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Catalytic activity of calcium for lignite char gasification in various atmospheres

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Gasification rates of a Texas lignite char, having calcium contents varying from 1.1 to 12.9 wt%, were measured in air, steam, CO₂, and H₂. Gasification rates increased rectilinearly with increase in calcium loading. The chemisorption of CO₂ at 298 K on the CaO present on the char surface was used to determine CaO particle dispersion. Knowing this dispersion, specific activities of calcium as a catalyst for the gasification reactions were calculated. The spread in specific activities in different atmospheres is large, it being a maximum when the char-air reaction is compared with the char-H₂ reaction.

(Keywords: gasification; catalysis; lignite)

It has been concluded that calcium is the most important *in-situ* catalyst for the gasification of lignite chars¹. North American lignites contain between about 2–3 meqg⁻¹ of carboxyl groups, and ≈25% of these groups have undergone exchange of their hydrogen by Ca²⁺. On heating the coal to pyrolysis (gasification) temperatures, the carboxyl groups decompose, liberating CO₂, and leaving behind well dispersed CaO on the surface of the microporous lignite char³. Previously, the enhancement of Texas lignite char reactivity to steam was studied by the addition of greater amounts of Ca than found *in situ*⁴. Twelve levels of Ca loading were studied. A rectilinear increase in reactivity was found as Ca loading in the char was increased between 1.1 and 12.9 wt%. Overall, increase in reactivity was approximately six-fold.

This paper reports the reactivity of these Ca-loaded lignite chars to air, CO₂, and H₂ and an estimation of the specific activity of Ca as a catalyst for lignite char gasification in these various atmospheres.

EXPERIMENTAL

Lignite

A bench sample of a Gulf Province lignite from the Darco Mine near Darco City, Texas was used in this study. Table 1 presents proximate and ultimate analyses for the sample, using ASTM procedures. From ion-exchange of Ca on the raw lignite, it was estimated that it contained 2.36 mmol of carboxyl groups per g of dry mineral-matter-free coal. Table 2 presents an ash analyses on the raw lignite. As discussed previously², of the alkali and alkaline-earth metals present, Ca is by far the most abundant.

Procedures and apparatus

Determination of lignite. Demineralization was effected by first passing 10% (by wt) HCl over the coal continuously for 2 h. At the end of this period, no Ca ions were detected in the liquid leaving the column. The acid-

washed lignite was then immersed in a 50–50 mixture of 50% HF and 10% HCl and held at boiling water temperature for 48 h. The solution was then decanted off and the lignite continuously washed with boiling water in a column for 2 h. At the end of this time, no Cl ions were detected in the exit stream. Table 2 presents an ash analysis on the demineralized (Dem) lignite.

Calcium exchange on the demineralized lignite. Schafer's method was used to effect ion exchange⁵. Complete details of exchange are given elsewhere⁶. Twelve levels of Ca ranging from 0.10 to 2.14 mmol of cation g⁻¹ coal (daf) were added by exposing the Dem lignite to calcium acetate solutions ranging in concentrations from 0.04 to 2.0 molar for 24 h.

Charring of the lignite. Conversion of raw, Dem, and ion-exchanged lignites (28 × 48 mesh fraction) to chars

Table 1 Analyses of lignite

Proximate analysis	Wt%, dry basis	Ultimate analysis	Wt%, daf ^a
Ash	9.4	C	71.7
VM	44.8	H	5.2
Fixed C	45.8	N	1.3
		S	0.72
		Cl	0.02
		O ^b	21.1

^a Dry, ash free

^b Oxygen was determined by difference

Table 2 Ash analyses for selected lignite samples

Sample	Ash, %	Oxides, % by wt of ash							
		CaO	SO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
Raw	9.4	10.4	17.6	36.7	21.6	9.4	1.9	0.53	0.47
Dem	0.5	22.0	—	21.9	10.2	9.6	1.2	0.29	0.21
1.1									
Ca-									
Dem	8.7	74.2	15.2	2.9	0.12	0.55	1.5	0.98	0.19

was carried out in a fluid bed. The sample was held in 0.1 MPa N₂ for 30 min at room temperature under fluidization conditions before heating in N₂ at a rate of 20 Kmin⁻¹ to 1073 K and holding for 2 h.

