Full Length Article

Effect of catalysts on char structural evolution during hydrogasification under high pressure

Xuhui Liu, Biao Xiong, Xiaohong Huang, Haoran Ding, Ying Zheng, Zhaohui Liu *, Chuguang Zheng

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

HIGHLIGHTS

- Catalytic char hydrogasification under high pressure was conducted.
- Alkali catalyst exhibited better catalytic activity than calcium in hydrogasification.
- CaO catalyst improved char reactivity by inhibiting ring condensation.
- The alkali catalysts changed the char hydrogasification pathways.
- Alkali catalytic reaction occured simultaneously on the surface of and inside char.

ARTICLE INFO

ABSTRACT

The catalytic hydrogasification of coal char was investigated in a high-pressure fixed-bed tube reactor using CaO, $CaCO_3$, Na_2CO_3, and K_2CO_3 as catalysts. Experimental results showed that the char reactivity could be greatly improved with the addition of catalysts. Analysis of char structural evolution was performed to further explore the catalytic mechanism by employing Raman spectroscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX). The results revealed that CaO catalyst inhibited the aromatic ring condensation of the char structure during hydrogasification. The catalytic reaction of CaO only occurred on the char surface. Na_2CO_3 or K_2CO_3 was reduced to metallic Na or K and diffused into the char under hydrogen atmosphere, enhancing the cracking of large aromatic ring systems into small ones, which were the active species for hydrogasification. The catalytic reaction of alkali catalyst occurred simultaneously on the surface of and inside the char. Therefore, the Na_2CO_3 and K_2CO_3 displayed higher catalytic activities than CaO in hydrogasification.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Coal hydrogasification is a promising process for producing substitute natural gas [1–4], especially in China, where coal reserves are abundant compared with natural gas and the consumption of natural gas is increasing annually. Coal hydrogasification consists of hydropyrolysis and hydrogasification of the char, and the latter process is much more slower than hydropyrolysis. Thus, char hydrogasification is the controlling procedure for coal hydrogasification [4].

Many factors can influence char reactivity, and these include reaction temperature, pressure, char structure, and the presence of a catalyst. The char hydrogasification reaction under different reaction conditions has been investigated for many years [5–8]

with the aim of quantifying the kinetics of hydrogasification for a broader range of applications [9,10]. Several studies have indicated that the hydrogasification reactivity decreased sharply as reaction proceeds. High reactivity and conversion efficiency of char can be achieved under high hydrogen pressure and high reaction temperature conditions [11]. However, char hydrogasification reaction forming methane is an exothermic reaction, thus the char-hydrogenation equilibrium is limited with reaction temperature rises. Utilizing catalysts is recognized as a significant approach to effectively obtaining high char reactivity and conversion efficiency under mild conditions (low temperature and pressure) [11,12], thus decreasing operation costs of hydrogasification.

Alkali and alkaline earth metals (AAEMs) as well as transition metals, such as Ni or Fe, can enhance char reactivity [13,14]. Transition metals have been considered important catalysts for hydrogasification and attracted significant research attention over the last few decades [11,15–18]. However, several research results

---

* Corresponding author.
  E-mail address: zliu@hust.edu.cn (Z. Liu).

revealed that the transition metals do not show catalytic effects during the hydrogasification of coal [17]. This limitation may be attributed to the deactivation of transition metal elements resulting from the high-temperature sintering and easy sulfur poisoning in the reaction process [15]. Many studies [12,13,19,20] on catalytic steam gasification and CO_2 gasification for producing syngas (CO and H_2) have revealed that AAEM catalysts exhibit higher catalytic performance than transition metals. Nevertheless, the catalytic effects of AAEM on hydrogasification for producing methane have been rarely reported.

Char structure and its development during catalytic gasification reflect the activity of catalysts [13,19–22]. Many different instrumental techniques, including Raman spectroscopy and scanning electron microscopy, have been developed and improved by many researchers to characterize the structure and carbon microstructures of char. These techniques have been proven as effective methods for estimating the structure of highly disordered carbon materials and surface morphology [20,22]. Some researchers have investigated the development of char structure under steam and CO_2 atmosphere. Amorphous carbon with small aromatic rings has been found to decrease as the reaction proceeds [23,24]. Li et al. [22] used Raman spectroscopy to examine the roles of AAEM metals in char gasification under different atmospheres. They reported that the AAEM catalyst can improve the reaction rate by changing the char structure during gasification. Li et al. [24] also used Raman spectroscopy to analyze the influence of the potassium catalyst on petroleum coke reactivity and structural development under steam atmosphere and found that the potassium catalyst could accelerate the cracking of large aromatic ring systems during steam gasification. However, the structural evolution and the exact roles or catalytic mechanisms of catalysts during char hydrogasification remain unclear. For this reason, investigations on char structural development are required to understand the mechanistic aspect of catalytic hydrogasification.

