



Research article

Catalytic steam gasification of coal char with alkali carbonates: A study on their synergic effects with calcium hydroxide



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ABSTRACT

The order of catalytic activity of three alkali carbonates (Li_2CO_3 , Na_2CO_3 , and K_2CO_3) towards the steam gasification of coal char varies depending on the presence and absence of the acidic mineral species and their enrichment in coal. In the gasification of an ash-rich coal char, Li_2CO_3 exhibits the severest catalytic deactivation among three alkali carbonates, whereas Na_2CO_3 is the most resistant to the deactivation. The impregnation of $\text{Ca}(\text{OH})_2$ to the ash-rich coal substantially increases the rate of char gasification for all three alkali carbonates as a consequence of the inhibited catalytic deactivation. In the gasification of an ash-free coal char, however, only the binary $\text{K}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ catalyst shows a synergic effect on promoting the gasification rate, whereas the $\text{Li}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ catalyst and the $\text{Na}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ catalyst have a worse catalytic activity than their respective alkali carbonates alone. The mechanisms of the concerted effects between alkali carbonates and $\text{Ca}(\text{OH})_2$ on the gasification of the ash-rich char and the ash-free char are discussed.

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1. Introduction

Catalytic gasification is widely perceived as an efficient way to convert various carbonaceous materials such as coal, petroleum coke and biomass to optional gaseous products, fuel gas, syngas, synthetic natural gas, hydrogen, and so on. It has thereby been attracting considerable research interests for a long period of time [1–14]. As early as 1867 du Montay and Marechal patented the catalytic gasification of carbonaceous materials with alkali and alkali earth metals [15]. Since then, voluminous literature (e.g., Refs. [16,17]) has testified that alkali and alkaline earth metals, especially in the form of carbonate, are the superior catalysts for the gasification reactions.

In a classic work [18], McKee and Chatterji investigated the catalytic activity of lithium, sodium and potassium carbonates for the steam gasification of graphite using a thermogravimetric apparatus. They found the easiest occurrence of gasification in the presence of the lithium salt, which showed an endothermic interaction with carbon at the lowest temperature among three alkali metals. Kapteijn et al. revealed the catalytic activities of all Group Ia metal carbonates in the following order: $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ when the activated carbon was gasified with carbon dioxide at the same carbon/metal atomic ratio [19]. Karimi and Gray confirmed that K_2CO_3 had a better catalytic activity than Na_2CO_3 for the steam gasification of bitumen coke at a fixed molar loading [20]. In the CO_2 gasification of Illinois No. 6 coal with alkali carbonates of a fixed weight loading, however, Spiro et al. observed the order

of catalytic activities was $\text{K} > \text{Na} > \text{Li}$ [21], just as a reverse order as reported by McKee and Chatterji [18]. Spiro et al. attributed the discrepancy to the plausible difference in reactivity and mineral matter between graphite and coal char, but the reasons were not fully clarified. Kwon et al. confounded the issue as they ranked the catalytic activities as $\text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Li}_2\text{CO}_3$ from the rates of steam gasification of a lignite char with 3 wt.% catalyst loading [22].

Apart from single alkali salts being used as catalyst, the binary and ternary alkali eutectoids have been tested with respect to their catalytic activity. McKee et al. observed that a Pittsburgh coal char containing a $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic catalyst was at least an order of magnitude more reactive for steam gasification than the sample containing the same total concentration of K_2CO_3 alone [23]. It was believed that the reduced melting points of the eutectic phase facilitated the mobility of catalyst on the char surface and consequently resulted in an enhancement in catalytic activity. As per the published phase diagrams, Yeboah et al. prepared several binary and ternary alkali eutectic salts for the CO_2 gasification of an Illinois No 6 coal char [24]. They affirmed that both the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ eutectoid and the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectoid had a much higher catalytic activity than any single alkali carbonate in the case of using the same weight loading, and the ternary eutectic catalyst was more effective than the binary one.

In a series of papers [25–28], Wang and his co-workers investigated an approach for mitigating catalytic deactivation of potassium carbonate by adding calcium species to coal, and found that pre-mixing cheaper calcium hydroxide with coal, especially by impregnation, significantly expedited the gasification of coal chars, particularly of those abundant in acidic clay minerals. A key mechanism underlying this

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promotion was verified to be the suppressed interaction between the potassium catalyst and clay during coal gasification due to the neutralized acidic sites of clay by calcium hydroxide [29]. Another important mechanism was the eutectic formation between K_2CO_3 and $Ca(OH)_2$ [27]. Zhang et al. carried out the steam gasification of a subbituminous coal in a drop tube reactor using relatively inexpensive Na_2CO_3 , $Ca(OH)_2$ and their mixture as catalysts [30]. They showed that the coal sample loaded with the mixture gasified at the fastest speed, but no explanation was given in the work. Sheth et al. made sure that each of lithium, sodium and potassium carbonates readily reacted with clay during coal gasification to form water-insoluble compounds [31]. The aim of this work is to shed light on whether and how $Ca(OH)_2$ plays a synergic part in the catalytic gasification of coal chars with Li_2CO_3 and Na_2CO_3 . Since the results with K_2CO_3 have been addressed in previous studies, they are presented as briefly as possible or only discussed for contrast.

2. Experimental

2.1. Coal samples and char preparation

A Chinese Jinyou bituminous coal (JBC) was used in this study. The coal sample was pulverized to the particle size of smaller than 0.15 mm. The proximate and ultimate analyses of the raw coal sample are shown in Table 1. Major metallic elements in the ash were 55.7% SiO_2 , 30.1% Al_2O_3 , 3.5% Fe_2O_3 , 3.4% CaO , 1.1% TiO_2 , 1.2% K_2O , and 0.3% MgO . JBC was enriched with mineral matter, primarily aluminosilicates.

