



A new active site/intermediate kinetic model for K_2CO_3 -catalyzed steam gasification of ash-free coal char



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HIGHLIGHTS

- A kinetic model is proposed to describe the K-catalyzed steam gasification of ash-free char.
- The model is strictly formulated based on an active site/intermediate mechanism.
- The model fits the profiles of gasification rate over the carbon conversion well.
- The model fits the variations of gas composition with carbon conversion well.
- The reaction rate constants estimated from modeling are reasonably explained.

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ABSTRACT

Experimental results showed that the K_2CO_3 -catalyzed steam gasification of ash-free char had two distinct characteristics of gas evolution. One was a broad maximum of gasification rate versus carbon conversion at a higher carbon conversion as a result of the sustained catalytic activity. Another was the variations of gas composition with carbon conversion arising from the complex reaction pathways. No model was reported to describe both characteristics in the literature. In this work, a new kinetic model was formulated in terms of an active site/intermediate mechanism with an assumption of the variations of effective carbon concentration with carbon conversion. The mechanism involved three potassium species and four reaction pathways for the catalyst cycle and gas release. The model was associated with five parameters including four rate constants and a catalysis factor, and it manifested a capability of predicting accurately the profiles of both gasification rate and gas composition over the entire range of carbon conversion. All four rate constants estimated from the modeling followed the Arrhenius equations with the reasonable activation energies. Moreover, the model could predict the formation, growth and decline of three potassium species during the gasification. The modeling result would deepen the understanding of the chemical processes of K_2CO_3 -catalyzed steam gasification of char.

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1. Introduction

Catalytic coal gasification has an advantage over the uncatalyzed coal gasification of being low-temperature operation and high-efficient throughput. Potassium carbonate is a prime catalyst, which performs high catalytic activity, low volatility and easy availability. From the standpoints of application and academy, K_2CO_3 -catalyzed coal gasification has received considerable attentions for a long history [1–6]. Currently, much interest is attracted to manufacture hydrogen by the K_2CO_3 -catalyzed steam gasification of coal, biomass and other carbon resources [7–10].

We proposed a conceptual two-stage catalytic gasification process for production of a hydrogen-rich gas with the inhibited yields of both carbon monoxide and methane [7]. However, potassium carbonate has a demerit of catalytic deactivation, which is caused by its strong interaction with acidic minerals in coal [11,12]. Wang et al. reported that the application of K_2CO_3 -catalyzed gasification to the HyperCoal or ash-free coal may provide a way to thoroughly avoid the catalytic deactivation [13]. Extended studies were done by other researchers on the K_2CO_3 -catalyzed gasification of ash-free coal [14,15].

Kinetic modeling of char gasification is of crucial importance in determining the rate of whole coal gasification. It has thereby been the subject of a number of early and recent studies [16–23]. This is also due to the problematic complexity. Volumetric model (VM),

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shrinking core model (SCM) and random pore model (RPM) are widely applied to fit the kinetic profiles of char gasification. However, it is usually futile to use VM and SCM for catalytic char gasification because these two models cannot describe a conversion-dependent reactivity of char which represents a critical feature of catalytic char gasification. In some instances, RPM can fit to the char gasification rate with the maximal gasification rate appearing in the range of carbon conversion between 0 and 0.393 [24]. Nevertheless, as claimed clearly by Zhang et al. [25], the kinetic predictions from RPM were rather unsatisfactory for both calcium- and potassium-catalyzed char gasification. They explored two RPM-based equations (called modified or extended RPM), which were found to have a good fit to the calcium- and potassium-catalyzed char gasification, respectively. In a later work, Kopyscinski et al. confirmed that the kinetics of K_2CO_3 -catalyzed CO_2 gasification of ash-free coal could be predicted only by the extended RPM (ERPM) rather than SCM and RPM [23].

In fact, all VM, SCM and RPM are established with only consideration of the geometry of the char particle. No mechanism of carbon active sites is involved in these models so that these models deem to be deficient in the predictive capability. ERPM, despite the success in correlation of catalytic char gasification, adds two more parameters into RPM without their physical and chemical meanings being rendered. The model is semi-empirical at best.

