CATALYSIS OF LIGNITE CHAR GASIFICATION BY EXCHANGEABLE CALCIUM AND MAGNESIUM

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INTRODUCTION

The high intrinsic reactivity of chars derived from lignite coals is primarily due to the presence of well dispersed metal oxide particles, which are formed when carboxyl groups on the lignite surface, having been exchanged with various cations from the local groundwater, decompose as the lignite is heated to gasification temperatures. Roughly half of the carboxyl groups on American lignites have undergone exchange, with Ca and Mg predominantly, and to lesser extents with other alkali and alkaline-earth cations (1). These cations have been shown to be good catalysts for lignite char gasification in air, CO_2 and steam (2).

It is noted, however, that lignite char reactivity decreases rapidly as final heat treatment temperature increases (3,4) or as soak time at temperature increases (4). Radovic and co-workers (5) have shown that the majority of this decrease can be correlated with a decrease in CaO dispersion in the case of Ca loaded demineralized (Dem) lignite chars.

Exchangeable cations play an important role in the behavior of lignite coals in coal conversion processes. It is, therefore, important that a fundamental understanding be attained, first of the possible interaction of exchangeable cations in lignites with each other, and, second, of the possible effects on the subsequent catalytic activity of the cations for lignite char gasification. The aim of this study was to develop such an understanding using the two most abundant cations in American lignites: Ca and Mg. The objective of this work was to study the effect which adding Mg, which is a poor gasification catalyst, to Ca, which is a good gasification catalyst, has on the catalytic behavior of Ca for lignite char gasification. That is, will the presence of Mg in some way affect the sintering of Ca and, hence, affect the catalytic activity of Ca?

EXPERIMENTAL

A Montana lignite (6) was subjected to essentially complete demineralization with HCl and HF in order to remove essentially all the inorganic constituents (exchangeable cations and mineral matter) present (1). The Dem lignite was then ion-exchanged with Ca or Mg using solutions of their acetate salts. Seven levels of Ca and three levels of Mg were obtained using loading solutions of varying concentrations. A sample of Dem lignite was also co-exchanged with Ca and Mg in order to study the effect of their interaction on subsequent char reactivity. Chars were prepared by slowly heating (10 K/min) the treated lignites in a box furnace equipped with an air tight retort under N_2 to final temperatures of 973 or 1273 K and held (soaked) for 1 h. Char reactivities were determined by isothermic thermogravimetric analysis (TGA) in 0.1 MPa air, 0.1 MPa CO_2 and 3.1 kPa steam (saturated N_2). The maximum slope (R_{max}) of the TGA recorder plot was used as a measure of gasification reactivity (normalized to initial weight of char, daf basis). From a series of preliminary runs (7) reaction conditions were selected in order to eliminate heat and mass transfer limitations. Therefore, reported reactivities are believed to be intrinsic, chemically controlled rates.

Selected chars were examined by x-ray diffraction (XRD) to identify Ca and Mg containing species present in the chars. Average crystallite diameters of selected species were determined using the line broadening concept and the Scherer equation (8).

RESULTS AND DISCUSSION

Figures 1 and 2 show the reactivity results in 0.1 MPa air for the 973 and 1273 K chars, respectively. As seen previously, Ca is a good catalyst for char gasification in air, while Mg is a poor char gasification catalyst (2). For Ca loaded chars at both heat treatment temperatures, it is seen that two distinct regions of reactivity behavior are present. For loadings up to ~4 wt% Ca, the reactivity increases linearly with increasing Ca content. For loadings greater than ~4 wt% Ca, however, reactivity remains essentially constant with increasing Ca content. This is contrary to the behavior seen by Hippo et al. (9)., who reported a linear increase in reactivity with increasing Ca content up to 12.9 wt% in 0.1 MPa steam for a Texas lignite. Since mass transport limitations are believed to be absent, the plateau is not due to diffusional effects. This suggests that the plateau is the result of a catalyst "saturation effect," that is, adding of catalyst beyond a certain amount does not further increase the observed rate. For the relatively small range of Mg contents a similar saturation effect appears to be operating. Examination of the cation exchanged 1273 K chars by XRD revealed that CaO and MgO were the major species present in the Dem+Ca and Dem+Mg chars, respectively.

