



## Physical and chemical changes of coal during catalytic fluidized bed gasification



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### ABSTRACT

Coal gasification was studied by analyzing samples of feedstock extracted from a fluidized bed gasifier at various times throughout the gasification process. The analysis techniques used included energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy for elemental concentrations in the bulk and at the surface, respectively; acidimetric titrations to quantify the concentration of certain oxygen functional groups; and the BET method to determine surface area and porosity. The changes in feed particle size and composition showed that the gasification reaction rate was slow compared to the gas diffusion rates inside the coal particle. Detailed analysis of the composition and oxygen functional groups showed that the catalyst was loaded in the coal by ion exchange with surface oxygen functional groups. As the gasification reaction proceeded, the oxidized carbon content increased in the coal loaded with catalyst, but decreased in the coal without catalyst. That result supports the idea that the catalyst increases the reaction rate by helping to oxidize the carbon and increasing the number of reactive sites, rather than by decreasing the energy barrier for carbon–carbon bond breakage.

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### 1. Introduction

Though the world is switching to renewable energy sources, coal remains the most abundant fossil fuel on the planet [1], and its use will continue in much of the world over the coming decades [2]. Catalytic coal gasification is an attractive method for extracting energy from coal while reducing the environmental impacts compared to directly burning the coal. Gasification allows the conversion of solid coal into syngas—a gaseous mixture of hydrogen, methane, and carbon monoxide—which can then be converted to many other valuable products using a host of well-known reactions, e.g., steam-methane reforming to produce methane, the Fischer–Tropsch reaction for liquid hydrocarbons, or the water–gas shift for H<sub>2</sub> [3]. Low rank coals such as lignite are especially attractive for gasification because their high impurity content can increase gasification efficiency, whereas those same impurities can produce ash that causes costly maintenance issues for coal-fired plants. In fact, lignite that will be gasified is usually treated with catalytically active additives to further increase the gasification rate. Overall, catalytic coal gasification allows the efficient use of low rank coals which would otherwise be too costly and inconvenient to utilize [4–10].

One of the common classes of catalysts for coal gasification is alkali metal salts, which have long been known to increase the carbon

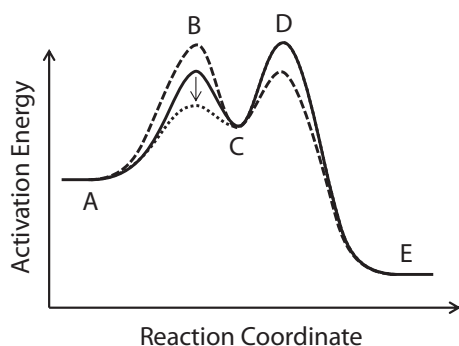
gasification rate [11–13]. Among alkali salt catalysts, the reaction rate has been found to increase with the cation atomic weight, i.e., uncatalyzed < Li < Na < K < Rb < Cs [14]. For a given cation, the highest reaction rate has been shown to occur with carbonate as the anion. Since Rb and Cs are prohibitively expensive, K<sub>2</sub>CO<sub>3</sub> is the catalyst of choice among alkali salts, and it was chosen for use in this study since it is cheap, effective, and widely used. Alkaline earth metal salts [15,16] and transition metal oxides [17,18] have also long been known to be effective gasification catalysts, and more recently co-gasification with biomass that contains catalytically active species has also been found to be effective [19–23].

While there has been a large amount of effort put towards understanding catalysis in gasification, much remains unknown about the form of the catalyst and its mechanism of action. Many researchers have proposed reaction mechanisms that address each discrete step in catalytic gasification, though there are two fundamental processes which always occur: (1) dissociative adsorption, where an oxidant molecule impinging from the gas phase becomes attached to the solid surface and oxidizes a carbon atom, and (2) the gasification reaction itself, where the bond between the bulk solid and the oxidized carbon is severed, allowing a CO or CO<sub>2</sub> molecule to enter the gas phase. Either of these processes could be rate limiting, and the alkali salt catalyst could act on either.

Fig. 1 shows a reaction diagram for the two generalized steps. The dashed line shows the case where the dissociative adsorption step is rate limiting, so it has a higher activation energy than the gasification

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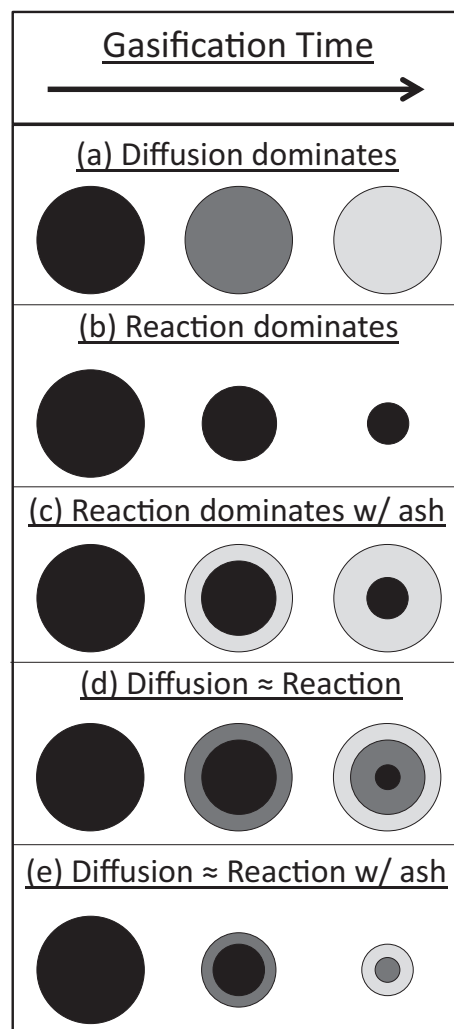