Reacting lignite chars. All reactivity runs were conducted at temperatures below that at which the chars were produced (1073 K). Further, conditions were selected such that reactivities in different atmospheres were similar and affected little by heat and mass transport considerations⁷. Reactivity measurements in 0.1 MPa steam were conducted in a fluid bed at 923 K, as described in detail elsewhere^{4,6}. At the exit of the reactor, unreacted steam was condensed and the product gas was passed through a wet test meter. Samples of gas leaving the wet test meter were taken at intervals to analyse for CO, CO₂, and H₂ using gas chromatography.

Reactivities in 0.1 MPa air (663 K) or CO₂ (1033 K) were measured in a 951 Dupont TGA apparatus. Reactivities in 5.4 MPa H₂ (1063 K) were measured in a 951 Dupont TGA unit which was enclosed in an autoclave⁸. These measurements were conducted at elevated pressure to enhance the rate of char gasification in H₂, since it is a relatively slow reaction⁷.

Characterization of chars. Surface areas of chars were determined from CO₂ adsorption at 298 K. The area taken for the CO₂ molecule was 0.253 nm².⁹ Pore volumes and char porosities were determined from He and Hg densities, measured at 298 K, as described in detail elsewhere¹⁰.

RESULTS AND DISCUSSION

Physical properties of chars

Table 3 presents results for surface areas and pore volumes of selected lignite chars. Surface areas on a dry-ash free basis were calculated assuming that CO₂ uptake on the inorganic fraction was negligible. A monotonic increase in surface area is observed with increase in calcium loading on the char. It is to be emphasized that these surface areas were calculated assuming only physical uptake of CO₂ and a molecular area for CO₂ of 0.253 nm². There is reason to believe that chemisorption of CO₂ is occurring on CaO sites in addition to physical uptake on all the surface. This supposition will be used to estimate the extent of dispersion of CaO on the char surface.

Unlike surface areas, pore volumes and porosities change little with the level of calcium loading on the chars. As discussed elsewhere, most of the pore volume in lignite chars is concentrated in the micropores <2.0 nm in diameter¹¹. It is physical uptake of CO₂ in these pores which contributes primarily to the surface areas calculated for the chars.

Table 3 Physical properties of selected chars

Property	Calcium loaded chars								
	Dem	Raw	1.1 ^a	1.9	2.6	4.5	5.3	8.5	12.9
CO ₂ surface area (m ² g ⁻¹ , daf)	680	800	720	740	760	760	770	800	850
He density (gcm ⁻³ , mmcb)	1.88	1.97	1.93	1.97	1.96	1.97	2.03	2.04	2.02
Hg density (gcm ⁻³ , mmcb)	1.18	1.33	1.30	1.35	1.34	1.33	1.37	1.33	1.36
Pore volume (cm ³ g ⁻¹ , mmcb)	0.31	0.24	0.25	0.23	0.30	0.24	0.24	0.26	0.24
Porosity (% mmcb)	37	31	33	31	33	32	33	35	33

^a Calcium in chars, wt%

Reactivity of chars in various atmospheres

Table 4 presents reactivity results for the lignite chars in the different atmospheres. Reactivities are normalized to starting weight of char. After the reactivity initially increased with burn-off, there was an extended burn-off range where reactivities changed little^{4,12}. Reactivities are given in this range. As seen previously⁴, char reactivity in steam increases rectilinearly with increasing amounts of Ca on the exchanged lignite chars. As Ca content in the chars increased from 1.1 to 12.9 wt%, reactivity increased about six-fold. Reactivities in other atmospheres also increased essentially rectilinearly with increasing Ca loading. Reactivity results are summarized in Figure 1. For each atmosphere, the reactivity was normalized to one for the char containing maximum Ca loading. Overall change in reactivity in air was similar to that found in steam; whereas, overall change in reactivity in CO₂ and H₂ were significantly less than that found in steam.

Specific catalytic activity of calcium for char gasification

The rectilinear increase in char gasification rate in different atmospheres over the range of Ca loading from 1.1 to 12.9 wt% suggests that catalyst dispersion is independent of loading. Using XRD, Radovic *et al.* have identified the calcium species found following lignite pyrolysis in N₂ as CaO³. The crystallite size of the CaO increases with increasing pyrolysis temperature and residence time at temperature.