An ash-free coal sample was prepared by demineralizing JBC by a sequential acid leaching method as described elsewhere [27]. The ash content in the demineralized coal finally decreased as low as 0.58% (dried basis). This demineralized coal sample, designated as ash-free coal (AFC), was used to investigate the influence of mineral matter on the catalytic gasification. In preparation of the calcium-added coal, JBC was mixed with the predetermined amount of $Ca(OH)_2$ in 200 mL of distilled water under stirring for 30 min. Then, the slurry evaporated in a vacuum oven at 65 °C without filtration until the sample was thoroughly desiccated. This coal is designated as calcium-added JB coal (Ca-JBC).

Three kinds of char samples were prepared by pyrolysis of JBC, AFC, and Ca-JBC in a tubular reactor in a stream of argon. Pyrolysis was carried out under a fixed condition (heating rate, 10 °C/min; final temperature, 750 °C; holding time, 30 min). The char was ground and sieved to a powdery sample with the particle size of smaller than 0.15 mm, and then stored in a capped glass bottle for use. The chars derived from JBC, AFC and Ca-JBC are referred to as JBC char, AFC char, and Ca-JBC char, respectively.

2.2. Char gasification

In gasification, the char sample was thoroughly mixed with one of anhydrous alkali carbonates (Li_2CO_3 , Na_2CO_3 and K_2CO_3) in an agate mortar. The amounts of alkali salts added to coal were predetermined to keep the same weight concentration of alkali salt in coal or the same molar concentration of alkali metal in coal. All three alkali carbonates and calcium hydroxide used in the study were the powdery reagents of analytical grade.

Table 1

Proximate and ultimate analyses of Jinyou bituminous coal (JBC) and the ash-free coal (AFC).

Sample	Proximate analysis ^a (wt.%)				Ultimate analysis (wt.%, daf)				
	M_{ad}	A_d	VM_{daf}	FC_{daf}	C	H	N	S	O ^b
JBC	4.27	19.82	7.76	72.41	88.05	3.03	1.08	0.94	6.70
AFC	2.41	0.58	18.42	80.99	83.68	2.32	2.23	0.48	11.29

^a M_{ad} , moisture content on an air-dry basis; A_d , ash content on a dry base; VM_{daf} , volatile matter content on a dry and ash-free basis; FC_{daf} , fixed carbon on a dry and ash-free basis.

^b by difference.

Char gasification was carried out in a horizontally installed tubular corundum reactor, as described elsewhere [7]. In each gasification experiment, a 0.2 g sample of char 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. Then, the gasification started by switching the argon stream to the steam/argon stream with the total flow rate of 1180 mL (STP)/min and the partial pressure of steam to ambient pressure of 0.44 ± 0.02 . The steam gasification was kept isothermally for a period of 50 min. Steam in the off-gas was removed through an ice/water-cooled condenser followed by a dehumidizer. The major gases (CO_2 , CO and CH_4) were measured online with a rapid GC (Agilent Micro 3000) using helium as a carrier gas. The flow rate of gas containing the purging gas and yielding gas was instantly measured at the position of gas analyzer by a mass flow meter at each interval of 1 s. H_2 was detected but not precisely determined because of a low detection sensitivity when helium was used as a carrier gas. The gas release rate is expressed as the molar numbers of a gas released per minute based on the carbon mass in char. The percentage of carbon gasified (PCG) 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.

2.3. Other analyses

Elemental analysis (C, H, N and S) was performed on an Elementar Vario EL III elemental analyzer for raw coal samples and chars. A XRF-1800 X-ray fluorescence analyzer was used to determine the ash composition in coal, which was operated at 50 kV and 40 mA. In this analysis, the coal sample was combusted to the ash at 550 °C, and then about a 3 g sample of ash was pressed to a tablet for XRF analysis. X-ray diffraction analysis was performed on a Rigaku D/max 2550VB/PC diffractometer. The sample was pressed into a rectangle glass sample holder and scanned with a speed of $0.2^\circ \text{ min}^{-1}$ over the angular range of 10–80° using 40 kV and 30 mA Cu $K\alpha$ radiation. Thermogravimetry and differential scanning calorimetry (TG–DSC) was conducted with the use of a METTLER Toledo TGA/DSC instrument. In each analysis, about 20 mg of sample was placed in a platinum crucible, and then heated to 1000 °C at 10 °C min^{-1} under a stream of argon. The flow rate of argon was 100 mL min^{-1} . Mass and caloric calibrations were performed before sample measurement whenever the instrument was turned on.

The surface morphology of coal samples were observed by using a Hitachi S-3400N scanning electron microscopy (SEM). The particle size of char was determined using a Malvern Mastersizer 2000 laser diffraction particle size analyzer. In this analysis, the particles were dispersed in distilled water contained in a beaker. An ultrasonic probe was used to strengthen the dispersion samples. A Model IRIS 1000 inductively coupled plasma atomic emission spectrometer (ICP–AES) was used to detect the solubility of Li, Na, and K present in the ash obtained after gasification. In this analysis, all residual ash samples were immersed in 100 mL of the distilled water under a supersonic stirring for 1 h. After filtration, the concentrations of Li, Na and K in the solution were determined. The dissolution is defined as the ratio of the amount of water-soluble alkali metal to the total amount of alkali in the sample. The total amount of alkali metal (Li, Na or K) in the ash was figured out in terms of the amount of alkali metal added to the char sample as well as the yield of ash obtained after gasification, with no loss of alkali metal.

3. Results and discussion

3.1. Catalytic gasification of JBC char

As shown in Fig. 1, the gas release rate of JBC char with Li_2CO_3 distinctly decreased soon after the steam gasification proceeded, while most of the carbon was not gasified at that moment. This behavior

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