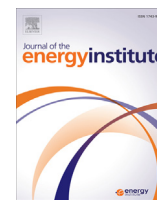




Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: <http://www.journals.elsevier.com/journal-of-the-energy-institute>

Catalytic effects of alkali carbonates on coal char gasification

Lu Ding, Zhenghua Dai^{*}, Juntao Wei, Zhijie Zhou, Guangsu Yu^{*}

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Shanghai Engineering Research Center of Coal Gasification, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:

Received 19 October 2015

Received in revised form

4 May 2016

Accepted 9 May 2016

Available online xxx

Keywords:

In-situ heating stage microscope

Catalytic gasification

K₂CO₃Na₂CO₃

Reaction mechanisms

ABSTRACT

In this work, effects of K₂CO₃ and Na₂CO₃ additives on catalytic gasification of Shenfu coal were studied by the combination of thermogravimetric analyzer (TGA) and an in-situ heating stage microscope. Effects of loading amounts of catalysts (2.2 wt.%, 4.4 wt.%, and 6.6 wt.%) and gasification temperatures (700–950 °C) on the interactions during the char–ash/slag transition were analyzed. The results show that the interactions of catalysts with coal at gasification phase varied with reaction temperature, and compared to K-form char, Na-form char showed a more significant melt and flow of catalysts when the temperature was higher than the melting point of catalyst. The different aggregation states of catalysts on the surface of char matrix and development degrees of pore structure of char matrix accounted for the differences in interaction forms of K catalyst and Na catalyst with coal char. The interaction mechanisms of catalysts with char matrix during char–ash/slag transition were proposed and were related to the variation of gasification reactivity of char with increasing reaction temperature. Moreover, the ratio of the initial reaction rate of char loading catalyst to that of raw coal char (the specific reactivity) and the optimal loading amount of catalysts were analyzed considering the optimal gasification efficiency. There is a threshold value of reaction temperature lower than the melting point of catalyst for the optimal gasification efficiency during the gasification processes of Na-form and K-form chars.

© 2016 Energy Institute. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Gasification is a competitive technology to convert carbonaceous materials including coal, biomass, petroleum coke, etc. into syngas or fuel gas [1,2]. The entrained flow gasification, one of the most promising technologies for large-scale conversion of carbonaceous materials, is generally operated at high temperatures and high pressures, typically in the range of 1200–1600 °C, 2–6.5 MPa [3,4]. Although the high operating temperatures of gasifiers are favorable for high carbon conversion, it may also bring technological problems associated with the ash melting such as sintering, agglomeration, poor slagging or corrosion during thermo-chemical conversion of coal and biomass, etc. [5,6]. Moreover, the harsh reaction conditions will also bring relatively high costs and risky operation of gasification units.

Recently, many researchers are engaged in studying coal catalytic gasification processes in order to avoid or solve the issues above. The catalytic technology could enhance the reactivity of coals and broaden the range of coals adaptable, and it is often applied at a modern temperature range (700–950 °C) [7,8], which will significantly reduce the production costs and operating risks. The catalytic technology has got great development since American Exxon Company developed the catalytic coal gasification technology for methane production directly from coal and steam at the presence of catalyst in late 1970s [9]. Most of the catalysts used for coal catalytic gasification are alkali metals (e.g., K⁺, Na⁺) [10,11], alkali earth metals (e.g., Ca²⁺, Mg²⁺) [12,13], and transition metals (e.g., Fe²⁺/Fe³⁺, Ni²⁺) [14,15], with the alkaline metals being the most active ones [16]. Effects of alkali metals, such as Na₂CO₃, on Victorian brown coal pyrolysis and gasification have been extensively studied by Li et al. [17–19]. Researches indicate that the catalytic gasification reactions were localized on the sites associated with the catalysts. The catalytic active phases might be preferentially accommodated on the carbons of aromatic nature. Karimi and Gray carried out steam gasification of coke using K₂CO₃, KCl, Na₂CO₃, CaCO₃, CaO, and MgO as catalyst additives, and they found that K₂CO₃ and Na₂CO₃ were most effective for all the gasification conditions (atmospheric pressure, 600–800 °C) adopted [16]. Alkali metal species showed significant mobility within the coke phase, which resulted in their high catalytic activities. Popa et al. held their catalytic gasification

* Corresponding authors. Tel.: +86 21 64252974; fax: +86 21 64251312.

E-mail addresses: chinadai@ecust.edu.cn (Z. Dai), gsyu@ecust.edu.cn (G. Yu).

experiments of a sub-bituminous coal in a fixed-bed reactor loading Na_2CO_3 as a catalyst [20]. Effects of gasifying agent compositions, catalyst adding amounts, and reaction temperatures on the associated coal pyrolysis and char gasification were explored. The optimal adding amount of Na_2CO_3 (~3 wt.%) was found in Popa et al.'s research for the catalytic gasification process. Kopyscinski et al. studied the interactions of a demineralized coal with the catalyst (K_2CO_3) in N_2 or CO_2 at 700 °C by in situ X-ray diffraction and thermogravimetric analysis (TGA) [21]. They found that K_2CO_3 was favorable for the proceeding of pyrolysis. The atmosphere during the pyrolysis processes produced a remarkable effect on the subsequent char gasification reaction. They concluded that the reduction of K_2CO_3 was optimal for rapid char gasification.