Reactivity results for the 1273 K chars reached in 0.1 MPa CO_2 and 3.1 kPa steam at 1053 K are shown in Figures 3 and 4, respectively. The same trends evident for the 1273 K chars reacted in 0.1 MPa air are also seen in these reactant gases. Two regions of reactivity behavior are present in both cases. Calcium is seen to be a good char gasification catalyst, while Mg has very little catalytic effect.

The purpose of this work was to study the effect that adding Mg to Ca has on the subsequent catalytic behavior of Ca for lignite char gasification. To study this effect, the chars of the co-exchanged Dem lignite were used. It was reasoned that the co-exchanged chars should have a Ca content which was in the region where reactivity increased with metal content, as to avoid the saturation region. Also, the char should contain more Mg than Ca on a molar basis, since an effect is more likely to be observed under these conditions. Metal contents of the co-exchanged chars are presented in Table 1.

TABLE 1

METAL CONTENTS IN THE CO-EXCHANGED CHARS (DRY BASIS)

	Calcium		Magnesium	
Char	mmol/g	wt%	mmol/g	wt%
973 K	0.54	2.2	0.91	2.2
1273 K	0.56	2.2	0.94	2.3

To determine if there was any effect, reactivity data of the mono-exchanged chars were used to calculate an expected reactivity. Calculation of these expected reactivities was straight forward, which assumed that the catalytic activities of Ca and Mg were simply additive. From the metal contents in Table 1, the contributions of Ca and Mg to the calculated reactivities could be determined from Figures 1-4 by reading the reactivity value corresponding to that amount of Ca or Mg directly from the appropriate figure. The reactivity of the Dem-char is subtracted once because it is included in both the Ca and Mg contributions, while it is included only once in the co-exchanged char. This step is not necessary when the rate of the uncatalyzed (Dem) reaction is low; but is necessary when the uncatalyzed rate is high, as is the case in CO_2 (Figure 3). For consistency, the Dem reactivity

was always subtracted once. The calculated reactivity is the sum of the Ca and Mg contributions, with the rate of the Dem reactivity subtracted once. By comparing the calculated reactivity with that actually observed for the co-exchanged chars, one will be able to tell if indeed there is an effect. The calculated and observed reactivities are given in Table 2 for the various gases.

TABLE 2

CALCULATED AND OBSERVED REACTIVITIES OF THE CO-EXCHANGED CHARS

Char	Reactivity Contributions (mg/mg h)			Reactivities (mg/mg h)	
	Ca	Mg	Dem	Calculated	Observed
			Air		
973 K	0.31	0.09	0.01	0.39	0.42
1273 K	0.34	0.22	0.03	0.53	0.60
			CO_2		
1273 K	0.60	0.34	0.32	0.62	0.64
			Steam		
1273 K	0.30	0.10	0.05	0.35	0.31

It is quite clear from Table 2 that the addition of Mg to Ca does not have a significant effect on the subsequent activity of Ca. The observed reactivities are, within experimental error, the same as the calculated reactivities. This shows that the catalytic effects of Ca and Mg are additive and they do not interact in a significant way to either increase or decrease their combined catalytic effects. This is perhaps due to the fact that MgO is not significantly soluble in CaO below 1900 K (10). The presence of MgO does not reduce the sintering of CaO. This is supported by examination of the 1273 K co-exchanged char by XRD. The average crystallite diameter of the CaO was calculated to be 30 nm. This is the same value obtained for a 1273 K Dem+Ca char that has a similar Ca content (1.4 wt%).

CONCLUSIONS

The addition of Mg to Ca does not have a significant effect on the subsequent activity of Ca for lignite char gasification under the slow heating conditions used in this study. Their catalytic effects were found to be additive, indicating that they did not interact in any significant way. This was supported by XRD results which showed that the sintering of CaO was not reduced by the presence of MgO.

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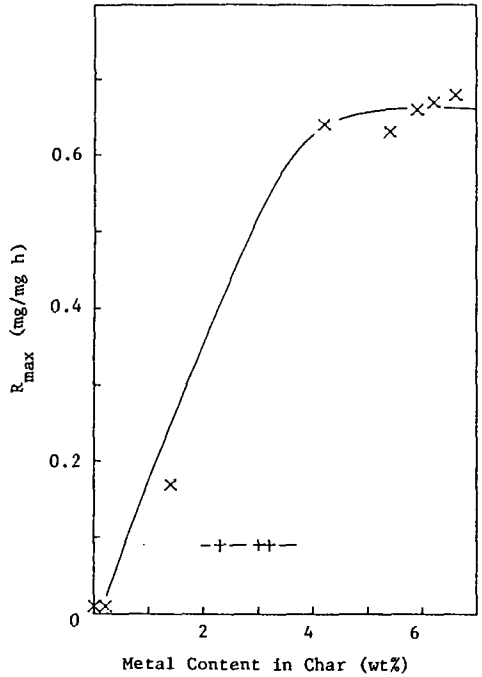

