

CATALYSIS OF CHAR GASIFICATION IN O₂ BY CaO and CaCO₃

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ABSTRACT

Catalysis by CaO and CaCO₃ of the oxidation of a well-defined, high purity synthetic char, Spherocarb, was investigated at low reaction temperatures using thermal gravimetric analysis (TGA). Oxidation rates were likewise measured for fresh, demineralized, and Ca-impregnated samples of a high temperature char prepared in a flat-flame burner at about 1300 K from Beulah Zap coal. Spherocarb and demineralized Zap char were impregnated with Ca using aqueous impregnation and ion-exchange techniques. The resulting kinetic parameters for Spherocarb indicate significant catalytic effects--up to a 100 fold increase in reaction rate for CaCO₃ and 3,000 in the case of CaO. The oxidation rates of CaO-catalyzed Spherocarb and Beulah Zap char are the same within experimental error, suggesting that the high reactivity of the Zap char is due in large part to catalysis by CaO.

INTRODUCTION

Char oxidation is a complex heterogeneous process which often governs the overall rate of combustion. Oxidation rates are partially governed by surface properties of the char and reactions catalyzed by minerals within the char matrix. To date studies on catalytic effects of inorganic minerals on char oxidation have been relatively few, and many important questions regarding effects and mechanisms of mineral catalysis, and the relevance of laboratory temperature data to actual operating conditions remain unanswered.

The objectives of this ongoing study are to address some of these questions by (1) studying rates and mechanisms of CaO catalysis of the oxidation of synthetic chars and rank representative demineralized coal chars, (2) determining active sites, surface functional groups, and surface mineral phases in these chars, and (3) investigating effects of surface area and catalyst dispersion.

This paper reports TGA measurements showing the effects of CaO and CaCO₃ catalysis on low temperature oxidation rates of Spherocarb, a well-defined, high purity synthetic char and of a Beulah Zap char prepared in air at high temperature in a flat-flame burner.

EXPERIMENTAL

Oxidation rates of pure Spherocarb and CaO loaded Spherocarb prepared by aqueous impregnation (1.2% CaO) and ion exchange (2.8% CaO) with a solution containing an excess of calcium acetate [1] were measured using a thermogravimetric (TGA) system described elsewhere [2]. We designate the samples prepared by aqueous impregnation and ion exchange methods as 1.2% CaO(aq)/Spherocarb and 2.8% CaO(ion)/Spherocarb respectively. Spherocarb samples (Analabs, Inc.; particle diameter of 120 microns) were burned off to 50% of the initial weight at a temperature in the intrinsic rate regime of 748 K in 10% oxygen prior to preparation of the calcium-containing samples to facilitate the penetration of the Ca acetate or Ca hydroxide into the pores. Critical temperature data (temperatures for 6.5 % per minute burnoff) were initially obtained in 10% oxygen (in nitrogen) by heating 2 mg samples at 40 K/min to 1223 K. Thereafter, rates of oxidation were measured isothermally in 10%

oxygen to various stages of burnoff in the neighborhood of the critical temperature and in the region of 150-200 K below the critical temperature.

The dispersion of CaO particles on Spherocharb was measured following the procedure of Radovic et al. [3], and Solano et al. [4] using selective CO₂ chemisorption at 573 K in a TGA apparatus. Samples containing calcium were decomposed at 1173 K for 10 minutes in nitrogen flow, cooled to 573 K and after 10 minutes, exposed to flowing CO₂ in nitrogen for about 30 minutes. From the weight of CO₂ chemisorbed values of surface area (S_{CaO}), crystallite diameter (d), and percentage dispersion (D) of CaO were estimated using the equations of Radovic et al. [3].

Surface areas were determined from nitrogen adsorptions carried out at 77 K, using procedures and a flow adsorption system described previously [5]. Nitrogen adsorption isotherms were analyzed using the BET equation, and an area for the nitrogen molecule of 0.162 nm² was used to obtain surface areas.

High temperature Beulah-Zap (Zap) char was prepared by devolatilization in a flat flame burner of 200-230 mesh particles of the Argonne premium coal. The details of this apparatus have been described previously [6]. Feed gas consisted of 8.6% methane, 72% nitrogen, and 19.4% oxygen. The flame temperature at the collection probe was found to be 1251 K, and the residence time of the particles in the burner was 130 ms.

