

## CATALYSIS OF CHAR GASIFICATION BY MINERALS

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### INTRODUCTION

It is well known that most minerals act more or less to catalyze carbon gasification (1,2). In coals, there are two broad classes of inorganic impurities -- the discrete mineral matter, which is usually present in particles greater than about 1  $\mu\text{m}$  in size, and the minor and trace elements, which are more or less associated with the organic phase or mineral phase in a highly dispersed state. Because of current interest in producing low and high BTU gases by coal gasification, it is desirable to know the extent to which inorganic impurities in chars (as a result of being present in the original coals) increases gasification rates. The aim of the present study is to investigate possible catalytic activity of major minerals found in coals for char gasification in air,  $\text{CO}_2$  and  $\text{H}_2$ . Since coals and, hence, chars are invariably associated with many inorganic impurities, a high purity polymer char having a structure similar to coal-derived chars has been used in the present study.

### EXPERIMENTAL

Char Preparation The high purity char was obtained by carbonizing Saran (a copolymer of PVDC and PVC in a ratio of about 9:1) at  $900^\circ\text{C}$  in the manner described previously (3). The char was ground and the 200x325 mesh fraction (44x74  $\mu\text{m}$  particle size) heated in  $\text{N}_2$  in a fluidized bed reactor up to  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . Soak time at  $1000^\circ\text{C}$  was 2 hr. The  $\text{N}_2$  ( $77^\circ\text{K}$ ) and  $\text{CO}_2$  ( $298^\circ\text{K}$ ) surface areas of the char were 900 and 1110  $\text{m}^2/\text{g}$ .

Minerals The following minerals were used: kaolinite, illite, calcite, dolomite, gypsum, quartz, rutile, pyrite and siderite. The minerals were obtained from Wards Natural Science Establishment, Inc., New York.

Preparation of Char-Mineral Mixtures Various char-mineral mixtures containing 5%, by weight, minerals were prepared by mixing the 200x325 mesh fraction of the minerals with the same size fraction of Saran char. The mixtures were blended for 4 hr in an electric rotating device.

Procedure Reactivities of various char-mineral mixtures were determined in air (1 atm) at  $550^\circ\text{C}$ ,  $\text{CO}_2$  (1 atm) at  $960^\circ\text{C}$  and  $\text{H}_2$  (20.4 atm) at  $940^\circ\text{C}$ . In each case, an electrobalance was used to monitor weight changes occurring during the gasification reaction. Details of the experimental procedure have been described previously (4,5). Briefly, a small amount of the mixture contained in a platinum pan was heated in an inert ( $\text{N}_2$  or He) atmosphere to the reaction temperature at a rate of  $20^\circ\text{C}/\text{min}$ . The sample was maintained isothermally at the reaction temperature for 15 min to ensure thermal stability. Following this, the inert atmosphere was replaced by the reactant gas. Weight changes occurring during gasification were then determined continuously.

Reactivity Measurement In the present study burn-off vs. time curves had a gradual induction period followed by a region in which burn-off increased with time. At higher levels of carbon burn-off, the rates started to decrease. Instantaneous reactivity ( $R_t$ ) at different reaction times was calculated from the following equation:

$$R_t = \frac{1}{w_t} \cdot \frac{dw}{dt}$$

where  $w_t$  and  $dw/dt$  are the weight of the unreacted char on a dry-ash-free (daf)

basis and slope of the burn-off vs. time plot at time  $t$ , respectively. For reactions in  $\text{CO}_2$  and  $\text{H}_2$ , the reactivity parameter  $R_c$ , which represents the constant rate in the region where the kinetics follow a first order rate expression with respect to amount of unreacted char, has been reported. For reaction in air,  $R_c$  increased monotonically with conversion so that  $R_c$  values cannot be given. Therefore, the reactivity parameter for the reaction in air has been calculated from the following equation:

$$R_o = \frac{1}{w_o} \cdot \frac{dw}{dt}$$

where  $w_o$  is the starting weight of char on a daf basis and  $dw/dt$  is the maximum rectilinear rate of weight loss.

