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Full Length Article

Impact of calcium on the synergistic effect for the reactivity of coal char gasification in H_2O/CO_2 mixtures

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HIGHLIGHTS

- Mechanism of synergistic effect during co-gasification was revealed.
- Catalytic effect of CaO facilitates the synergistic effect.
- H_2O can make CaO smaller in size and higher in dispersity.
- Interaction of H_2O and CO_2 with Ca participation promotes the pore development.
- Sintering of CaO at higher temperature causes the weak synergistic effect.

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ABSTRACT

In this paper, the effect of calcium on coal gasification in mixture agents containing both H_2O and CO_2 was investigated by comparing the gasification behaviors of the demineralized coal and calcium-loaded coal using Wucaiwan (WCW), a calcium-enriched low rank coal, as the raw material. TG analysis of pure $CaCO_3$ was conducted at different conditions to reveal the catalytic mechanism of calcium. The properties of the chars as well as partially-gasified chars were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Moreover, pore structures of partially-gasified chars were obtained by BET analysis. It was found that under calcium catalysis, the normalized gasification rate *K* increased more than 20 times in H_2O/CO_2 mixtures, and this value was much higher than that in pure H_2O and pure CO_2. The results suggest that under the influence of calcium, there is a synergistic effect between H_2O and CO_2 during co-gasification when temperature is lower than 900 °C. The reason for this enhanced gasification is the fact that CaO, the main form of calcium mineral during coal catalytic gasification, can catalyze coal gasification in H_2O/CO_2 mixtures much more effectively and create a strong synergistic effect. H_2O can decrease the size of the CaO particles and increase their dispersity, thus facilitating CO_2 adsorption on CaO. Furthermore, with CaO participation, interaction between H_2O and CO_2 can allow both of them to enter the interstices or pores of the coal char more rapidly, which accelerates the reaction rate and results in the synergistic effect. The synergistic effect becomes weaker as the temperature rises, which can be attributed to reduced adsorption of CO_2 on CaO and the sintering of CaO at higher temperature.

1. Introduction

Coal gasification is one of the most important technologies for the development of modern coal chemical industry and it is considered as a clean and environment-friendly approach for coal utilization [1]. With the demands of saving energy and reducing emission of pollutants, recycling of CO_2 during chemical processes is considered to be an effective way to utilize CO_2 [2,3]. Especially in the fixed bed dry bottom gasifier, addition of CO_2 to replace partial H_2O can not only reduce the amount of phenolic wastewater but also limit the emission of CO_2 [4]. Moreover, this method can make full use of the carbon source. Nevertheless, introducing CO_2 into the gasifier may reduce the gasification reaction rate of coal with H_2O. However, our previous work demonstrated that the reactivity of coal char gasification with H_2O/CO_2 mixtures was better than that with H_2O or CO_2 alone, which can be attributed to the synergistic effect between H_2O and CO_2 on the gasification

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reactivity [5]. Wang et al. [6] found that the synergistic effect disappeared after the coal was demineralized by HCl, and it was further revealed that the synergistic effect depends on the catalytic action of calcite inherent in coal. Therefore, catalytic coal gasification in mixtures of H_2O and CO_2 may be a reasonable and available way to ensure gasification efficiency.

Catalytic gasification is an attractive option due to its low operating temperature, high gasification reaction rate, and selective reaction pathways towards production of desired gases [7–11]. Calcium, an important alkaline earth metal, can show superior catalytic activity, but it reacts to a much lesser degree with clay minerals in coal and hardly volatilizes during the heating process [12,13]. Owing to the superiority of calcium among other potential catalysts including potassium and sodium [14–16], it has been favored by more and more researchers and is a better choice for catalytic gasification.

Hengel and Walker [17] studied the gasification reactivity of calcium-loaded coal in air, CO_2 and steam separately. The coal with added calcium showed outstanding activity in any gasifying agents. Murakami et al. [18] investigated the catalytic performance of $CaCO_3$ in the steam gasification of Indonesian sub-bituminous coal. The results showed that catalytic activity of $CaCO_3$ was as high as that of $Ca(OH)_2$, and $CaCO_3$ continued to display excellent performance even at low catalyst loading. Shuai et al. [19] prepared calcium-loaded coal by wet-mixing method and found that H_2 concentration was greatly improved due to the catalytic effect of $Ca(OH)_2$ on the water gas shift reaction.

