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Steam gasification of coal char catalyzed by K_2CO_3 for enhanced production of hydrogen without formation of methane

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ABSTRACT

Steam gasification of coal char catalyzed by potassium carbonate was investigated on a laboratory fixed-bed reactor to examine the catalytic effects not only on the reaction rate but also on the reaction selectivity, and non-catalytic gasification of coal char was performed by way of contrast. It was observed that the catalytic gasification of coal char with steam occurred significantly in a temperature range of 700–750 °C, producing a hydrogen-rich gas with slight formation of carbon monoxide and virtually no formation of methane. An oxygen transfer and intermediate hybrid mechanism of the catalytic char gasification with steam is proposed for understanding of the experimental data regarding both the kinetic behaviors and reaction selectivity. The study has highlighted the advantages of the catalytic gasification of coal char over the conventional coal gasification with respect to the reaction selectivity. The catalytic steam gasification of coal char makes it possible to eliminate or simplify the methane reforming and water–gas shift processes in the traditional gas-to-hydrogen purification system.

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1. Introduction

Coal gasification is one of the cheapest ways to manufacture hydrogen on a large scale in industry. Coal-based hydrogen accounts for about 19% of the worldwide production of hydrogen [1]. Nowadays hydrogen is primarily used as synthesis and refining gases. It has the potential to become a routine energy carrier with widespread application of advanced fuel cell techniques for transportation and stationary power generation in the foreseeable future. However, the current coal gasification technologies do not yet offer a cost-competitive way to produce hydrogen in place of gasoline and diesel. It is necessary to develop more cost-effective coal gasification technology.

Conventional coal gasification uses no catalyst, and it requires a temperature of higher than 1000 °C using steam and oxygen as reactants. The gaseous product is generally a mixture of H_2, CO, CO_2, CH_4, and other minor gases, although it varies in the composition depending on coal type, gasification process and operating condition. For example, the gas produced from Lurgi dry ash gasifier (1000 °C) contains 38–39% H_2, 15–18% CO, 10–12% CH_4, and 31–32% CO_2. Hydrogen is traditionally produced by a sequence of post-conversion, separation and purification of raw gas. The major processes include the steam reforming of methane and the water–gas shift reaction [2,3]:

$$CH_4 + H_2O \rightarrow CO + 3H_2,\ \Delta H^\circ = 206.0\ \text{kJ mol}^{-1} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2,\ \Delta H^\circ = -45.2\ \text{kJ mol}^{-1} \tag{2}$$

The former is a strong endothermic reaction, and it takes place at 790–820 °C using a Ni-based catalyst. The latter is generally accomplished via the two steps. The first one operates at higher temperatures (350–450 °C) using a Fe–Cr catalyst, and the second one does at lower temperatures (240–250 °C) using a CuO–ZnO–Al_2O_3 catalyst. Both the steam methane reforming process and water–gas shift reaction process cause a great energy loss [4]. Elevating gasification temperature promotes reaction rate, but it leads to an increase in the yield of CO and also in the energy loss during the gas cooling. Converting CO of high concentration to a low level may even require a three-step process of water–gas shift reaction. Gambini et al. [5] have reported that the overall energy efficiency of an advanced high-temperature coal gasification coupled with hydrogen production and electricity generation is rather low.

Catalytic coal gasification has long received the bulk of research attention because of its kinetic advantages of low-temperature operation and high efficient throughput [6–14]. Some later interests have expanded to improve hydrogen production by taking advantage of the favorable reaction selectivity of some common catalysts including alkali [15,16], lime [17], iron-based compounds [18], and calcium-iron composites [19]. In pressurized steam coal gasification, slaked lime acts as an absorbent of gaseous CO_2, and it thus hinders CO formation and enhances H_2 production via changing the equilibrium of water–gas shift reaction [17].

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Iron-based catalysts can reduce CO formation but they only have limited effect [19].

Potassium carbonate is well known to have superior catalytic properties. In late 70s, Exxon Co. demonstrated a pilot-scale process of coal gasification using this catalyst [9,10]. A fluidized bed gasifier was developed, and it was run at 3 MPa and 700 °C using a mixture of steam/H_2 for fluidization. It was reported that this process produced a methane-rich product. Hauserman [15] and Timple et al. [16] at University of North Dakota investigated a process of catalytic coal gasification for integration with fuel cells. They reported that the potassium-catalyzed steam coal gasification yielded more hydrogen but methane was still a major product. Owing to the potential for commercial application, there are numerous fundamental studies concerning the potassium-catalyzed coal gasification [6,7,11,13]; however, studies of the catalytic selectivity are surprisingly scarce. The work by Wigmans et al. was an early but in-depth investigation into the reaction selectivity [20]. They found that potassium carbonate dramatically decreased CO/CO_2 ratio. However, no attention was paid to the formation of H_2 and CH_4. Recently, Wang et al. [21] and Sharma et al. [22] investigated the K_2CO_3-catalyzed steam gasification of ash-free coals for high yield of hydrogen. Their studies have raised strong curiosity about how abundant hydrogen is formed by the catalytic gasification.

