



Calcium-promoted catalytic activity of potassium carbonate for steam gasification of coal char: Effect of hydrothermal pretreatment

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HIGHLIGHTS

- ▶ We proposed the hydrothermal pretreatment (HT) with $\text{Ca}(\text{OH})_2$ for K_2CO_3 -catalyzed coal gasification.
- ▶ HT had a promoting effect on the rate of catalytic char gasification depending on coal type.
- ▶ The alkalinized mineral matter in coal became inactive for deactivating the potassium catalyst.

ARTICLE INFO

Article history:

Received 20 January 2012

Received in revised form 22 June 2012

Accepted 26 June 2012

Available online 20 July 2012

Keywords:

Coal char

Catalytic gasification

Potassium carbonate

Calcium hydroxide

Hydrothermal treatment

ABSTRACT

Hydrothermal pretreatment of coal with the addition of $\text{Ca}(\text{OH})_2$ was found more effective for promoting the K_2CO_3 -catalyzed char gasification than the physical addition way for both JY anthracite coal and HB bituminous coal used. The effect of hydrothermal pretreatment was more remarkable for JY coal which suffers significant catalyst deactivation due to its high mineral content. For this type of coal, employing more severe hydrothermal pretreatment conditions was proven to significantly enhance the gasification rate. It was observed that kaolinite and quartz in coal hydrothermally reacted with calcium forming hydrated calcium aluminosilicates, which, unlike the original minerals, was inactive for the deactivation reactions of potassium. Consequently, the hydrothermal pretreatment allowed more potassium to persist as a water-soluble entity during the gasification. This was a main mechanism underlying the promoted catalytic gasification by the hydrothermal treatment.

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1. Introduction

Coal gasification, as a key process of coal conversion, is increasingly expanding its scale of commercial installation in the world, preponderantly in developing countries. Fundamental study of the coal gasification is, hence, still the subject of many recent publications [1–4]. Catalytic gasification is always an attractive topic with respect to its chemistry and engineering, by virtue of its salient advantages of low operating temperature, high efficiency of energy conversion, low capital cost, and selective reaction pathways towards production of desired gases. Extensive work has been performed to investigate the catalytic coal gasification with alkali and alkaline earth metals (AAEMs) [5–9], because of their superior catalytic activity and low cost, and also because some coals are inherently abundant in AAEMs [10]. Recently, we have focused on the K_2CO_3 -catalyzed steam gasification of coal for production of hydrogen-rich gas [11] and the promoted catalytic activity of K_2CO_3 for char gasification by physical addition of calcium hydroxide to coal

[12,13]. We found that the addition of calcium hydroxide to coal gave rise to a marked increase in the reactivity of char for the catalytic gasification with K_2CO_3 [12]. The plausible explanations for this observation were taken into account in two respects. One reason was the inhibited interaction between potassium and mineral components in coal (mainly clay) by the added calcium, enabling more potassium to survive in a water-soluble or catalytically active form during gasification. Another reason was the mineral-unrelated synergies between potassium and calcium [13]. In previous work, however, calcium species was added to coal in a physically mixing manner. In this work, we propose a new approach to use calcium hydroxide more effectively for promoting the catalytic gasification via hydrothermal pretreatment.

2. Experimental

2.1. Preparation of treated coal samples

An anthracite Jinyou coal (JY coal) and a bituminous Huaibei coal (HB coal) were used in this study. The coal samples were

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pulverized and sieved to the particles size of smaller than 0.15 mm. Table 1 lists the properties of two coal samples.

Hydrothermal pretreatment was carried out using a stainless steel autoclave with a volume of 300 mL. For each run, approximately 4.0 g sample of coal was slurried together with the prescribed amount of pulverized slaked lime in 250 ml of distilled water under stirring. The autoclave was heated to a predetermined temperature (i.e. 150–300 °C) at 7.5 °C/min, held isothermally for a period of time. The vapor pressure was autogenously formed. After cooling down, the slurry was then taken out from the autoclave, followed by filtration and drying at 105 °C. The sample prepared in this manner is named the hydrothermally treated coal.

In some cases, the hydrothermally treated coal was further washed with acid to remove mineral matter. In each run of acid washing, about 0.4 g of the hydrothermally treated coal sample was leached with 70 mL of 6% acid (HCl, HNO₃ or H₂SO₄) under stirring for 1 h at room temperature. The acidified coal was filtered and washed with a sufficient amount of distilled water until the washings became neutral, and then dried in the oven at 105 °C. The sample prepared after acid washing is named the demineralized coal sample.