The Zap char was demineralized using concentrated acids (37 wt.% HCl and 49 wt.% HF). One gram of char was placed into a beaker and 200 ml of concentrated HCl was added. The beaker was heated to 333 K and stirred for two hours. Following HCl treatment, the char was washed 4 times using 1 liter of 365 K water for each wash. The HCl treatment was performed on the char 3 times, following which the same treatment was performed using HF. Following the final acid treatment the char was washed 8 times using 1 liter/wash of distilled water at 365 K and dried in a vacuum oven at 383 K overnight.

RESULTS AND DISCUSSION

Spherocharb. BET surface areas from nitrogen adsorption of untreated Spherocharb and 50% burned-off Spherocharb were determined to be 895±7 and 1039 m²/g respectively; the value for the untreated Spherocharb compares favorably with values of 864 and 965 m²/g reported by Waters et al. [7] and Dudek et al. [8]. In these two previous studies [7,8] surface area was observed to increase up to a conversion of 10-15% and then monotonically decrease with increasing conversion (reaching 650-660 m²/g at 65-80% conversion); however conversion temperatures in these studies ranged from 780 to above 1300 K. In the present investigation conversion in the intrinsic rate regime at 748 K (10% oxygen) caused a 16% increase in surface area. This result suggests that densification/graphitization processes [9] are important at higher oxidation temperatures (above 750 K).

Arrhenius plots of oxidation rates for preburned (to 50%) and untreated Spherocharb are plotted in Fig. 1. The rates at any given temperature and activation energies (153 and 150 kJ/mol respectively) are the same within experimental error. Accordingly, the low temperature burnoff treatment at 748 K to open up pores for Ca impregnation does not affect the intrinsic reactivity of the Spherocharb char. The oxidation rate of Spherocharb at 667 K corrected to 21% oxygen (assuming an oxygen order of 0.6) is 2.8 μg/gs in very good agreement with a value of 2.3 μg/gs determined by Hurt et al. [10]. The activation energies from this study of 150-153 kJ/mole for oxidation of Spherocharb are in excellent agreement with the value of 153 kJ/mole determined for Spherocharb from the data of Hurt et al. [10] but somewhat lower than the value of 184 kJ/mol reported by Waters et al. [7] for Spherocharb and

very near values of 167-170 kJ/mole reported for oxidation of various synthetic mineral-free carbons [11,12]. Accordingly, the rate data and activation energies are valid for the intrinsic surface oxidation of carbon and are not influenced by pore diffusional or film mass transfer resistances.

Critical temperatures (6.5% wt. loss/min corrected for ash) for unloaded Spherocarb, 1.2% CaO(aq)/Spherocarb and 2.8% CaO(ion)/Spherocarb were found to be 968, 906 and 797 K respectively, indicating a large catalytic effect.

Rate data plotted in Arrhenius form are shown in Figure 2 for unloaded Spherocarb, 1.2% CaO(aq)/Spherocarb at 55 burnout and 2.8% CaO(ion)/Spherocarb at 50% burnout after pretreatment at 823 or 973 K. From the Arrhenius plots preexponential factors and activation energies were obtained for the unloaded Spherocarb and the two different catalytic loadings, one after pretreatment at two different temperatures (see Table 1). The activation energies for unloaded, 1.2% CaO(aq)/Spherocarb and 2.8% CaO(ion)/Spherocarb samples after pretreatment at 823 and 978 K are 150, 121, 96, and 139 kJ/mole respectively in the temperature range of 570-900 K, the magnitude of these values again indicating that the rates are probably not influenced by pore diffusional resistance in this range of conditions, since values of 125-200 are reported for mineral-catalyzed coal char combustion [13], although a value of only 64 kJ/mole was reported for Ca-impregnated char [14].