This work focused on the catalytic behaviors of CaO, $CaCO_3$, Na_2CO_3, and K_2CO_3 on demineralized coal char reactivity by employing a high-pressure fixed-bed reactor (HPFR) under a hydrogen pressure of 5 MPa at 1123 K. The effects of the catalysts on char and the catalytic hydrogasification reaction rates of coal char were investigated. Char structure were analyzed by Raman spectroscopy and SEM-EDX. The char structural development during catalytic hydrogasification was also investigated to gain some insights into the catalytic mechanism.

2. Experimental setup and analysis method

2.1. Sample preparation and heat treatment

Hailar lignite was obtained from Hailar Basin in northeastern Inner Mongolia, China, which was characterized by low-ash and low-sulfur content. The coal samples were pulverized below 98 μm. Coal demineralization were performed using the HCl-HF demineralization method [25]. The coal demineralization was as follows. Hailar lignite (100 g) was first treated with hydrochloric acid (500 mL, 5 M) and stirred at 333 K for 24 h. The HCl-treated coals were washed with deionized water to remove chloride ion. The HCl-washed coals was then treated with Hydrofluoric acid (500 mL, 5 M) using the same process as the HCl treatment. The sample was thoroughly washed with deionized water when the pH value was close to that of the deionized water. The demineralized coal was dried under vacuum at 378 K for 24 h.

The demineralized coal char sample was produced in an temperature-controlled fixed-bed reactor heated to 1173 K at a heating rate of 10 K/min in N_2 atmosphere, and the final temperature was maintained for 1 h before cooling to room temperature.

The samples were collected and stored for further use and analysis. The obtained chars were abbreviated uncatalyzed char.

CaO, $CaCO_3$, Na_2CO_3, and K_2CO_3 were dry mixed with 2 g (daf) of demineralized char samples in an agate mortar for 15 min, respectively. The amount of catalyst was added to the char in equi-molar amounts and the molar ratio of metal to carbon in char was maintained at 10 wt.% for each catalyst/char mixture.

The properties of the demineralized coal and uncatalyzed char were given in Table 1. Proximate analysis were performed by a thermogravimetry analyzer (TGA Thermostep, Eltra) based on the ASTM D7582-12 standard. The elemental composition of carbon, hydrogen and nitrogen contents were analyzed using a CHN analyzer (Vario Max, Elementar) following ASTM D 5291-91 standard and sulfur content was determined using an sulfur elemental analyzer (Rapid S Cube, Elementar) following ASTM D 4239 standard.

2.2. Char hydrogasification reaction rate measurement

An HPFR (20 mm inner diameter) system (Fig. 1) depicted in an earlier study [26] was employed to test the char hydrogasification reaction rate under high pressure. The experimental system was designed to operate at hydrogen pressures up to 7 MPa. The pressure of the system was controlled by using a back pressure regulator and the reactor temperature was tested with four K-type thermocouples. The sample (about 2 g) was placed in the reaction zone. Before the formal experiment, the system was fully purged and pressurized with N_2 until it reached the target pressure (5 MPa). The reactor was pressure tested at this condition to ensure safe operation. The system was subsequently heated to the final temperature of 1123 K. Once the desired pressure and temperature were achieved, the N_2 was switched to H_2 (1.5 N L/min, 99.999%) to start the reactions. The hydrogen flowing from the top passed through the sample layer.

The product gas was continuously dried and then analyzed by an online flue gas analyzer (Gasboard-3100, Cube).

The hydrogasification reaction rate and carbon conversion (X) of chars were calculated by Eqs. (1) and (2) [4]:

$$dX/dt = -1/n_0 \cdot dn_c(t)/dt \tag{1}$$

$$X = 1 - n_c(t)/n_0 \tag{2}$$

where $n_c(t) = n_0 - \int_0^t Q_t \cdot (V_{CH_4} + V_{CO} + V_{CO_2})/22.4 \cdot dt$ and $n_0 = m_{char} \times W_C/M_C$ was the carbon moles number of the samples at time t and initial, Q_t was the instantaneous gas flow rate. V_{CH4}, V_{CO}, V_{CO2} was the mole content of CH_4, CO and CO_2 in the product gas, respectively. M_C was the carbon mole number. W_c was the carbon content in the char. m_{char} was the initial weight of the char.

The hydrogasification of uncatalyzed char under the same conditions were conducted for four times to obtain the repeatability of

Table 1
Proximate and ultimate analysis of samples.

	Demineralized coal	Uncatalyzed char
Proximate analysis (wt.%, ab)		
Moisture	0.3	1.6
Ash	0.1	0.7
Volatile	41.2	3.4
Fixed Carbon (by difference)	58.5	94.3
Ultimate analysis (wt.%, daf)		
Carbon	73.6	97.6
Hydrogen	4.2	0.9
Nitrogen	0.8	0.7
Sulfur	0.3	0.3
Oxygen (by difference)	20.8	0.5