release of sodium played an important role [9,10]. Adding adsorbents into the furnace, mainly the clay minerals, is a frequently employed method for its easy operability and good economical efficiency.

Kaolin has been widely identified as an effective sorbent capturing alkali metals in coal-fired boilers [11–14]. Kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), the main component of kaolin, is a kind of two-layer aluminosilicate clay with a basic unite layer consisting of a sheet of tetrahedral silica and an octahedral sheet coordinated to Al^{3+} [15]. The mechanism of kaolinite adsorbing alkali metals in the furnace can be summarized as follows. In the range of 450–550 °C, kaolinite is gradually converted into amorphous metakaolinite through dehydroxylation, which is the intermediate product during the thermal decomposition of kaolinite [16]. Due to the loss of hydroxyl groups, metakaolinite is unsaturated-coordinated and alkali metals are likely to occupy the vacant positions, realizing the chemical adsorption of alkali metals through the formation of alkali aluminosilicate [17]. As the temperature continues to rise, metakaolinite finally turns into crystalline mullite above 1100 °C, which is widely regarded as a mineral with little adsorption capacity [18]. At higher temperatures, cristobalite is generated through the expulsion of some silica and the alumina reverts back to octahedral coordination [17,18]. It can be easily seen that the process of kaolin capturing alkali metals in furnace is closely related to the thermal behavior of kaolinite.

In our former work [19], we firstly employed the intercalation-exfoliation method in mineral material science to modify kaolinite and successfully boosted the performance of kaolinite adsorbing alkali metals at 1000 °C. Test results indicated that the improvement of adsorption capacity at this temperature was due to the effect of modification on the structure of kaolinite. However, the best adsorption performance of modified kaolinite at different temperatures is still unclear, which directly determines the application temperature of kaolinite in boilers. Finding out how modification affected the structural change of kaolinite at different temperatures, i.e. thermal behavior of modified kaolinite, helps reveal relevant mechanisms.

The discussion above raised a fundamental question: can a connection be made between the adsorption capacity and thermal conversion process of kaolinite? If detailed answers can be found, then they can potentially lead to the convenient selection among various aluminasilicates used as efficient sorbents in boilers. Therefore, in this study, the adsorption capacity of kaolinite before and after modification was quantified by adding these two adsorbents during the combustion of Zhundong coal at different temperatures. In order to further reveal relevant mechanisms, the effect of modification on the thermal behavior was also studied by outlining the dehydroxylation process, the transformation of functional groups, phase transition and coordination condition (both Al and Si) during the heat treatment process. Moreover, the correlation between thermal behavior and adsorption capacity of modified kaolinite was identified in this study.

2. Experimental section

2.1. The preparation of samples

Raw kaolin (labeled as RKaol) used in this study was highly purified. The modified kaolin (labeled as MKaol) was prepared by intercalation-exfoliation method, which has been described in detail before [19]. The modification procedure could be briefly summarized as intercalation process and exfoliation process. Intercalation was realized by treating the mixture of kaolinite and intercalation agents (mass ratio of 1:1) at 50 °C for 48 h. Exfoliation process was achieved by ultrasound treating the intercalated compound at 50 °C for 30 min. The results of X-ray fluorescence (XRF) analyses are summarized in Table 1, and it could

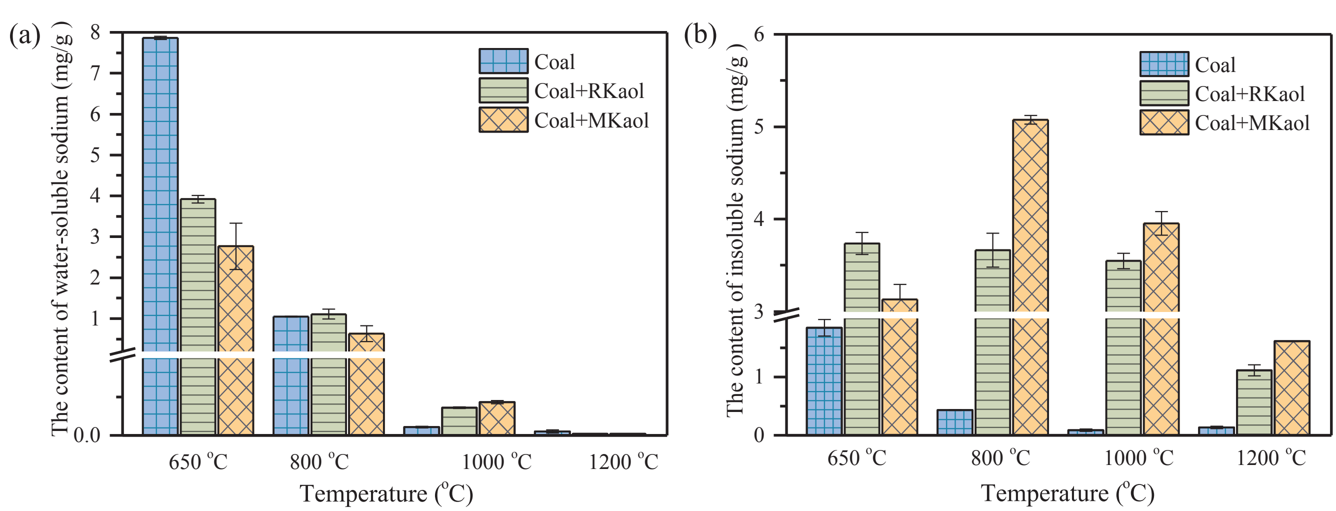


Fig. 1. Sodium adsorption capacity of RKaol and MKaol during the combustion of Zhundong coal: (a) water-soluble sodium content (b) insoluble sodium content.