Table 1. Activation Energies and Pre-Exponential factors of oxidation of CaO-Loaded and Unloaded Synthetic and Zap Char Samples in 10% oxygen

Sample	Ea (kJ/mole)	Pre-Exponential (g/sample s)
2.8% CaO(ion)/Spcb (823 K)	139	3.0 x10 ⁸
2.8% CaO(ion)/Spcb (973 K)	96	0.19 x10 ⁴
1.2% CaO(aq)/Spherocarb	121	3.6 x10 ⁴
Unloaded Spherocarb	150	99 x10 ⁴
Zap Char	112	1.4 x10 ⁶
1.86% CaO/Zap	117	6.9 x10 ⁶
Zap, demineralized	151	3.3 x10 ⁸

Rates calculated at 600 K from Figure 2 indicate that the 1.2% CaO(aq)/Spherocarb sample is more reactive than the unloaded sample by a factor of about 12 while 2.8% CaO(ion)/Spherocarb pretreated at 823 K is more reactive by a factor of about 100 (Table 2). This enhancement in rate is consistent with that of up to two orders of magnitude reported by Levendis et al. for CaO catalysis at low temperatures [14]; however, the 2.8% CaO(ion)/Spherocarb pretreated at 973 K is 30 times more active than these other Ca-containing chars with a rate enhancement factor relative to the uncatalyzed sample of 2800. Apparently, the pretreatment temperature has a dramatic effect on activity. As will be shown later, the significantly higher activity after pretreatment at 973 K is due to the presence of CaO while CaCO₃ is present after pretreatment at the lower temperature. A smaller but still significant factor is the method of preparation; this is probably because the aqueous impregnation technique results in a dispersion that is inferior to that obtained by other techniques such as ion exchange [14].

TEM and SEM studies of unloaded and CaO loaded Spherocarb samples were also conducted to determine the distribution of CaO in the samples. The TEM results were inconclusive regarding the dispersion of CaO in the micro and mesopores of the carbon. However, the SEM pictures provided strong evidence that the aqueous impregnation deposits copious quantities of CaO on the exterior of the carbon spheres, while the ion exchange

technique provides a uniform dispersion and greater penetration of pores, especially into partially burned-out Spherocharb. Indeed, the extent of loading, dispersion, and surface area of CaO are greater for samples prepared by ion exchange than those prepared by an aqueous impregnation method (Table 3). Thus, smaller size crystallites of CaO are formed during the ion exchange process leading to better dispersion and higher surface area. Calcium loading by ion exchange probably allows calcium ions to enter into micro and mesopores of Spherocharb possibly accounting for its higher intrinsic reactivity (per surface area of CaO; see Table 2).

Table 2. Catalytic Effects of Ca in Oxidation of Spherocharb at 600 K

Sample	10^6 rate (g/gchar s)	10^4 rate (g/gCaO s)	10^6 rate (g/m ² CaO s)
2.8% CaO (ion -exch.) /Spherocharb (973 K)	237	85	
2.8% CaO (ion -exch.) /Spherocharb (823 K)	8.3	3.0	2.7
1.2% CaO (aq.-impr.) /Spherocharb	1.0	0.83	0.62
Ca-Free Spherocharb	0.085	-	-

Table 3. Effect of Method of Calcium Loading on CaO Dispersion

Sample	S_{CaO} (m ² /g CaO)	d (nm)	D (%)
1.2% CaO(aq)/Spherocharb	134	11.5	10.8
2.8% CaO(ion)/Spherocharb	180	8.5	14.5

The substantially higher reactivity of the 2.8% sample pretreated at higher temperature suggests the possible formation of a new catalytic phase. Indeed, TGA experiments of complete burning of 1.2% CaO(aq)/Spherocharb, 2.8% CaO(ion)/Spherocharb and pure calcium acetate performed in 10% O₂/90% N₂ atmosphere by ramping slowly from room temperature to 1173 K show that calcium acetate decomposes in two stages (Table 4). Comparison of weight changes observed from TGA experiments and values calculated assuming CaCO₃ and CaO as intermediate and final product respectively agree very well. This indicates that calcium in Spherocharb exists as CaCO₃ at temperatures below 823 K and CaO above this pretreatment temperature. Thus, CaO has substantially higher catalytic activity than CaCO₃.

