



Calcium-promoted catalytic activity of potassium carbonate for gasification of coal char: The synergistic effect unrelated to mineral matter in coal



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HIGHLIGHTS

- Calcium additive synergized with K_2CO_3 towards gasification of ash-free chars.
- A main mechanism for the synergistic effect (SE) was the formation of a eutectic.
- Another mechanism for SE was due to the organic binding of calcium on char.

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ABSTRACT

The purpose of this work is to investigate the synergistic catalysis between calcium species and K_2CO_3 for the char gasification. Graphite and four mineral-free chars including an anthracite coal char, a bituminous coal char, a lignite coal char and a pine wood char were gasified at 750 °C in a stream of steam/argon under atmospheric pressure. It was found that each of three calcium species ($Ca(OH)_2$, $Ca(CH_3COO)_2$ or $Ca(Ac)_2$, and $CaCO_3$) synergistically promoted the catalytic activity of K_2CO_3 for the gasification of all samples, and the extent of promotion was dependent on calcium species and carbon or char samples. The formation of a eutectic from the calcium species/ K_2CO_3 catalyst was proved to be an important mechanism for its better catalytic effect. The presence of the organically bound calcium on the char was also likely to be responsible for the promoted catalytic gasification.

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1. Introduction

Catalytic coal gasification has long been the subject of a large number of researches in the field of coal conversion [1–14]. It is well known that K_2CO_3 , although a superior catalyst for coal gasification, easily suffers the deactivation because of the interaction with acidic minerals in coal. In our companion papers [15–18], renewed interests have been directed to dealing with the catalytic deactivation problem. It was found that the addition of a cheaper additive, $Ca(OH)_2$, to coal promoted the catalytic activity of K_2CO_3 for char gasification [15]. The extent of promotion varied depending on coal type, especially on the content of kaolin in coal [16]. For kaolin-rich coals, the promoting effect was quite striking. In the gasification of high-sulfur coal, the addition of $Ca(OH)_2$ was favorable for the formation of K_2SO_4 , along with the suppressed transformation of K_2CO_3 to a water-insoluble and catalytically

inactive component [17]. Apart from $Ca(OH)_2$, $Ca(Ac)_2$ and $CaCO_3$ were also proved positive in the promoting effect, but $CaCO_3$ showed a relative weakness [16]. Moreover, it was observed that the impregnation way to add $Ca(OH)_2$ to coal was remarkably better than the common mixing way [18].

In the light of the studies aforementioned, the mechanisms for the calcium-promoted catalytic activity of K_2CO_3 have been considered in two broad respects. One mechanism is related by the deactivation of K_2CO_3 to the minerals present in coal. Calcium additive acts as a deterrent to the reaction of K_2CO_3 with acidic minerals such as kaolin in coal by way of passivating the reactivity of the minerals. In a later investigation of model reactions [19], it was confirmed that interaction indeed occurred between $Ca(OH)_2$ and kaolinite at a temperature much lower than that needed for the bulk reaction to afford crystalline calcium aluminosilicate or even at room temperature. The addition of $Ca(OH)_2$ to kaolinite by impregnation appreciably facilitated this interaction. In contrast, $CaCO_3$ exhibited little affinity to kaolinite. Another mechanism may have nothing to do with mineral matter present in

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coal. A finding revealed early by Pereira et al. [20,21] from gasification of graphite and several chars was that bimetallic oxides (KCaO_x) was more catalytically active than either mono-metallic oxide. KCaO_x was morphologically observed to be homogeneously dispersed on graphite, which, by the catalytic action, was gasified in an edge recession rather than a channeling mode. Therefore, it was postulated that a mineral-unrelated synergy between calcium additive and K_2CO_3 also contributed to the calcium-promoted catalytic gasification of coal char. However, no direct evidence underpinned this postulation because the issue was complicated in the presence of mineral matter in coal. The aim of this study is, hence, to address whether and how calcium additives catalytically co-functions with K_2CO_3 in steam gasification of varying mineral-free chars.

2. Experimental

2.1. Preparation of char

Three Chinese coals of different ranks including an anthracite coal (A coal), a bituminous coal (B coal), and a lignite coal (L coal) as well as a pine wood sample and a commodity of graphite were used in this study. The proximate and ultimate analyses of three coals and the pine wood are shown in Table 1. The graphite sample had a purity of carbon greater than 99.9% and a content of ash smaller than 0.15%.

It could be seen from Table 1 that all three coals were enriched with mineral matter. To remove mineral matter from coal, staged leaching was carried out. Coal was first leached with 5 mol/L HCl at 50–60 °C for 60 min, then leached with a dilute HNO_3 solution (1:7 v/v) at boiling temperature for 30 min, then leached with 8.4 mol/L HF at 70 °C for 360 min, and finally washed with excess distilled water to neutrality. For A coal, the HF-leaching step was repeated once. The demineralized coal sample was dried at 105 °C. After the sequential leaching and drying, the ash contents in coal decreased finally to 0.20%, 0.19%, and 0.48%, respectively, for A coal, B coal, and L coal. Since the pine wood sample was low in the content of ash, it was not subjected to the demineralization.

