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Research Paper

Effect of $CaCO_3$ addition on ash sintering behaviour during K_2CO_3 catalysed steam gasification of a Chinese lignite

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HIGHLIGHTS

- K_2CO_3 decreased ash sintering temperature and enhanced ash melting in gasification.
- $CaCO_3$ addition enhanced ash melting and lowered ash sintering temperatures.
- $CaCO_3$ reacted with SiO_2 to form fluxing phases and amorphous materials.
- $CaCO_3$ addition inhibited the potassium aluminium silicate formation.
- $CaCO_3$ addition preserved the catalytic activity of potassium.

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ABSTRACT

The ash sintering behaviour of a Chinese lignite (LLI) with different amounts of $CaCO_3$ addition during K_2CO_3-catalysed gasification was investigated. 0–10 wt% K_2CO_3 was doped into the lignite for catalytic gasification, and $CaCO_3$ was added into the K_2CO_3-doped samples, varying in the range of 0–20 wt% relative to the lignite, for understanding its impact on ash sintering and catalytic gasification activity. Ash samples were prepared by completely gasifying the lignite samples with steam in a fixed-bed catalytic gasification system operating at 1073 K and atmospheric pressure. Sintering temperature, mineralogy and morphology of the ash samples thus obtained were determined using a pressure-drop sintering device, XRD and SEM-EDS, respectively. The results showed that the ash sintering temperature decreased as the K_2CO_3 addition increased, indicating that K_2CO_3 as the catalyst for gasification would promote ash sintering. SEM imaging analysis showed that all the ash samples from LLI with K_2CO_3 addition were composed of agglomerated particles with smooth surfaces, indicating the ashes had incurred partial melting. The degree of melting became more apparent as the K_2CO_3 addition ratio increased. These molten phases were identified as K-bearing arcanite and kaliophilite, which contributed to the formation of liquid phases at lower temperatures, resulting in lowered ash sintering temperatures. It was also revealed that the addition of $CaCO_3$ decreased the sintering temperatures of ash samples, indicating that the ash sintering was further enhanced by $CaCO_3$ addition. The surface texture of the ash particles, with the same K_2CO_3 addition level, changed from slightly melting to seriously melting or fusion as the $CaCO_3$ addition ratio increased. This is because the addition of $CaCO_3$ suppressed the formation of refractory silicon oxide and generated more fluxing feldspars and lime as well as the amorphous phases. However, the addition of $CaCO_3$ inhibited the formation of water-insoluble kaliophilite and thus helped preserve the catalytic activity of K_2CO_3, promoting K_2CO_3 catalysed gasification.

1. Introduction

Coal gasification is a clean method for the production of gas that can be used for power and/or heat generation or as a synthesis

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precursor for liquid transportation fuel production [1–12]. Pursuing higher gasification rates at relatively lower reaction temperatures, some alkali, alkali-earth, and iron-based catalysts, particularly potassium carbonate (K_2CO_3), have been trialled as catalysts for coal gasification [5,13–15]. However, it was reported that potassium could interact with other minerals and form low melting point eutectics [16], leading to even severer ash sintering [17]. Ash sintering plays an important role in the entire ash deposition process, especially in the initial phase of the deposit growth. Besides, the mineral matter in coal such as kaolinite would react with potassium to form water insoluble potassium aluminium silicate, resulting in the deactivation of the potassium catalyst for coal gasification [7,8].

In an effort to mitigate potassium deactivation, different strategies have been proposed such as finding a substitute for potassium catalyst, removing the mineral matter in coal, or using additives to inhibit the interaction between potassium and the mineral matter in coal [7,8]. Jiang et al. pointed out that calcium-bearing additives were effective in promoting catalytic activity of K_2CO_3 by inhibiting the interactions between K and aluminium silicate during K_2CO_3-catalysed gasification [18,7]. However, Ca-bearing minerals such as $CaCO_3$, CaO, and $Ca(OH)_2$ are also known fluxing minerals during combustion, which would decrease the ash fusion temperatures unless its content was sufficiently high. Song et al. [19] studied the effect of CaO addition on the ash fusion temperature and found that the ash fusion temperatures decreased as the CaO addition ratio was increased up to 35 wt%. Thus, although the calcium additives can increase the gasification rate of coal, even severer and more problematic ash sintering and bed agglomeration may also occur in the reactor [20]. In order to effectively utilise $CaCO_3$ as an additive to prevent potassium deactivation, it is essential to understand the effect of $CaCO_3$ on the mineral interactions and sintering behaviour of the generated ash during K_2CO_3-catalysed gasification. However, studies of the ash sintering characteristics and mineral interactions during K_2CO_3-catalysed gasification of lignite with $CaCO_3$ addition are scarce.