It is well known that CO₂ chemisorbs on alkaline-earth metal oxides¹³. Radovic *et al.*, confirmed such chemisorption on calcium-loaded lignite char³. Results presented in Table 3 support this conclusion in the present study. Whereas the pore volume (almost entirely micropore volume) changes little with calcium loading on the char, the surface area, as measured by CO₂ uptake at

Table 4 Char reactivities in different atmospheres

Ca in char, wt%	Reactivity, gg ⁻¹ h ⁻¹ (daf)			
	CO ₂	air	steam	H ₂
2.0	Raw lignite char			
	0.37	0.24	0.05	-
0.02	Dem lignite char			
	0.25	0.02	0.005	0.37
1.1 1.9 2.6 4.5 5.3 8.5 9.1 12.9	Ca exchanged lignite chars			
	0.47	0.21	0.11	0.40
	0.51	0.22	0.13	-
	0.60	0.45	0.17	0.43
	0.60	0.53	0.23	0.50
	0.86	0.65	0.30	-
	0.97	0.98	0.43	-
	1.15	1.00	0.45	0.47
	1.55	1.40	0.63	0.60

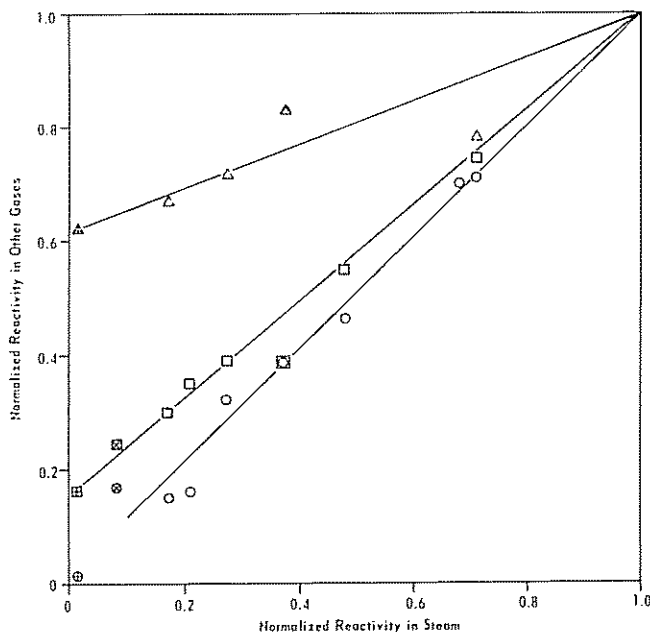


Figure 1 Normalized reactivities in air, CO_2 , and H_2 versus those in steam. Reactivities change with calcium loading and are normalized to 1.0 at maximum loading of 12.9 wt%: \circ , air; \square , CO_2 ; \triangle , H_2 ; \times represents raw char and $+$, dem char

298 K, increases monotonically as calcium loading is increased. It is suggested that the char surface area, like the pore volume, changes little with calcium loading and that the reported increase in surface area with loading is due to increasing chemisorption on CaO sites. If this assumption is correct, the number of CaO sites (or Ca atoms) in the surface of the catalyst can be calculated knowing that one CaO site has a surface area of 0.115 nm^2 and that one CO_2 molecule chemisorbs on one CaO site. The best estimate of this dispersion should be made from CO_2 surface areas on samples having a maximum difference in calcium loading, where the difference in surface areas is a maximum and least susceptible to imprecision of individual surface area measurements. An increase in Ca loading in going from the 1.1 wt% Ca char to the 12.9 wt% Ca char, or 19.7×10^{20} Ca atoms g^{-1} , is assumed to have resulted in an increase in surface area of $130 \text{ m}^2 \text{ g}^{-1}$ due to CO_2 chemisorption. The $130 \text{ m}^2 \text{ g}^{-1}$, resulting from the original assumption of only physical uptake of CO_2 , is equivalent to an uptake of 5.1×10^{20} CO_2 molecules g^{-1} . The assumption of one CO_2 molecule chemisorbing per Ca atom, yields a dispersion (d) for the CaO of 25.8%. From the formula, $d = 124/D^3$, the average diameter (D) of the CaO particles on the lignite char surface is estimated to be 4.8 nm. It is expected that a particle size of CaO which is this small (with the crystallite size of 4.8 nm or smaller), even for maximum loading on the char, would not generate detectable CaO XRD peaks³. Such was found to be the case in this study.

