



Full Length Article

Direct production of high hydrogen syngas by steam gasification of Shengli lignite/chars: Significant catalytic effect of calcium and its possible active intermediate complexes



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ABSTRACT

The catalytic effect of calcium on the steam gasification of Shengli chars was studied in this work. The calcium-added chars were prepared by pyrolysis under argon atmosphere from calcium oxide added demineralized Shengli lignite. The chars were characterized in detail by SEM-EDX, XRD, Raman, FTIR and XPS and were tested on a fixed-bed reactor to evaluate its performances steam gasification. Calcium was found to have significantly promotional effect on the steam gasification of char samples with reduces of activation energy. It was observed the presences of 5 wt% or above in the char significantly enhanced H₂ productions, which resulted in high H₂/CO ratio of syngas. The SEM-EDS and XRD results suggested calcium was highly dispersed within the char particles, CaO and CaS presented in the char samples, but the hydrochloric acid treatment of the char caused significant loss of these calcium compounds. The steam gasification rate of the acid-treated samples was still much higher than that of the no-calcium-added char, which elucidates that superior steam gasification performance of the Ca-added chars was not the simple CaO species in the char, instead, a special calcium lignite intermediate complex “R₁-O-Ca-O-R₂” (R representing aromatic or aliphatic constituents), formed within char during the pyrolysis. Thus the crosslink-like intermediate complexes “R₁-O-Ca-O-R₂” structure between calcium and chars was postulated to be the decisive factor to promote the steam gasification of Shengli chars with more production of high hydrogen syngas.

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1. Introduction

Hydrogen is an ideal and efficient energy resource with the highest calorific value (about 142.6 MJ/kg). It is the most promising source of energy in the future among the known environmentally friendly fuels [1]. Currently, among the various commercial technologies for the production of hydrogen or hydrogen rich syngas, the steam gasification of low-rank coal showed strong competitive advantage due to coal natural structure [2,3]. Catalytic steam gasification of coal could remarkably improve the reaction rate at low reaction temperatures.

In the early 1980s, researchers [4,5] observed that the gasification of low-rank coals could be efficiently catalyzed by calcium compounds. The calcium components could catalyze the steam

gasification reaction at relatively low temperatures, which overcame the thermodynamic limitations of producing hydrogen rich syngas [6–8]. Some results [9–13] indicated that the catalytic effect of calcium compounds on the gasification of low rank carbon resource was tightly associated with the inherent oxygen-containing groups. Significant catalytic effect of Ca(OH)₂ on the gasification of the low rank coals were found by Ohtsuka [14,15]. The calcium ions was found to react with coal or coke matrix to form Ca-matrix complexes or CaC₂ during the thermochemical reaction [16,17], which could react readily with -COOH groups in low-rank coals by ion-exchange. Meanwhile, Kuznetsov et al. [18] proposed that the catalytic effect of calcium mainly depended on the naturally calcium-containing carboxylates. It was shown that the catalytic effect of inherent calcium species was greater than that of the externally added CaCO₃. During the gasification reaction at 750–800 °C, the calcium catalysts were reported to initially exist as finely dispersed calcium species after pyrolysis,

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which effectively catalyzed the steam gasification of subbituminous coal even with low catalyst contents [19]. However, Clemens et al. [20] claimed that the inorganic crystalline calcium was more likely to be active species in the char because of only a small fraction of the available ion exchangeable sites in the coal. Wang et al. [10,21–23] systematically studied the combined catalytic effect of calcium and potassium on the gasification of chars and found that the calcium additive acted as a deterrent to suppress the potassium deactivation and thus promoted the catalytic gasification [23]. These studies suggested types of coal and calcium species greatly affected the gasification reactions. However, the results obtained so far were inconsistent or even contradictory, which was mainly owned to the complexity of coal microstructures and the complicated mechanisms of calcium catalysis during the gasification reaction.

Several reaction mechanisms for the catalytic gasification of coals had been proposed in the early 1980s and are still widely used today. The mechanisms could be divided into two categories: electron-transfer and oxygen transfer [24–30]. Lobo et al. [25] found that both mechanisms failed to explain the kinetic behavior in some case; instead, the carbon bulk diffusion mechanism was applicable to kinetics of coal gasification reaction. Shen et al. [31] found that the carbon bulk diffusion mechanism were more suitable to characterize the kinetic behavior of nickel-catalyzed CO₂ rice husk char gasification. Our previous studies [32,33] indicated that the hydrogen rich syngas could be produced readily by the steam gasification of Shengli lignite, one of low rank coals from Inner Mongolia of China. Li et al. [32] found that the inherent mineral in Shengli lignite could significantly improve its steam gasification. The calcium component of the inherent minerals was proved to play a key role in the catalytic gasification reaction of Shengli lignite. Li et al. [33] further demonstrated that the calcium ion could inhibit the graphitization of lignite structure during pyrolysis, which was used to speculate the catalytic mechanism of steam gasification. Despite there have been many studies dealing with the catalytic species and mechanism of calcium on the steam gasification of coal, it is still not clear what active complexes play key factor of catalytic effect on the steam gasification of lignite. Thus it is highly necessary to re-examining the steam gasification reaction over the effect of calcium on lignite.