Against this backdrop, this work was aimed to comprehend the mineral interactions and the sintering behaviour of the ash with the addition of $CaCO_3$ during K_2CO_3-catalysed gasification. A Chinese lignite was firstly doped with 0–10 wt% K_2CO_3, after which $CaCO_3$ was added into the K_2CO_3-doped lignite samples varying in the range of 0–20 wt%. The coal samples thus prepared were then gasified in a fixed bed reactor and the ash samples were collected and analysed for their sintering temperatures, ash mineralogy and morphology. It is expected that the results would shed lights upon how $CaCO_3$ interacts with K_2CO_3 or other minerals and affects the ash sintering behaviour.

2. Experimental

2.1. Materials

A lignite from Yili coal mine in China, referred to as LLI, was employed in the present work. The lignite sample was air dried, pulverized and sieved to less than 200 μm in size. The proximate and ultimate analyses of the lignite were determined following the Chinese standards GB/T212-2008 and GB/T476-2008, respectively. The lignite ash was prepared by heating the lignite sample in air in a muffle furnace from room temperature to 1088 K and hold for 2 h (GB/T212-2008). The ash chemistry was then determined using X-ray fluorescence (XRF), and ash fusion temperatures were measured according to the Chinese standard GB219-2008. The results are shown in Table 1.

The K_2CO_3-doped lignite samples were prepared by adding K_2CO_3 to the lignite sample using an impregnation method [21,22] so that the mass fractions of K_2CO_3 in the samples were 0%, 1%, 5%, and 10%. In order to investigate the effect of $CaCO_3$ on the ash sintering behaviour during K_2CO_3-catalysed gasification, $CaCO_3$ was then added to the K_2CO_3-doped lignite samples, with $CaCO_3$ mass fractions of 0%, 5%, 10% and 20% relative to the lignite. After thorough mixing by vigorous stirring, the samples were dried in an oven at 378 K for 24 h.

2.2. Catalytic gasification

Ash samples from catalytic gasification of the above LLI samples were prepared. A schematic diagram of the catalytic gasification system is shown in Fig. 1. The fixed-bed gasification reactor (500 mm in length, 50 mm o.d. and 36 mm i.d.) was heated in a vertical electric furnace. During experimentation, a sample of approximately 4 g was placed in the gasification reactor. A flow rate of 1000 ml h^{-1} N_2 was then induced into the reactor and the furnace temperature was increased to 1073 K and maintained for 5 min for the lignite to undergo pyrolysis before the gasification process. Water was then pumped into the reactor from the bottom to provide a steam atmosphere at a flow rate of 500 ml h^{-1}. The N_2 carrier gas with the same volume flow rate as the steam was used to facilitate water evaporation and provide consistent steam atmosphere throughout the reactor. The whole system was maintained at 1073 K for 4 h to ensure complete gasification of the sample.

2.3. Ash sintering temperature measurement

The ash samples were subjected to measurement of ash sintering temperature in N_2 atmosphere using a pressure-drop sintering device. A schematic diagram of the pressure-drop sintering device is shown in Fig. 2 [21,22]. Briefly, an ash pellet of approximately 0.4 g produced from gasification was compacted into an ash pellet in the middle of an alumina mullite tube which was then inserted into an electric furnace. A stream of N_2 was passed through the pellet at a flow rate of 240 ml h^{-1}. The furnace was heated from ambient temperature at a heating rate of 480 K h^{-1} and the pressure-drop across the pellet as a function of temperature was recorded. In the current experimentation, the ash sintering temperature was defined as the temperature when the pressure-drop across the pellet reached to the maximum [23,24]. The sintering temperatures determined using this technique had a repeatability of ±10 K.

2.4. XRD and SEM-EDS analysis

The morphological characteristics of the ash particles and spot composition analysis were performed using a TESCAN-Vega-3-XM scanning electronic microscopy (SEM) aided with an Oxford X-ray energy dispersive spectroscopy (EDS). The mineralogical characteristics of the ash samples were identified using a PANalytical X-ray diffractometer with copper Kα radiation. The qualitative powder XRD analysis was performed with an accelerating voltage of 40 kV, a current of 40 mA at a scanning speed of $0.0847^\circ\ s^{-1}$ between 5° and 70° of the 2θ.

3. Results and discussion

3.1. Ash sintering temperature

Fig. 3 shows the ash sintering temperatures of the various LLI lignite samples with different $CaCO_3$ addition ratio during the K_2CO_3 catalysed gasification. It is obvious that, regardless of K_2CO_3 concentration, the sintering temperature of the ash sample decreased as the amount of $CaCO_3$ increased from 0% to 20%. This