Figure 1

Reactivities of the 973 K Chars
in 0.1 MPa Air at 603 K.
x Dem+Ca, + Dem+Mg

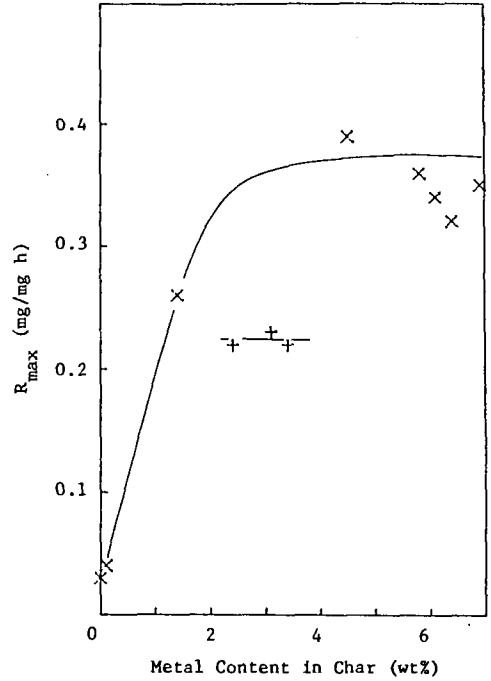

Figure 2

Reactivities of the 1273 K Chars
in 0.1 MPa Air at 603 K.
x Dem+Ca, + Dem+Mg

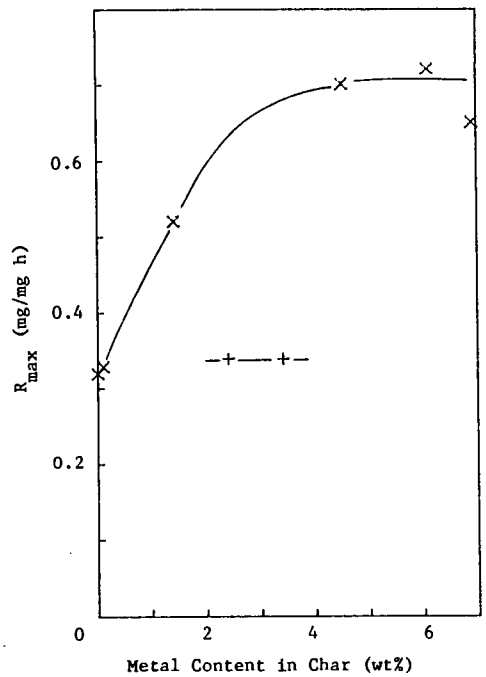

Figure 3

Reactivities of the 1273 K Chars
in 0.1 MPa CO_2 at 1053 K.
x Dem+Ca, + Dem+Mg

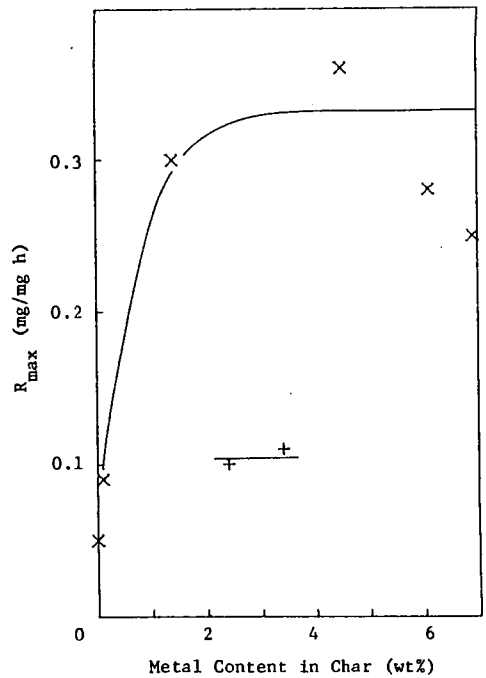

Figure 4

Reactivities of the 1273 K Chars
in 3.1 kPa Steam at 1053 K.
x Dem+Ca, + Dem+Mg