Up to now, most of the studies have mainly focused on the catalytic action of calcium on the gasification of coal or char with single agents. There is limited research on the catalytic effect of calcium on the gasification of char with H_2O and CO_2, and it is still unclear how calcium catalyzes coal char gasification in mixture of H_2O and CO_2. Thus, the purpose of this study is to examine the catalytic effect of calcium on coal gasification with H_2O/CO_2 mixtures and attempt to reveal the catalytic mechanism of calcium for co-gasification. Wucaiwan (WCW), a calcium-enriched low rank coal, was used as the raw material. The effect of calcium on coal char gasification was evaluated by comparing the gasification behaviors of the demineralized coal and calcium-loaded coal in different gasifying agents including pure H_2O, pure CO_2 and H_2O/CO_2 mixtures. The chemical forms and dispersion of calcium on the surface of coal char were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Moreover, the pore structures of coal chars were analyzed by N_2 adsorption and the dissociative-chemisorption behavior of CO_2 on CaO was studied by thermal gravimetric analysis (TGA).

2. Experimental

2.1. Coal sample

A sub-bituminous coal from Wucaiwan (WCW), Xinjiang province in China was used in this study. The sample was ground and sieved to a particle size less than 0.178 mm. Proximate and ultimate analyses of WCW are listed in Table 1 and the chemical composition of the coal ash is given in Table 2.

2.2. Preparation of demineralized coal sample and calcium-loaded coal sample

HCl and HF were used to wash WCW in order to remove the minerals inherent in coal. The specific demineralization process has been described in our previous work [5]. The final demineralized coal obtained after drying was named as WCWD and was stored in the desiccator. The ash content of WCWD is as low as 0.2 wt.%, so it can be considered as ash-free coal.

In order to investigate the effect of calcium on coal char gasification, calcium was loaded on the demineralized coal by an impregnation method and the calcium loading level was kept the same as the calcium content in raw coal. The precursor of calcium used in this study was calcium acetate and the detailed calcium-loading procedure is as follows: a certain amount of $Ca(OAc)_2$ powder was firstly put into a beaker. Then 1 g of the demineralized coal sample was added into the beaker along with deionized water to make coal-water slurry, and this slurry was stirred for 12 h at room temperature. Finally, this mixture was dried at 60 °C in a vacuum oven for 12 h to obtain the calcium-loaded coal. The calcium-loaded coal was named as Ca-WCWD and was also stored in the desiccator.

2.3. Coal gasification experiment

The gasification experiments of demineralized coal and calcium loaded coal were performed on a thermal gravimetric analyzer (NETZSCH STA 449 F3, Germany). The detailed description and schematic diagram of the apparatus have been provided in our previous work [6]. Each gasification experiment was conducted at atmospheric pressure and desired temperature including 800 °C, 850 °C and 900 °C. Before the gasification experiments, the internal diffusion effect and external diffusion effect were eliminated due to the significant influence of particle size and flow rate of gasification agent on gasification reactivity [20,21]. It was found that the carbon conversion curves would not vary provided that the particle size of coal sample was less than 0.38 mm and flow rate of gasification agent was higher than 150 mL/min. In this study, approximately 10 mg coal sample with a particle size less than 0.178 mm was placed on a plate crucible, heated at a heating rate of 10 °C/min from room temperature to defined temperature with Ar as protective gas and purge gas, and then maintained at constant temperature for 30 min. Then, 200 mL/min of the different gasifying agents was introduced and the sample was gasified under either 100% H_2O, 100% CO_2 or 66.7% H_2O + 33.3% CO_2 for 30 min. During the gasification process, the mass of sample was recorded every 2 s.

Carbon conversion during coal gasification was calculated by the following equation [6]:

$$X = \frac{w_0 - w_t}{w_0 - w_{ash}} \quad (1)$$

where X is carbon conversion, w_0 is the initial sample mass, w_t is the mass at time t, and w_{ash} is the mass of ash after coal char gasification.

Gasification reactivity of coal char was evaluated by normalized gasification rate [22] and it was calculated by:

Table 1
Proximate and ultimate analyses of WCW.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
M_{ad}	A_d	V_{daf}	C	H	O*	N	S
14.8	3.6	33.8	76.0	2.9	19.9	0.7	0.5

[ad]Air-dried basis, [d]Dry basis, [daf]Dry and ash-free basis, *By difference.