### RESULTS AND DISCUSSION

Reactivity parameters for various char-mineral mixtures in air,  $\text{CO}_2$  and  $\text{H}_2$  are listed in Table 1. Reactivities could be duplicated within  $\pm 2\%$  in all cases.

TABLE 1

#### REACTIVITY RESULTS

Mineral	Reactivity, $\text{mg hr}^{-1} \text{mg}^{-1}$		
	$R_o$ in Air	$R_c$ in	
		$\text{CO}_2$	$\text{H}_2$
none	1.1	1.9	2.3
siderite	1.0	1.8	5.6
pyrite	1.1	1.3	3.9
dolomite	1.0	2.0	2.0
illite	1.0	1.8	1.4
quartz	-	2.0	2.1
gypsum	1.0	1.5	1.6
rutile	1.1	2.0	1.6
kaolinite	1.2	1.6	1.2
calcite	1.0	1.7	0.6

Reactivity in Air Values of  $R_o$  for various samples vary between 1.0 and 1.2. Furthermore, instantaneous rates at a given conversion for different mixtures were found to be essentially the same as for the Saran char itself. These results thus indicate that there is little or no catalytic effect of the minerals studied on char reactivity in air.

Most of the minerals investigated are known to undergo chemical and/or structural changes upon heating to higher temperatures. In order to see if such changes modify activity of the various minerals towards char gasification in air, a few char-mineral mixtures prior to making reactivity measurements at  $550^\circ\text{C}$  were heated to  $900^\circ\text{C}$  in an inert atmosphere. The reactivities following heat treatment at  $900^\circ\text{C}$  were found to be essentially the same as when the heat treatment temperature was  $550^\circ\text{C}$ . Thus, the chemical or structural forms of the minerals investigated have no detectable catalytic effect on char gasification in air.

Reactivity in  $\text{CO}_2$  It is seen (Table 1) that pyrite, gypsum, kaolinite and calcite inhibit the reaction in  $\text{CO}_2$ ; the effect is most pronounced for pyrite. It is noteworthy that although both  $\text{C-CO}_2$  and  $\text{C-O}_2$  gasification reactions involve an intermediate oxygen transfer step (1,2), the aforementioned minerals inhibit the reaction in  $\text{CO}_2$  whereas they have no such effect in  $\text{O}_2$ . This shows high catalytic specificity of these minerals for gasification reactions in different oxidizing atmospheres.

The observed inhibitive effect of pyrite may be due to the following. Carbon monoxide is produced during the C-CO<sub>2</sub> reaction. Before CO is desorbed into the gaseous phase, it has a two-dimensional mobility on the surface. During this mobility, CO may collide with pyrite particles producing COS which in turn may dissociate at the reaction temperature into CO and S. This sulfur may be chemisorbed on the char surface. It is known that sulfur and oxygen are chemisorbed essentially at the same active carbon sites (6). Since the first step in the overall gasification process is the dissociative chemisorption of the reactant gas at the active carbon sites, it is obvious that following chemisorption of sulfur the extent of oxygen chemisorption and, hence, gasification rate will be retarded.

Reactivity in H<sub>2</sub> Most of the minerals have an effect, either catalytic or inhibitive, on the hydrogasification reaction. Siderite and pyrite show large catalytic activity. Both these minerals contain iron as a major component. X-ray diffraction studies revealed that during the hydrogasification reaction both these minerals are reduced to elemental iron. It is well known that metallic iron catalyzes the C-H<sub>2</sub> reaction. Illite, gypsum, rutile, kaolinite and calcite have an inhibitive effect on the hydrogasification reaction. The inhibitive effect is most pronounced for calcite. Although it is difficult to explain unequivocally the inhibitive effect of various minerals, we suggest the following reason for the observed behavior. Most inorganic impurities catalyze carbon gasification by providing active sites at which dissociation of reactant molecules can readily occur (2). The dissociated species then diffuse across the substrate surface and react with the active carbon atoms. It is suggested that in the case of the minerals which have an inhibiting effect on char reactivity the reverse of molecular hydrogen dissociation is predominant. That is, H<sub>2</sub> is dissociated at active sites on the char surface producing hydrogen atoms. Some hydrogen atom recombination on the surface of the minerals results in a reduction in the rate of char hydrogasification.

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