The char sample was prepared by pyrolysis of demineralized coal sample or pine wood in a tubular reactor under a stream of argon. The pyrolysis experiment was carried out under a fixed condition (heating rate, 10 °C/min; the final temperature, 750 °C; holding time, 30 min), unless stated otherwise. After cooling down, the char was taken out, and then ground and sieved to a powder with the particle size of smaller than 0.15 mm. The char samples were stored in sealed bottles. Four chars produced from A coal, B coal, L coal, and pine wood are named A char, B char, L char, and P char, respectively, in the following sections.

2.2. Char gasification

Gasification experiment was carried out in a tubular fixed-bed reactor under a stream of steam/argon. The details about the

experiments were described elsewhere [22]. In the case of using K_2CO_3 alone as a catalyst, the char sample was mixed with K_2CO_3 using agate mortar and pestle, prior to gasification. In the case of using calcium species/ K_2CO_3 as a catalyst, the char sample was first mixed with calcium species and then with K_2CO_3 in the same manner. In each gasification experiment, about 0.2 g of the mixture of char and catalyst was thinly spread on a platinum boat, and then heated in the reactor at 10 °C/min from room temperature to 750 °C under a stream of argon (500 mL/min). As soon as the temperature was raised to 750 °C, the argon stream was switched to a steam/argon stream to start the steam gasification. The partial steam pressure (the ratio of steam pressure to atmospheric pressure) was 0.5 ± 0.02 . Steam in the off-gas was completely removed through an ice-cooled condenser followed by a moisture trap. The major gases (CO_2 , CO and CH_4) were measured online with a rapid GC (Agilent Micro 3000) which used helium as a carrier gas. H_2 was determined with a GC (Agilent 6820) which used argon as a carrier gas, by collecting the gaseous product with gas bags.

2.3. Other analyses

Calcium K-edge X-ray absorption near edge structure (XANES) analysis was implemented on beamline 4B7A at Beijing Synchrotron Radiation Facility (BSRF). Calcium K-edge XANES spectra of all chars and reference samples were obtained using total electron yield (TEY) mode. The absolute energy position of the calcium K-edge white line was taken at 4045.3 eV. The spectra were normalized and then quantified by the least squares fit using a linear combination of the spectra of all reference compounds by means of Athena program package [23]. The reference calcium compounds used in the study included calcium sulfate (CaSO_4), calcium carbonate (CaCO_3), calcium oxide (CaO), calcium hydroxide (Ca(OH)_2), calcium sulfide (CaS), and calcium acetate (Ca(Ac)_2).

Elemental analyses of coal, pine wood and char samples were carried out with the use of an Elementar Vario EL III elemental analyzer. X-ray diffraction analysis was performed on a Rigaku D/max 2550VB/PC diffractometer. Scanning electron microscopy (SEM) was implemented on a modeled JEOL JSM-6360LV scanning electron microscope. Thermogravimetry and differential scanning calorimetry (TG-DSC) was conducted with the use of a METTLER TOLEDO TGA/DSC instrument.

3. Results and discussion

3.1. Verifying the synergistic effect

Fig. 1 shows the release rates of major gases and carbon conversion versus the heating time obtained from the gasification of A char using K_2CO_3 alone or calcium species/ K_2CO_3 as a catalyst, where three calcium species Ca(OH)_2 , Ca(Ac)_2 , and CaCO_3 are examined, with the loadings that are intended to guarantee the equal amount of calcium added in the mixture. All calcium additive or K_2CO_3 loadings are represented on the basis of the mixture. The gas release rate is expressed as the molar numbers of a gas released per minute based on the carbon mass in char. The carbon conversion is defined as the cumulative amount of carbon released as three carbon-containing gases (CO_2 , CO and CH_4) over the heating, divided by the initial amount of carbon in the char sample. The amount of CH_4 produced was so small that it was almost indiscernible in the figure.

From Fig. 1 it was seen that the release of both CO_2 and CO became significant immediately after the beginning of the steam gasification, whereas in the heat-up stage, only very small amounts of CO_2 and CO were released. Whichever catalysts were used, the char was completely gasified, and the carbon conversions reached as

Table 1
Properties of three coals and pine wood.

	A coal	B coal	L coal	Pine wood
<i>Proximate analysis (% air dried basis)</i>				
Moisture	3.25	5.76	17.92	2.35
Ash	19.68	15.65	16.67	0.35
Volatile	4.74	33.51	37.99	83.01
<i>Ultimate analysis (% daf. basis)</i>				
C	90.2	89.8	67.7	48.7
H	5.1	4.1	4.7	6.0
N	0.5	1.5	2.1	0.1
S	0.7	0.4	0.9	<0.05
O (by diff.)	3.5	4.2	24.6	45.2

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