In this paper, we have re-examined the effects of potassium carbonate on catalytic steam gasification of coal char, with an emphasis on the gas composition. An oxygen transfer and intermediate hybrid mechanism has been proposed for elucidating both the reaction rate and the reaction selectivity. Also, a conceptual process has been put forward to generate a hydrogen-rich and methane-free gas by separating coal pyrolysis from K_2CO_3-catalyzed steam gasification of coal char. As stated above, if the gas contains CH_4, the subsequent steam reforming of CH_4 not only consumes extra energy but also is a negative due to re-generation of CO via reaction 1. From the standpoint of hydrogen production, it is desirable to minimize the formation of both CO and CH_4.

2. Experimental

2.1. Coal sample and char preparation

A Chinese Huaibei bituminous coal was used in this study. The coal was crushed and pulverized to the particles with diameter sizes of less than 0.15 mm. The proximate analysis showed that the coal contained 10.8% ash, 14.4% volatile matter, and 74.8% fixed carbon, on dry basis. The ultimate analysis showed that the coal consisted of 84.8% C, 5.7% H, 1.4% N, 0.4% S, and 7.7% O (by difference), on dry ash-free basis. X-ray diffraction analysis showed that the coal contains some quartz and kaolinite minerals. The coal char was prepared by a method similar to the standard method (ASTM D3175-07) which was used for measurement of the volatile matter in coal. Briefly, a sample of coal was accurately weighed, and filled in an alumina crucible, which was loosely capped to isolate the sample from air but to allow emission of the volatile matter. The crucible was promptly placed into a heated furnace under a natural atmosphere at 500 °C, 700 °C, or 900 °C for 30 min. The resultant char was weighed, and then ground with agate mortar and pestle. The powdery char sample (particle size, < 0.15 mm) was used for coal gasification. The coal chars prepared at 500 °C, 700 °C, and 900 °C are named the 500 °C char, the 700 °C char, and the 900 °C char, respectively. Elemental analysis showed that the 500 °C char contained 79.1% C, 3.0% H, and 1.1% N; the 700 °C char contained 79.4% C, 2.0% H, and 1.3% N; the 900 °C char contained 81.0% C, 0.7% H, and 1.1% N, all on dry basis, indicating the increased extent of carbonation with temperature.

2.2. Steam gasification

The gasification reactor system was mainly composed of a steam generator and a horizontally placed corundum tubular reactor (i.d., 50 mm) which was heated by an electric furnace. In the run of catalytic steam gasification, the char sample was thoroughly mixed with anhydrous potassium carbonate (purchased from Shanghai Lingfeng Chemicals Co.) in an agate mortar. It should be noted that whether using a physical blending method or using a solution impregnation method, the catalytic char gasification did not behave much differently because of the good mobility of this catalyst [6,22]. About 0.2 g sample of the mixture was thinly spread on a platinum boat, and then placed at the central zone of the tubular reactor where the temperature was homogeneous. The use of small amount of sample is intended to reduce the external mass transfer because catalysis only occurs in the case of the gasification rate of chemical reaction or internal diffusion control. The sample was heated at a heating rate of 10 °C/min by the electric furnace to a predetermined temperature under a stream of argon. Then, the gasification started isothermally at atmospheric pressure by sweeping steam gas into the reactor. The partial steam pressure was about 0.5 using argon as a sweeping gas. The argon flow rate was 500 ml/min, which was controlled by the mass flow meters. The outgoing gas passed through a water condenser and two moisture trappers. The major product gases including CO, CH_4 and CO_2 in the desiccated gas were quantitatively determined online by a rapid gas chromatograph (Agilent Micro 3000) with a thermal conductivity detector. On this gas chromatograph, helium was used as the carrier gas to improve the analysis precisions of CO and CH_4. Quantification of hydrogen was carried out on gas chromatograph (Agilent 6820) using argon as the carrier gas, through the collection of the gas in gas bags. The gas flow rate at the gas outlet was measured by a film volumetric method.

2.3. Other analysis methods

XRD was performed on a diffractometer (Rigaku D/max 2550VB/PC). Elemental analysis (C, H, and N) was carried out on an elemental analyzer (Elementar Vario EL III). Sulfur analysis was accomplished on a Coulomb sulfur analyzer (CLS-2).

3. Results

3.1. Gas release patterns of typical non-catalyzed gasification and catalytic gasification

Fig. 1 shows the gas release patterns of the typical non-catalyzed char gasification and catalytic char gasification, where the gas release rate is on the basis of the unit weight of carbon in the fed char. In the case of the non-catalyzed gasification, the char sample was first heated to 1000 °C in a stream of argon, then the gasification started by switching the argon stream to the steam/argon stream and it was held isothermally for a period of time; in the case of the catalytic gasification, the gasification was operated in a similar manner and only the gasification temperature was changed to 750 °C. The amounts of gases released in the heat-up stage was insignificant for both the non-catalyzed gasification and the catalyzed gasification, compared to those released in the gasification stage. After switching to the steam/argon stream, the release of CO and CO_2 became remarkable with some formation of CH_4 for the non-catalyzed gasification, whereas for the gasification catalyzed by 17.5% K_2CO_3 at 750 °C, the release of CO_2 was even more remarkable with substantially less formation of CO and virtually no formation of CH_4. The appreciable release of H_2 was qualitatively observed in the gasification stage for both the non-catalyzed

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