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

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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%.

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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 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
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 (Al2O3·2SiO2·2H2O), 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 SiO2 and Al2O3, 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-N2H4, 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 H2SO4) 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 4100).

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-
Ric analysis (TGA) was carried out in Pyris1 TGA instrument (PerkinElmer Instruments), and the samples were heated from room temperature to 1100 °C at a heating rate of 20 °C/min. The Fourier transform infrared (FTIR) patterns between 4000 and 400 cm\(^{-1}\) were recorded using a VERTEX 70 Fourier infrared spectrometer produced by Bruker Corporation, and the semi-quantitative data was obtained by a precise control of the mass ratio (1 wt.%) of samples and KBr pellets. The X-ray diffraction (XRD) curves were collected on a Japan Shimadzu XRD-7000S X-ray diffractometer (40 kV, 30 mA) with Cu irradiation at the scanning rate of 5 °/min in the 2\(^\theta\) range of 5–65°.

3. Results and discussion

3.1. Adsorption performance of different samples

The adsorption performance of seven samples can be assessed by a comparison of sodium content in absorbed products. Particularly, the insoluble sodium indicates that the sodium was fixed in kaolin in the form of sodium aluminosilicate [8]. While the soluble portion represents the physically absorbed sodium species, possibly with some non-volatile NaCl remained in the mixture. Basically, a desired sorbent may show high loading capacity as well as high adsorption efficiency [30]. Fig. 2(a) depicts the adsorption efficiency of seven samples and Fig. 2(b) focused on the loading capacity. The percentage of insoluble sodium in raw Kaolin was 55%, suggesting that almost half of the sodium was fixed in aluminosilicate before modification. For six modified sorbents, either soluble or insoluble sodium was improved, and the degree of promotion varied from 5% to 20% in spite of the existence of inert component (quartz). So a better adsorption capacity is likely to achieve for modified kaolin with higher purity. It is particularly conspicuous that insoluble sodium in K-KAc accounted for 83%, with the sodium-loading capacity increasing from 77 mg/g to 100 mg/g. So it can be considered that the modified kaolin samples performed much better than raw kaolin, i.e. intercalation-exfoliation method is able to enhance the adsorption property of kaolin at high temperature. However, it is not clear that how modification affects the adsorption performance of kaolin, so the best performing sample (K-KAc) was selected as a representative to further investigate the sodium-capturing mechanism by modified kaolin.

3.2. Porosity structure analysis

In general, materials with a large volume and many large pores are more likely to be excellent sorbents, which are crucial for the mass transportation of gaseous phases [31]. The BET specific surface area and pore volume are listed in Table 2, and it is shown that pore volume was expanded after modification. It is indicated that intercalation-exfoliation method developed the porosity structure of kaolin, which is beneficial to sorbents in physical aspect.

![Flowchart for the preparation of samples.](image)

Fig. 1. The flowchart for the preparation of samples.

![Sodium-capturing performance of seven kaolin samples at 1000 °C.](image)

Fig. 2. Sodium-capturing performance of seven kaolin samples at 1000 °C (a) adsorption efficiency (b) sodium loading capacity.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET specific surface area/m(^2) g(^{-1})</th>
<th>Pore volume/cm(^3) g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>5.83</td>
<td>0.029</td>
</tr>
<tr>
<td>K-KAc</td>
<td>5.53</td>
<td>0.035</td>
</tr>
</tbody>
</table>
On the other hand, the pore size plays a crucial role in adsorbate entering into sorbents. It is generally believed that, micropores are pores with a diameter below 2 nm, macropores are pores with a diameter over 50 nm, and pores with a diameter between this range are referred to as mesopores [32]. Fig. 3 shows the pore size distribution of Kaolin and K-KAc. Both samples have a bimodal pore size distribution, with two apexes at 6 nm, 80 nm, respectively. It is clear that pores distributed around the first apex decreased, meanwhile pores with a larger diameter increased impressively. After modification, the average pore diameter of kaolin increased from 15.7 nm to 23.3 nm. Therefore it is much easier for sodium to get the access to kaolin, i.e. expansion of porosity structure is one of the explanations of better adsorption performance.

3.3. Thermal analysis

The thermal behaviors of Kaolin and K-KAc were possessed by thermogravimetric analysis. Only one mass loss peak is observed in Fig. 4(a) and (b), which is attributed to the water loss of kaolinite [14]. The widely believed explanation for the mass reduction of kaolinite can be simplified as dehydroxylation, which is referred that a water molecule is formed by the connection of one proton-transferred hydroxyl group with another hydroxyl group. Meanwhile the kaolinite changed into metakaolinite. The reaction process can be demonstrated as Eqs. (1)–(3) [14].

\[
\begin{align*}
\text{OH}^– &\rightarrow \text{H}^+ + \text{O}^2^- \quad (1) \\
\text{H}^+ + \text{OH}^- &\rightarrow \text{H}_2\text{O} \quad (2) \\
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} &\rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O} \quad (3)
\end{align*}
\]

It is noteworthy that the weight loss rate of both samples were 10.6% and 6.8%, respectively, suggesting that the weight loss rate reduced by 3.8% during modification process with potassium acetate. This indicates that the reduction of mass loss rate may be ascribed to the decline of hydroxyl groups in quantity, which is to be directly verified by FTIR test.

3.4. FTIR spectroscopic analysis

Fourier transform infrared spectroscopy patterns are recorded in Fig. 5. Firstly, no significant shifts can be observed in the spectrum of Kaolin and K-KAc, and there is no vibration band for potassium acetate. It is indicated that layer structure of kaolinite remained after modification and inserting molecules were removed completely.

