

## Studies on Catalysis of Metallic Species during CO<sub>2</sub> Gasification of Lignite Char

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## 論 文 内 容 の 要 旨

### Thesis Summary

In the transitional phase to renewable energy, avoiding direct combustion of coal is indispensable. The endothermic gasification with CO<sub>2</sub>/steam would be a key process of carbon resources conversion for chemicals and power production in the near future since it allows more efficient and more eco-friendly conversion of the coal. To further promote the efficiency of a gasifier, the reaction mechanism during the gasification need to be understood well, generally by applying a kinetic model, so that the rate of char conversion can be maintained optimally. However, the development of the conventional kinetic models is mostly based on the assumption that the change in char reactivity is only caused by that in char structure. These models described well the kinetics of gasification of highly ordered carbonaceous materials but failed to explain changes in the char reactivity of lignite and biomass, which contain inherent catalyst species. Recent studies also found the correlations of the rate of catalytic gasification with the metallic species composition. It was thus suggested that the kinetics model should take into account not only the char properties but also the catalysis of metallic species. Thus, the application of the parallel reaction model, which assumed the progress in parallel of catalytic and non-catalytic gasification, seems to be more reasonable to describe quantitatively the kinetics of gasification of lignite char. It is also noted from the review that there have been no trials to explain the differences in catalytic behavior between inherent and extraneous metallic species during CO<sub>2</sub> gasification of lignite char. Moreover, while the use of composite catalysts from AAEM species becomes a popular subject recently, very few studies made a focal point to understand the interaction mechanism of these species.

So, the focuses of this thesis is to understand the kinetics and mechanism of CO<sub>2</sub> gasification of lignite char under the catalysis of inherent metallic species and also that of extraneous (*i.e.*, intentionally added) metallic species using the parallel kinetic model, striving for a quantitative description of the overall rate of gasification, as a function of char conversion ( $X$ ) over the entire range of  $X$ . The initial catalytic activity and the rate of catalyst deactivation of these types of metallic species are also compared and discussed. This thesis also aimed to explain the kinetics of the K-catalyzed CO<sub>2</sub> gasification by proposing a new approach to evaluate the catalytic activity of K and its change during the gasification.

This thesis have proven the important roles of inherent and extraneous metallic species on determining the overall rate of CO<sub>2</sub> gasification of lignite char, which was successfully described over the entire range of conversion by employing the parallel kinetic model (PRM). Thesis contents are arranged as follows:

Chapter 1 introduces the background and outlines of this study.

In Chapter 2, CO<sub>2</sub> gasification of lignite chars at 900°C was investigated. The twenty chars, which having different contents/chemical types of inherent metallic species, were prepared by multistage washing of two-parent lignites and subsequent pyrolysis. The time-dependent changes in char conversion up to 0.999 for all the chars are quantitatively described by a kinetic model that assumed the progress of non-catalytic and

catalytic gasification in parallel, and employed multicatalytic species with different initial activities and deactivation kinetics. A single piecewise linear function, which followed a nucleation-growth mechanism of catalysts, showed the relationship between the total concentration of Na, K, Ca, and Fe and the initial total catalytic activity (ICA-2) for the chars. The overall rate of catalyst deactivation (ICD-2) was given by a single linear function of ICA-2 and a factor for the composition of metallic species. This function was also applicable to previously reported ICA-2/ICD-2 relationships for chars from lignite and biomass, showing fast deactivation of Fe catalyst and an important role of Mg in the promotion of catalyst deactivation.

Chapter 3 investigated the interaction mechanisms of Ca with Mg or K during catalytic CO<sub>2</sub> gasification of lignite char. Two demineralized lignites, prepared by multi-stage removal of inherent inorganic species, were loaded with varying amounts of Ca, Mg, and K, separately or jointly, by ion exchange, then pyrolyzed and subsequently gasified at 900°C. The measured kinetics of the gasification of chars with different contents of metallic species was described quantitatively over a range of char conversion, 0–0.999, by the model that employed the progress of non-catalytic gasification and catalytic gasification in parallel, together with the presence of multicatalytic components with different characteristics. For Ca-catalyzed gasification, its initial rate was correlated well and linearly with the Ca concentration in char (0.14–1.33 wt%-daf-char). When bi-metal catalysts were used, the kinetic analysis revealed that the Mg/MgO deactivated a portion of the most active Ca catalyst prior to and during the gasification. In contrast, the K showed synergistic performances with Ca. Its overall catalytic activity was similar to Ca on an equal mol basis, but its deactivation rate was much lower. It was also found that the catalytic performance of the extraneous metallic species was lower than that of inherent metallic species.

Chapter 4 developed a new method to observe the change in catalytic activity of K with the char conversion during CO<sub>2</sub> gasification of lignite char at 800–900°C. Several physical and chemical properties of char that potentially influence the catalytic activity were examined. The char samples were prepared from an Indonesian lignite by a sequence of complete removal of inherent metallic species and mineral matter, K-loading by ion-exchange, and pyrolysis. The catalytic activity of K ( $k'_{\text{cat}}$ ) was defined as the rate of catalytic gasification (after elimination of the rate of non-catalytic gasification and that of K volatilization from total mass release rate from char) per amount of K retained by the gasifying char.  $k'_{\text{cat}}$  increased by a factor of 5–20 with  $X$  over its range up to 0.98–0.99, depending on the initial K concentration in the char ( $m_{\text{cat},0}$ ) ranging 0.16–1.4 wt%-daf. Such significant increase in  $k'_{\text{cat}}$  was due to change in not the intrinsic reactivity of char but its porous nature, *i.e.*, the size and volume of pores that retained the K catalyst. At  $X < 0.4$ , the entire portion of K catalyst was confined in micropores (width < 2.0 nm) having relatively small  $k'_{\text{cat}}$ , although it increased gradually. At  $X > 0.4$ , the gasification created greater mesopores (width > 2.0 nm), providing spaces for growth in the size of the K catalyst and allowing promotion of its activity. However, for low  $m_{\text{cat},0}$ , its major portion continued to stay in micropores with a limited increase in  $k'_{\text{cat}}$ .

Chapter 5 summarizes the findings described in the preceding chapters.