Beulah Zap. BET surface areas from nitrogen adsorption of Zap char and demineralized Zap char were determined to be 322 and 348 m²/g respectively. The value for the Zap char prepared with a residence time of 130 ms is somewhat higher than the value of 229 m²/g reported by Hecker et al. [2] for a residence of time of 104 ms; however, this is expected since surface area of chars prepared in the flat flame burner increases very significantly with increasing residence time [2]. The larger surface area for the demineralized char is consistent with removal by acid treatment of mineral matter from micro or mesopores or pore entrances, since it is the micro and mesopores that account for most of the surface area of chars [5].

Table 4. Stoichiometry of Decomposition of Calcium Acetate by TGA

	Experimental(TGA)		Calculated	
	Raw data (wt.%)	after water correction (wt.%)		(wt.%)
Ca(Ac) ₂	100.000		Ca(Ac) ₂	100.000
Water	5.400			
1st decomposition	60.167 (724 K)	63.601	Ca(Ac) ₂ → CaCO ₃	63.331
2nd decomposition	33.658 (1048 K)	35.579	Ca(Ac) ₂ → CaO	35.476

*values in the parentheses are the temperatures of maximum decomposition rate

Arrhenius plots of rate data are shown in Fig. 3 for oxidation of Zap, 1.86% CaO/Zap (prepared by ion exchange), and demineralized Zap chars. It is evident that the reactivities of Zap and 1.86% CaO/Zap chars are very close while that of the demineralized Zap is much lower, suggesting that the high reactivity of Zap is due to the presence of Ca minerals. Activation energies for the three Zap chars are summarized in Table 1. The value of 112 kJ/mol for untreated Zap char is in excellent agreement with the value of 113 kJ/mol reported by Hecker et al. [2] for a Zap char prepared under very similar conditions in a flat-flame burner. The value of 151 kJ/mol for demineralized char is the same within experimental error as the value determined for pure Spherocharb (see Table 1), suggesting that oxidation of the demineralized char occurs by the same mechanism as the synthetic, mineral-free char.

Fig. 4 compares rate data in Arrhenius form for oxidation of catalyzed and uncatalyzed Spherocharb with those for Zap and demineralized Zap chars. The data for Zap and 2.8% CaO/Spherocharb fall nearly along the same line while rates for demineralized Zap are lower than for Zap but higher than those for uncatalyzed Spherocharb. Again, these results strongly suggest that the higher reactivity of Zap relative to demineralized Zap is due to the presence of CaO minerals in the Zap char. These results are quite consistent with data reported by Radovic et al. [15] for Zap, demineralized Zap, and CaO-catalyzed Zap pyrolysis chars prepared at a relatively high residence time (0.3 s) at 1275 K; in this latter study [15] the demineralization and CaO exchange were done on the coal. These workers likewise observed similar reactivities for Zap and CaO-catalyzed Zap chars, while that for the demineralized char was substantially lower. Apparently, significant differences in pretreatment of the coal and preparation of the chars do not affect the qualitative results, although quantitatively they are different.

CONCLUSIONS

1. The intrinsic reactivity of Spherocharb, a relatively mineral free synthetic char, is not affected by 50% oxidation at 748 K in 10% oxygen. In other words, there is no evidence of graphitization or densification under these conditions. However, there is a significant (16%) increase in BET surface area as a result of this mild oxidation treatment.

2. Kinetic parameters obtained in this study indicate a significant catalytic effect of CaO involving at least a 2800-fold increase in oxidation rate of Spherocharb compared to a 100-fold increase in rate for CaCO₃.

3. Ion exchange results in better dispersion and penetration of calcium into Spherocharb than other methods investigated in agreement with previous studies of synthetic chars.

4. The higher reactivity of Zap relative to demineralized Zap or uncatalyzed Spherocharb is due in large part to the presence of Ca minerals in the form of CaO.

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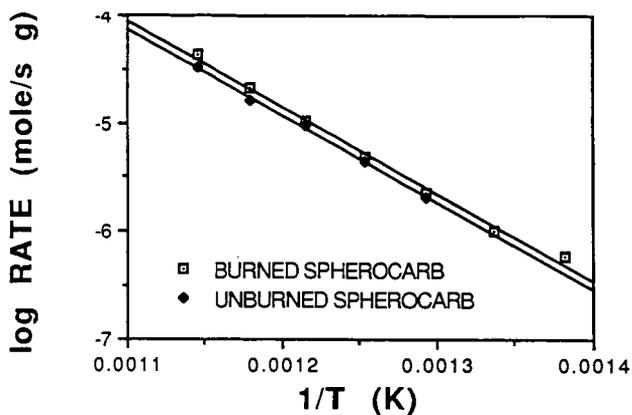


Figure 1. Arrhenius plots of oxidation rates of SpheroCarb and partially oxidized SpheroCarb (50% conversion at 748 K in 10% oxygen in nitrogen).