**Fig. 1.** A reaction diagram for a generalized two-step process describing carbon gasification. The reaction could be limited either by the gasification rate, represented by the solid line, or by the rate of dissociative adsorption of oxidant, represented by the dashed line. The dotted line shows the further reduction in activation energy for dissociative adsorption in the presence of catalyst. The reaction coordinates are: (A) reactants—gaseous oxidant, solid carbon; (B) transition state for dissociative adsorption; (C) oxidized carbon; (D) transition state for carbon gasification; (E) products—carbon monoxide gas.

step ( $E_{\text{diss-ads}} > E_{\text{gasification}}$ ); the solid line shows the opposite situation where the gasification step is rate limiting. If the alkali catalyst reduces the activation energy of the rate limiting step, then the overall activation energy of the process should be reduced. Some studies have shown that the presence of catalyst bound to the carbon substrate does reduce the carbon–carbon bond strength, which leads to a small decrease in  $E_{\text{gasification}}$  [14,24–28]. However, Bell et al. [29] compiled many different studies to show that, though the reaction rate did increase markedly, the overall activation energy was not strongly influenced by the presence of a catalyst [14,30–32]. Thus, the primary role of the catalyst must be to reduce  $E_{\text{diss-ads}}$  (shown by the dotted line in Fig. 1), which causes a greater concentration of oxidized carbon species to be available for gasification. The catalytic mechanism in this case could be an oxidation–reduction cycle, where catalyst that is initially oxidized transfers oxygen to the carbon substrate, then the reduced catalyst readily reacts with gaseous oxidant species [33–35].

Determining the correct mechanisms for coal gasification has proven to be challenging for a few reasons. For a given catalyst, the chemical form and dispersion of the catalyst in the substrate is critical to its activity [15,36,37]. Possible active forms of the alkali catalyst could be highly dispersed metal ions, discrete clusters or particles, atoms covalently bound to surface oxygen functional groups such as carboxylates or phenolates, or some combination thereof [38]. There was also some confusion at one point where some studies showed that the activation energies for gasification were different with different catalysts [5], but these probably arose due to the huge range of measured activation energies: the measured values span an order of magnitude and are highly dependent on the type of coal and reaction conditions [30,39].

In practical systems, understanding catalytic gasification is even further complicated because the carbon substrate is a porous solid. Fig. 2 shows generalized reaction schemes for porous, solid particles reacting in a gas, either with (c, e) or without ash species present (a, b, d). If the reaction rate is very high, the reaction occurs mostly at the surface (b,c); if the reaction rate is low, then the reactive gas will have enough time to diffuse into the particle before reacting (a) [40–42]. When the reaction and diffusion rates are similar, there may be a more complex structure that develops (d, e). The difference between the reaction models at relatively high or low reaction rate can be seen from the change in the particle structure as the solid mass decreases. In the random pore model (a), the gasification reaction occurs throughout the network of pores in the solid particle. As gasification proceeds, the pores become larger, and the mass of the particle decreases, but the diameter of the particle remains unchanged [43]. In the shrinking core model (b), the particle porosity is constant, and the particle diameter decreases until only ash remains [29]. Knowing the



**Fig. 2.** Reaction models for solid reactant particles consumed in a gasification reaction, adapted from ref. [42].

proper reaction model is useful for producing more accurate kinetic and computational fluid dynamic models for a gasifier [42,44–47], and also gives insight into how to improve the reactor design and operation, since different modifications would be needed depending if the diffusion or the surface reaction is the limiting step.

In this work, we use a variety of *ex situ* analysis techniques of the coal, char, and ash particles retrieved from a gasifier at various stages of the reaction to track the changes during gasification. SEM imaging allows a rough estimate of the size distribution of the particles. Surface area measurements reveal the porosity of the coal particles. EDX and XPS give chemical compositions of the particles for the bulk and surface, respectively. IR spectroscopy and acidimetric titrations show the evolution of functional groups in the coal. A general model for the reaction was found by analyzing the physical changes in the samples, which provided insights into the relative rates of diffusion and reaction in the gasifier. We also follow the distribution and form of the catalyst and the oxidation of the carbon substrate as they evolve throughout the reaction. The *post mortem* analysis outlined here provided valuable insight into the gasification process, and could be similarly applied by others to better understand a variety of systems.

## 2. Materials and methods

All studies in this paper used a low-rank coal (lignite) from Inner Mongolia, China that was pre-ground. The proximate analysis showed

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