Knowing the increase in total number of Ca atoms in the surface and the increases in gasification rates in different atmospheres as Ca loading on the char is increased from 1.1 to 12.9 wt%, the specific activity of the catalyst can be calculated as a turnover frequency (TOF) in units of atoms of carbon gasified per surface atom of Ca per second. These results are summarized in Table 5 for the experimental gasification conditions used in this study. If we assume that the gasification rate in H_2 is proportional to the first power of H_2 pressure¹⁴, the TOF for the C- H_2 reaction is also given at 0.1 MPa pressure.

The specific activity of inorganic species for catalysing char gasification is expected to not only be a function of the particular element(s) involved but also the active surface area (ASA) of the char¹⁵. For a given catalytic phase, the TOF should increase as the ASA of the char increases. Therefore, the TOF's given in Table 5 are not expected to be universal specific activities for calcium at the particular temperature and pressure conditions used for gasification. Radovic *et al.* show that the ASA's of a North Dakota lignite char, produced by slow heating in N_2 and holding for 1 h at maximum temperature, are 108 and $25 \text{ m}^2 \text{ g}^{-1}$ following pyrolysis at 975 K and 1475 K, respectively¹⁵. They also found that ASA decreased with increasing pyrolysis residence time following rapid heating to 1275 K. Thus the specific activity of a particular catalyst is expected to depend upon pyrolysis conditions used to convert the coal to char. The ASA of the Dem char produced in this study, using oxygen chemisorption, was not measured.

Estimates of specific activities for calcium catalysis of char gasification in this study over a range of temperatures can be made from knowledge of activation energies for the different gasification reactions. These activation energies are taken where gasification is predominantly catalysed by calcium, that is gasification of either raw lignite chars or chars derived from Ca-loaded lignites. Activation energies, in kJmole^{-1} , in air, steam, CO_2 , and H_2 atmospheres are as follows: $130^{3,16}$, 170^4 , 200^{17} , and 200^{14} . Figure 2 presents results on an Arrhenius plot over the range of gasification temperatures

Table 5 Specific activity of calcium as a gasification catalyst

Atmosphere	Temperature, K	Pressure, MPa	TOF, $\text{s}^{-1} \times 10^2$
Air	663	0.1	3.23
Steam	923	0.1	1.41
CO_2	1033	0.1	2.93
H_2	1063	5.4 (0.1)	0.54 (0.010)

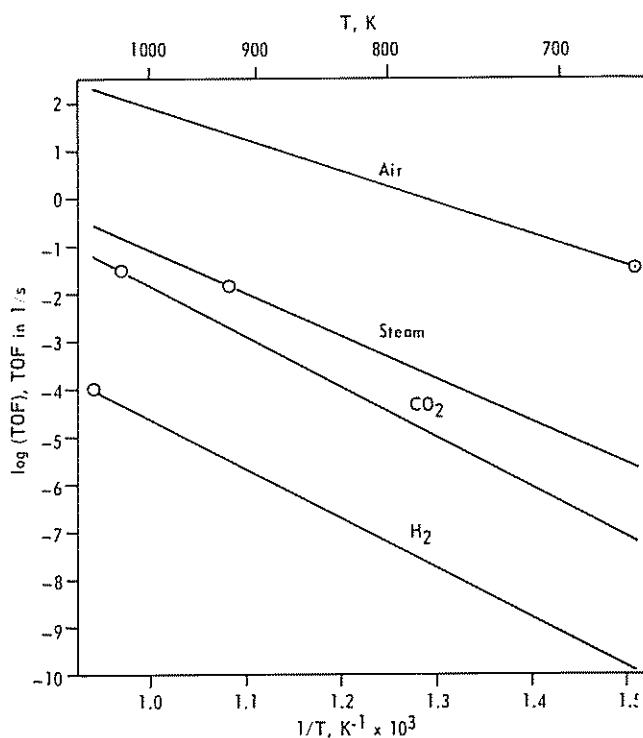


Figure 2 Arrhenius plots for TOFs for calcium catalysed char gasification in various atmospheres at 0.1 MPa pressure

used in this study, that is 663 K to 1063 K. Very large differences in the activity of calcium to catalyse the gasification reactions are noted. For example, at 700 K the TOF for the calcium-catalysed char-air reaction is some 10^8 greater than the TOF for the char- H_2 reaction. Differences in TOF's will depend markedly upon the particular catalyst present. For example, iron is an excellent catalyst for the C- H_2 reaction; whereas in air, iron becomes oxidized and loses much of its catalytic activity¹⁸. In this case the TOF's would be much closer together.