The hydroxyl groups on Al-coordinated sheets divide into two parts, inner surface hydroxyls facing to adjacent layers and inner hydroxyl groups towards intralayer cavity [33]. The bands at 3696, 3668 and 3654 cm\(^{-1}\) are attributed to OH stretching modes of inner surface hydroxyl groups, and the 3620 cm\(^{-1}\) bands belong to inner hydroxyl groups [19]. In the case of K-KAc, the peaks corresponding to above four wavenumbers are lower than that of Kaolin, reflecting that hydroxyl groups indeed decrease after modification and the deduction of thermogravimetric analysis was confirmed. According to the research of Gale and Wendt [13], metal vapors may react with the Al-coordinated surfaces of metakaolinite. So it can be deduced that active sites of adsorption are located in the activated Al-coordinated surfaces, which were
formed through the loss of hydroxyl groups during modification process.

The bands at 1101 cm\(^{-1}\) (Si connects with apical oxygen in the same plane with OH), 1033 and 1009 cm\(^{-1}\) (Si bonds with the O in the plane) are assigned to stretching vibration mode of Si–O bonds [34]. It is discovered that peak at 1101 cm\(^{-1}\) became lower with peaks at 1033 cm\(^{-1}\) and 1009 cm\(^{-1}\) unchanged, suggesting that hydrogen bonds between apical oxygen atoms and potassium acetate were broken and therefore the amount of silicon-oxygen bonds decreased. Stretching vibration bands at 937 cm\(^{-1}\) and 914 cm\(^{-1}\) are noticed to decrease in the Al–O region. In a similar manner, plenty of hydrogen bonds were formed during intercalation process, linking hydrogen atoms in alumina octahedral sheet with potassium acetate. And the subsequent fracture of hydrogen bonds during exfoliation process resulted in the reduction of Al\(^{3+}\)–O–H bonds.

When the K-KAc samples were calcined with NaCl at high temperature, the higher frequency bands (3695, 3668, 3654 and 3620 cm\(^{-1}\)) and bands at 937, 914 cm\(^{-1}\) disappeared while adsorption peaks in Si-O region were still observed, which reflected that the structure of alumina octahedral sheet became disorderly with silica tetrahedral sheet unchanged.

3.5. X-ray diffraction analysis

To find out the effect of modification on crystal structure and the reaction product of kaolinite capturing sodium chloride, the XRD tests were conducted on modified and calcined samples (see Fig. 6). According to the pattern of raw kaolin, it is clear that the main component is indeed kaolinite while quartz is the main impurity. Compared with Kaolin, the diffraction peaks of K-KAc have no significant shifts, suggesting that the main crystal structure of Kaolin remained after modification. In the curve of calcined kaolin sample, the peaks attributed to kaolinite vanished while a new species nepheline appeared. Therefore, the adsorption mechanism of modified kaolin is the same as that of kaolin. Similar to the results of previous research [8], modified kaolin reacted with absorbed NaCl and the product was nepheline. The reaction equation may be described chemically as follows.

\[
2\text{NaCl} + \text{H}_2\text{O} + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{HCl} \quad (4)
\]

3.6. The possible mechanism of modification

A general understanding of modified kaolin adsorbing sodium chloride at high temperature was obtained through a series of tests and analysis. Based on above results, the mechanism of modification on kaolin using intercalation-exfoliation method and adsorption of sodium by modified kaolin was deduced in Fig. 7. Corresponding to the modification process separated into two parts-intercalation and exfoliation, there were three kinds of kaolinite including raw kaolin, the kaolin after intercalation process and the modified kaolin. It is easy to find that the unit layer consists of Si-coordinated tetrahedral sheet and Al-coordinated octahedral sheet, with hydrogen bonds connecting adjacent layers. In intercalation process, the intercalation agents inserted between layers. Taking potassium acetate as an example, hydrogen bonds were formed between the hydroxyl groups on the Al-coordinated sheets and acetate anions and thus the interlayer spacing was expanded [19]. Afterwards, the acetate anions fell off from kaolinite due to the ultrasonic wave and centrifugation treatment in exfoliation process. Then the newly formed hydrogen bonds were bound to break and consequently the amount of hydroxyl groups reduced, which could provide sites for sodium-capturing at high temperature.
temperature. Therefore, the mechanism of intercalation-exfoliation depicted in Fig. 7 is a possible approach to improve the adsorption performance of kaolinite through a combination of two effects, i.e. the expansion of interlayer spacing and the loss of hydroxyl groups during modification.

4. Conclusions

In this research, six representative intercalation agents were selected to prepare modified kaolin samples using the intercalation-exfoliation method. Sodium chloride was the alkali source and kaolin samples were the sorbents in adsorption experiments. After evaluating the adsorption performance of all samples, the mechanism of improved adsorption by modified kaolin was discussed. The main conclusions are as follows:

(1) The intercalation-exfoliation method was proven to improve the adsorption performance of kaolinite at high temperatures. Under the experimental conditions described in this article, K-KAc (kaolinite intercalated with potassium acetate) has the best adsorption capacity. During this run, sodium was almost completely absorbed with the sodium-capturing capability increasing from 77 mg/g to 100 mg/g.

(2) According to the analysis of K-KAc, the intercalation-exfoliation method increased the chance to enter the kaolin by doubling the pore volume as well as increasing the average pore size from 15.7 nm to 23.3 nm. Combined with the reduction of hydroxyl groups during modification process, more sodium was chemically fixed by forming nepheline during the adsorption process.

Acknowledgments

The authors gratefully acknowledge the financial supports provided by International Science & Technology Cooperation Program of China (2015DFA60410) and National Natural Science Foundation of China (51506064, 51606075). A portion of experiment was conducted with the facilities in Analytical and Testing Center of Huazhong University of Science and Technology.

References