2.2. Coal pyrolysis and char gasification

In char preparation stage, five kinds of coal samples were used: (1) raw coal; (2) coal physically mixed with calcium hydroxide; (3) coal loaded with calcium hydroxide in an impregnation way that the coal sample was stirred with a prescribed amount of calcium hydroxide in distilled water at room temperature, followed by drying without filtration; (4) hydrothermally treated coal; (5) demineralized coal. The method for the preparation of coal char was similar to the coal volatile matter test (ASTM3175-07). The coal sample was enclosed in an air-isolated alumina crucible, and then pyrolyzed or charred in a furnace preheated to 750 °C for 30 min. After cooling down, the char was ground with agate mortar and pestle, sieved to a powder with the particle size of smaller than 0.15 mm.

Gasification was carried out in a fix-bed reactor. For each run, about 0.2 g of the mixture of char sample and K₂CO₃ was thinly spread on a platinum boat, and then heated in the reactor to 750 °C at 10 min/°C under a stream of argon. The gasification started by switching the argon stream to a steam/argon stream once the temperature reached 750 °C, which was detected by a

thermocouple pointed at the sample crucible inside the reactor, and then maintained isothermally (± 5 °C) for 60 min. The flow rate of argon was 500 ml/min, which was controlled by the mass flow meters. The outlet gas passed through a water condenser and two moisture adsorbers. The carbon-containing gases (i.e. CO, CH₄ and CO₂) were determined online with a rapid gas chromatograph (Agilent Micro 3000).

2.3. Determination of soluble potassium

Experiments were performed to measure the solubility of potassium present in the ash. An accurately weighed sample of the ash was dissolved in excess distilled water under a magnetic stirring for 30 min. After filtration, the solution was used for determination of potassium by means of inductively coupled plasma atomic emission spectrometry (ICP–AES, model IRIS 1000). Dissolution of potassium is defined as the amount of soluble potassium divided by the total amount of potassium in the ash sample, represented in percentage. The total amount of potassium in the ash sample was determined in terms of the amount of potassium added to the char sample and the yield of the ash obtained after gasification, based on an assumption that no potassium was lost in the gasification process.

2.4. Other analyses

XRD was performed on a diffractometer (Rigaku D/max 2550VB/PC). Carbon, hydrogen and nitrogen analysis was carried out on an elemental analyzer (Elementar Vario EL III). FT-IR analysis was implemented on a Fourier transform infrared spectrophotometer (Magna-IR 550).

3. Results and discussion

3.1. Effects of different addition ways

Fig. 1 illustrates the release rates of gases during the K₂CO₃-catalyzed gasification for the four kinds of chars prepared from JY coal in different ways. The release rate of gas is represented on the basis of the initial amount of carbon in the char sample. The carbon conversion is defined as the cumulative amount of carbon released as three major carbon-containing gases (CO₂, CO and CH₄) divided by the initial amount of carbon in the char sample. In the case of no addition of calcium (Fig. 1a), the gasification was quite insignificant. The release rates of CO₂ and CO were indeed increased after the pursuing gas was switched from argon to the mixture of argon and steam, with reference to the result at the stage of heat-up; however, the release rates tended to decrease soon after the steam gasification commenced, suggestive of a noticeable deactivation of potassium upon the gasification [12,13]. The carbon conversion reached only of the order of 30% until the experiment was shut down. In contrast, the addition of calcium to coal even in a physical way (Fig. 1b) resulted in an appreciable increase in the gasification rate, with a high carbon conversion at the end of experiment. The action of calcium species added in a physical way was reported previously [12,13]. Herein, a new observation achieved was that the impregnated calcium (Fig. 1c) was more effective in promoting the gasification of char than the physically added one (Fig. 1b). Such an action on the gasification rate was further intensified by the coal hydrothermal pretreatment (Fig. 1d). Both the impregnation and the hydrothermal pretreatment attained a carbon conversion of no less than 90%. A carbon conversion inaccessible to 100% was due to miscellaneous part of carbon undetermined in the gasification. It should be noticed that in all cases of adding calcium to coal, more gases, especially more CO₂, were liberated during the

Table 1
The properties of the coal samples.

	JY coal	HB coal
<i>Proximate analysis, air-dried (%)</i>		
Moisture	3.25	1.04
Ash	19.68	10.73
Volatile matter	4.74	14.46
<i>Ultimate analysis, daf. (%)</i>		
Carbon	90.21	84.86
Hydrogen	5.55	5.82
Nitrogen	0.54	1.26
sulfur:sulphur	0.66	0.54
Oxygen (by difference)	3.04	7.52
<i>Ash composition (%)</i>		
SiO ₂	55.72	52.07
Al ₂ O ₃	30.11	30.78
Fe ₂ O ₃	3.54	6.67
CaO	3.44	3.29
SO ₃	2.95	2.29
TiO ₂	1.12	2.37
K ₂ O	1.26	1.17
MgO	0.29	0.37

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