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Reduction activities of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts with hydrogen sulphide and hydrogen

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Diphenylmethane and diphenylether were reacted under a $\text{H}_2/\text{H}_2\text{S}$ gas mixture in the presence of a series of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts. In general, the activity of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ increased as the surface area increased, but decreased when the catalyst preparation involved the use of sodium hydroxide or sulphate ions. The supported iron catalysts displayed higher activity, in terms of conversion, toward the aromatic-alkyl (Ar-C) bond cleavage than the aromatic-ether (Ar-O) bond cleavage. Some of the $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts were more effective than $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$ for cleaving diphenylmethane and did so with less aromatic ring hydrogenation. The hydrocracking ability with regard to the Ar-C bond rupture correlated well with the acidity of the catalysts as determined by butylamine adsorption. Both hydrocracking and hydrogenation abilities of the catalysts were important in the Ar-O bond rupture which appeared to be influenced by acid and base sites.

(Keywords: catalyst; reduction; hydrocarbon)

An important aspect of coal liquefaction research is the development of effective catalysts for the various chemical conversions involved in the process. It has been demonstrated that H_2S is beneficial for the pyrolysis of some pure hydrocarbons^{1,2}, the hydrodenitrogenation of aromatic compounds^{3,4}, the $\text{CO}/\text{H}_2\text{O}$ shift reaction⁵ and the hydrocracking of diphenylmethane (DPM)⁶. Moreover, the various effects of H_2S on coal liquefaction have been reported by several researchers⁷⁻¹⁵. It was found to be beneficial for improving the hydrogen-carbon (H/C) ratio of the products^{11,13,16}, enhancing coal conversion, and increasing the yield of distillate oils^{11,16}.

A recent hypothesis concerning the activity of pyrite (FeS_2) in coal liquefaction is that the catalyst is the H_2S , produced from the reduction of pyrite^{14,17}. The preliminary studies suggest that H_2S is participating in the reactions and appears to be an effective hydrogen transfer catalyst as evidenced by the conversion of coal to THF-solubles and the H/C ratio of the products.

To further enhance the yield of distillate in coal liquefaction, catalytic agents other than H_2S may be required. The effect of H_2S with pyrite¹³ and/or pyrrhotite¹⁸ in coal liquefaction, especially for enhancing the yield of distillate, has been reported and exemplified by the hydrocracking of DPM^{6,19}. Moreover, it has been shown for many metal oxides that the catalytic activities on coal conversion increase when used together with H_2S ²⁰. A more recent study^{21,22} involving the reductive cleavage of DPM suggests that a synergism between H_2S and some of the Fe_2O_3 binary oxide catalysts exists.

Because the catalytic activity of heterogenous catalysts generally varies with factors such as the nature of the support and the methods of preparation, a series of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts has been synthesized and the results are reported in the present study. These catalysts were

tested for their hydrocracking ability with regard to two model compounds in the presence of $\text{H}_2/\text{H}_2\text{S}$. DPM and diphenylether (DPE) were selected as model compounds because they represent two types of bonds, aromatic-alkyl (Ar-C) and aromatic-ether (Ar-O), that would be desirable to rupture in the liquefaction process. This study is centred on the effects of catalyst preparation, surface area and acidity/basicity. For comparison, commercial $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$ was also studied.

EXPERIMENTAL

DPM and DPE from Aldrich (>99.5% pure as determined by gas liquid permeation chromatography) were used as received. Research-grade hydrogen and hydrogen-sulphide were used without further purification.

The preparation of silica gel from tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ at pH 11 was done by dissolving 140 g of $\text{Si}(\text{OC}_2\text{H}_5)_4$ in 340 ml of ethanol. To this solution, 340 ml of H_2O were added producing a nonhomogeneous suspension. Approximately 40 ml of concentrated $\text{NH}_3(\text{aq})$ or NaOH were added, with constant stirring until the solution was clear. Then an additional 20 ml of base was added with constant stirring, and the solution was left to stand for 30 min. The solution was stirred for 10 min to ensure gel formation while the pH was monitored and adjusted if necessary. The precipitate was heated in a water bath for 3 h and then vacuum filtered using Whatman No. 1 filter paper. The pH of the filtrate was also checked. The precipitate was then washed with 100 ml of ethanol followed by 1000 ml of H_2O . This washing took $\approx 6-8$ h and the surface of the precipitate was worked with a spatula as needed. The precipitate was then dried overnight at 110°C followed by calcination at