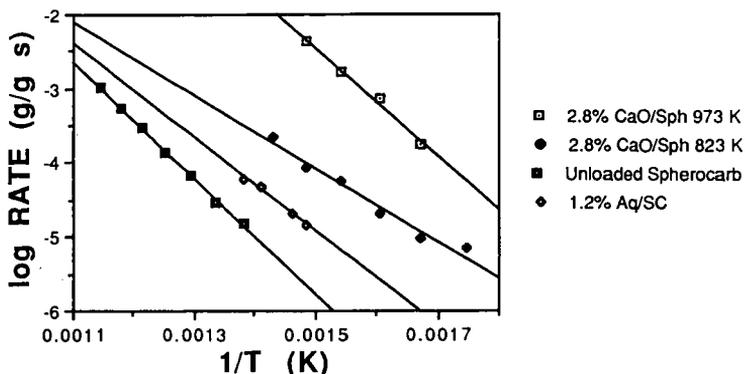


Figure 2. Arrhenius plots of oxidation rates for 2.8% CaO(ion)/SpheroCarb (pretreated at 823 and 973 K), 1.2% CaO(aq)/SpheroCarb, and uncatalyzed SpheroCarb in 10% oxygen.

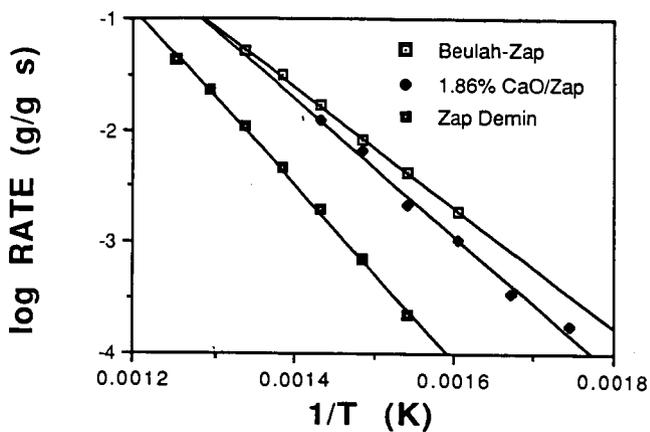


Figure 3. Arrhenius plots of oxidation rates for Zap, 1.86% CaO/Zap (prepared by ion exchange), and demineralized Zap chars in 10% oxygen.

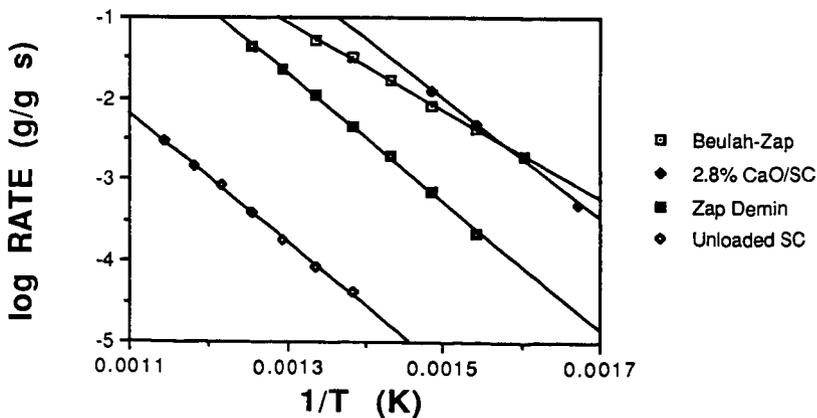


Figure 4. Arrhenius plots of oxidation rates for catalyzed and uncatalyzed Sphercarb and for Zap and demineralized Zap chars in 10% oxygen.