In this paper, we continue to study the catalytic effect of calcium on the steam gasification of Shengli lignite. The possible calcium structure serving as active species of during the steam gasification of char was analyzed using XRD, Raman, FT-IR, and XPS. This work is committed to advancing the catalytic mechanism of calcium on steam gasification of low rank coals for the production of hydrogen-rich syngas from low rank coals.

2. Experimental

2.1. Materials

Argon (purity: >99.99%) was provided by the Beijing Analytical Instrument Company. Calcium oxide (analytically pure, purity: >98%), hydrochloric acid (analytically pure, 38 wt%) were purchased from Tianjin Fengchuan Chemical Reagent Co. All the chemicals were used as received.

2.2. Sample preparation

The used lignite samples labeled as SL were from Shengli coal-field (Inner Mongolia Autonomous Region, China). The proximate analysis showed that received SL contained 47.6% moisture, 7.70% ash, 17.3% volatiles and 27.4% fixed carbons, respectively.

The received SL was crushed and sieved to 0.15–0.18 mm for subsequent treatment.

- 1) The demineralized SL sample was prepared by hydrochloric acid leaching. Approximately 50 g of SL was mixed with 500 mL 17% hydrochloric acid, aqueous solution and stirred for 4 h at room temperature. The resulting slurry was filtered by a vacuum filter and then rinsed continuously with distilled water to remove the residue chloride ions dried at 105 °C for 4 h. The solid products were labeled as SL⁺. The metal ions in inherent minerals and their contents in the received lignite samples, which were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES, Optima 7000, PerkinElmer) on the basis of coal or ash, are listed in Table 1. Table 1 shows the amount of metal ions in the SL⁺ sample decrease significantly compared with the original SL sample. It is proved that most of the inherent minerals (i.e. Al³⁺, Na⁺, Ca²⁺, Feⁿ⁺, K⁺, Mnⁿ⁺) within SL were removed by the hydrochloric acid leaching procedure.
- 2) The calcium addition char samples were prepared in a stainless steel reactor (40 × 1000 mm) which was heated by an electric furnace. About 5.0 g of the SL⁺ sample was first thoroughly mixed with certain amount of calcium oxide and then were placed in the center part of the tubular reactor; the reactor was heated to 1100 °C at a heating rate of 15 °C/min and was held for 1 h at a constant flow rate of 500 ml/min Argon followed cooling down to room temperature. The prepared chars containing 0.0, 2.5, 5 and 10% of Ca were labeled as SL⁺, SL⁺-2.5, SL⁺-5 and SL⁺-10 respectively. The sample SL⁺-10⁺ was prepared by the hydrochloric acid leaching of SL⁺-10. The percent of calcium within the char samples were determined by SEM-EDS and listed in Table 2.

2.3. Steam gasification experiments

The reaction system (Scheme 1) consists of a steam generator and a fixed-bed reactor that is made from stainless steel (8 × 350 mm). The reactor is heated by an electric furnace. For each experiment, 0.5 g of coal sample was loaded in the central zone of the tubular reactor sandwiched by quartz wool and quartz sand in order to maintain homogenous temperature. The steam generator was preheated to 300 °C, and pressure in the reactor was adjusted to 0.6 MPa by introducing argon (purity: ≥99.99%) at a flow rate of 200 mL min⁻¹. The off gas passed through an ice-water trapper followed by a cooler maintained at –30 °C to prevent steam and tarry matters from entering into the GC analyzer. The concentrations of hydrogen (H₂), carbon monoxide (CO), methane (CH₄), and carbon dioxide (CO₂) in the off gas were quantitatively determined using an online gas chromatography (Agilent 7890A).

- 1) Isothermal steam gasification (ISG): The reactor was heated to 850 °C at the heating rate of 15 °C min⁻¹. The gasification started by switching the argon stream to a steam/argon stream at 850 °C.
- 2) Temperature programmed steam gasification (TPSG): The test process was similar to ISG except that the heating rate is 1.2 °C min⁻¹. The steam (0.12 mL min⁻¹) was introduced into the steam generator when the reaction temperature reached 200 °C.

The instantaneous gas release rates of H₂, CO, CO₂, and CH₄ (*r_i*), the carbon conversion to gases (*X*), the instantaneous gasification rate (*R*) and the cumulative H₂/CO molar ratio (*CR*) are calculated by the following equations:

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