As early as the last 80s, Radovic et al. cognized that the rate of char gasification is proportional to the amount of carbon active sites [26]. They pointed out that a fundamental understanding of the kinetics of coal gasification requires the knowledge of the role of carbon active sites. The amount of carbon active sites cannot be obtained simply in terms of the total surface area of reacting carbon because of the varying concentrations of carbon active sites with the elapse of char gasification. In a later work, they affirmed some relation between the char gasification reactivity and the amount of oxygenated complex on char [27]. To our knowledge, however, no model was established to mathematically express a relation between the gasification rate and the amounts of carbon active sites until Liliedahl and Sjoström suggested a kinetic model from the following gasification mechanism [19]:



where C^* denotes an active carbon site which is in a non-steady state. Through some non-strict derivation steps, they deduced two equations:

$$X = \cosh(kk_1t) \exp(-kt) \quad (2)$$

$$X = (1 + kk_1t) \exp[-k(k_1 + 1)t] \quad (3)$$

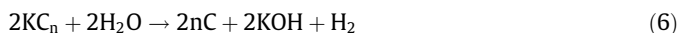
where X is carbon conversion, t is the time, k_1 is a rate constant depending on the nature and pressure of the gasifying agent, and k is a parameter related to the rate constant and equilibrium constant but defined ambiguously. As commented by Molina and Mondragon [20], although good agreement was claimed between the predicted results and the experimental ones for the case of CO_2 char gasification at 770–830 °C, to what gasification cases each equation is adaptable is not addressed. In a most recent study [28], we proposed a kinetic model for the calcium-catalyzed char gasification based on a simplified active sites/intermediate mechanism (named as Ca-ASIM below). An easily manageable equation with three parameters is eventually formulated to express the conversion-time or rate-time relationship. An encouraging outcome is that the model is accurately predictive for the calcium-catalyzed gasification and well reflective of some characteristics of calcium-catalyzed char gasification. Moreover, Ca-ASIM is flexible to match the uncatalyzed char gasification. In this case, the model is retrogressed to VM.

Nevertheless, Ca-ASIM cannot conform to the K_2CO_3 -catalyzed gasification of ash-free char. A typical result is illustrated in Fig. 1. The K_2CO_3 -catalyzed gasification of ash-free char exhibited a broad maximum of gasification rate positioned at a carbon conversion around 0.5 in contrast to a narrow summit of gasification rate occurring at a lower carbon conversion around 0.2 for the calcium-catalyzed gasification. This discrepancy is because the potassium catalyst behaves with no deactivation in the case of gasifying ash-free char, whereas the calcium catalyst gradually deactivates as the calcium loses its amorphism and high dispersion during gasification [29]. Ca-ASIM failed to track the belated climax of gasification rate characteristic of the K_2CO_3 -catalyzed gasification of ash-free char. In addition, from the maximum onward, the predicted rate dropped invariably along a concave curve, inconsistent with the experimental result.

In this context, the present work is undertaken to develop a new model for quantitatively describing the kinetic profile of the K_2CO_3 -catalyzed steam gasification of ash-free char. This model (named as K-ASIM) is built on the basis of the knowledge of K_2CO_3 -catalyzed char gasification and its active sites/intermediate mechanism, fundamentally differing from ERPM. K-ASIM is capable to describe not only the profiles of total carbon conversion but also the profiles of each gas production (CO , CO_2 and H_2) over the whole process of gasification. As far as the authors are aware, no such a prediction has been ever made by any models in the literature.

2. Model development

Numerous researches have been done regarding the mechanism of K_2CO_3 -catalyzed char gasification. The following mechanism and its simplified versions are widely disseminated in the early literature [2,5,30,31]:



These series of reactions seem to reasonably construct a redox cycle of the catalyst and an active intermediate for catalyzing carbon gasification. However, an essential flaw of this mechanism is

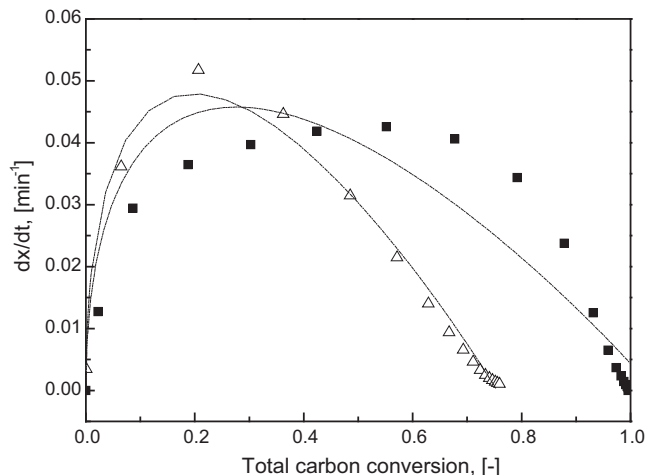


Fig. 1. The Ca-ASIM fit (dot lines) to the reaction rates versus the carbon conversion obtained by the gasification of a calcium-rich char at 750 °C (void triangle symbols) and by the potassium-catalyzed gasification of an ash-free char at 750 °C (black square symbols).

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