Despite the extensive researches on reaction mechanisms of coal catalytic gasification, there are still rare literatures reporting the in-situ analysis and comparisons of morphology changes during char–ash/slag transition of the catalytic processes, which could be helpful for grasping the interactions of catalysts with char matrix, and the corresponding catalytic reaction mechanisms for different catalysts. In the present work, an in-situ heating stage microscope and TGA were employed to explore catalytic effects of K_2CO_3 and Na_2CO_3 additives on Shenfu coal gasification. Effects of the interactions between char matrix and catalysts at different gasification temperatures on the reactivity of coal chars were analyzed, and gasification reaction mechanisms considering the interactions during char–ash/slag transition were proposed. Moreover, the optimal loading amount of catalysts and reaction temperatures were discussed considering the ideal gasification efficiency.

2. Experimental

2.1. Samples preparation

A typical bituminous coal in China (Shenfu coal) was adopted as a raw carbonaceous material in this study, which was denoted as SF, and the size range of coal particles was controlled in 80–120 μm . The characteristic data of coal sample are shown in Table 1. The loading catalysts, i.e. K_2CO_3 and Na_2CO_3 (purity > 99.0%), were obtained from Sinopharm Chemical Reagent Co., Ltd.

The K-form or Na-form coals were prepared thorough incipient wetness impregnation [22]. The nominal loadings of K^+ or Na^+ on the coal were 2.2 wt.%, 4.4 wt.%, and 6.6 wt.% on a dry basis, respectively. Taking loading K_2CO_3 as a representative, SF coal with different amounts of K_2CO_3 additive were designated SF-raw-2.2K, SF-raw-4.4K, and SF-raw-6.6K, respectively. The pyrolysis experiments of coal samples at 800 °C were held in a high frequency furnace, which were reported in our previous researches [22,23]. The corresponding pyrolysis char of SF-raw-2.2K is hereafter referred to as SF-2.2K-800P, and the nomenclature of Na contained samples referred to that of K contained samples. During the pyrolysis experiments, the constant time at the final temperature was kept for 5 min so as to remove most of volatile matters in coals. Ultimate analysis of tested samples with catalysts was shown in Table 2. Flame atomic absorption spectrometry (FAAS, analytikjena novAA350) was used to determine the total contents of water soluble and ion-exchanged Na or K in raw material and char, and the detail method could refer to Chen et al.'s work [24]. The solid samples were grinded to ~30 μm before experiment, and all the experiments of FAAS analysis were carried out for three times, and the standard deviation is less than 2%.

The actual Na or K content in char samples were converted to the same basis as coal samples (dry basis of the corresponding raw coal loading catalysts) for comparison. Contents of alkali metal in coal/char samples and the mass ratio of alkali metal to carbon are shown in Table 3. It is shown that when loading Na_2CO_3 or K_2CO_3 , the actual content of soluble and ion-exchanged K/Na in coal was nearly the same with the theoretical loading amount of K/Na. However, the total contents of water soluble and ion-exchanged Na or K decreased after heat treatment at 800 °C due to the form of aluminosilicate and metasilicate [25,26].

2.2. In-situ CO_2 gasification of char in heating stage microscope

The interactions of catalysts with char matrix during gasification processes were explored by using a heating stage microscope. The detailed diagram of this device is shown in Fig. 1. The main components are heating suit, microscope, and image analysis software. Typical 2 mg samples were introduced into the holder of the heating unit at room temperature. The superficial morphological changes of solid samples were observed by an Olympus light microscope (Olympus Optical Corporation, Tokyo, Japan). Images were on-line captured during char- CO_2 gasification process. The magnification used in this study was 100 \times . Char samples loading different amounts of catalysts were heated to the specified temperature (800 °C) under a continuous nitrogen flow of 100 mL min^{-1} . After keeping in N_2 atmosphere for 5 min, the gas atmosphere was switched to CO_2 (100 mL min^{-1}) for another 10 min at 800 °C, and finally the samples were heated up to 900 or 950 °C under CO_2 atmosphere to observe the melting interactions between alkali metal compounds and char matrix. The heating rate was controlled at 25 °C min^{-1} .

2.3. Measurements of isothermal CO_2 gasification reactivity of char samples

Gasification reactivity experiments of char samples were carried out with NETZSCH thermogravimetric analyzer (STA 449 F3). About 8 mg sample was placed in an alumina pan and heated at 25 °C min^{-1} to the prescribed temperature (700–950 °C) under a continuous

Table 1
Properties of tested samples.

Sample	Proximate analysis/d, wt.%			Ultimate analysis/d, wt.%				Ash fusion temperature/°C			
	VM	FC	Ash	C	H	N	S	DT	ST	HT	FT
SF	35.42	58.29	6.29	79.14	2.32	1.12	0.77	1152	1167	1175	1179

Note: VM – volatile matter; FC – fixed carbon; d – dry basis.

Download English Version:

<https://daneshyari.com/en/article/8109011>

Download Persian Version:

<https://daneshyari.com/article/8109011>

[Daneshyari.com](https://daneshyari.com)