

THE CATALYTIC EFFECT OF CALCIUM IN AIR GASIFICATION OF A SUBBITUMINOUS COAL CHAR

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INTRODUCTION

Low rank coals contain alkali metals and alkaline-earth metals (especially Ca) which catalyse the gasification by O_2 , CO_2 and H_2O .

A great deal of information is still needed concerning the nature and dispersion of the active species, the interaction between these species and organic matter...

A correlation of catalytic activity of CaO, as obtained during pyrolysis performed before gasification, with its dispersion, was observed by Radovic et al. (1).

EXPERIMENTAL

1) Sample preparation

The coal was a Brazilian subbituminous coal. It was demineralized by HCl and HF at 333 K, (CD), in order to observe only the catalytic effect of calcium. (CD) was pyrolysed in helium (heating rate : $4 K min^{-1}$) up to 1073 K (CD1073). This char was oxidized by HNO_3 15N (CD1073oxi), in order to increase its ion exchange capacity ; the procedure was used by Linares-Solano et al. (2). A cationic exchange was then performed with an 0.1 molar aqueous solution of calcium acetate, as described by Hippo et al. (3) ; drying of the sample (CD1073oxiCa) was carried out under reduced pressure (0.1 Pa) at 383 K. Finally a fraction of this material was pyrolyzed for 2 hrs in helium at 1073 K (CD1073oxiCa1073).

2) Sample characterization

Chemical analysis was used for the organic elements and for Ca. XPS Spectroscopy allowed determination of the surface concentration of Ca ; the depth of analysis was about 1.5 nm. X Ray Diffraction analysis was applied to appreciate the Ca phases. The microtexture was evaluated from the Dubinin-Raduskhevitch (4) method, and assuming a slit shape of the pores from CO_2 adsorption measurements at 273 K. The radical density and the linewidth value were obtained by ESR measurements.

3) Sample reactivity

The gasification experiments were performed under atmospheric pressure of dry air, heating rate $0.8 K min^{-1}$ and in absence of mass and thermal transfer limitations according to Barthe et al. (5). CO_2 and CO formation was followed by chromatographic analysis.

RESULTS

Table 1 and 2 give the chemical analysis data and the microporous texture data, respectively, for the initial samples CD, CD1073, CD1073oxi and CD1073oxiCa.

Table 3 gives the surface and bulk Ca/C atomic ratios, of the CD1073oxiCa sample either ungasified, or gasified at 30 or 60 %.

We did not detect any crystalline phase of some Ca species in either CD1073oxiCa1073 or in CD1073oxiCa.

Fig.1 shows the gasification versus temperature profiles for the samples CD1073, CD1073oxi, CD1073oxiCa and CD1073oxiCa1073. A strong catalytic effect of Ca is apparent from the comparison of the (c) and (d) curves to the (a) and (b) curves.

Table 4 shows the selectivities in CO versus CO + CO₂, which did not vary more than 10 % in course of the gasification experiments. Ca does lower the selectivity in CO.

Table 5 shows the microporous texture data for the CD1073oxi and CD1073oxiCa samples, gasified between 0 % (unconverted materials) and 60 %. The microporous volume, the surface area, and the micropore size are decreased in presence of Ca.

The ESR data are shown in Table 6. The radicals concentration is much smaller in CD1073oxiCa than in CD1073oxi (ungasified samples). That difference tends to cancel out as the burn off increases.

DISCUSSION

Initial sample characterization

The Ca⁺⁺ of the CD1073oxiCa sample are presumed to be selectively exchanged with carboxylic groups of the CD1073oxi sample. In fact, the pH value of the Ca acetate solution was not high enough to allow cationic exchange with hydroxyl groups according to Schafer (6). From the results of surface analysis of Ca (Table 3 ; ungasified sample), Ca should be homogeneously distributed between the surface and the bulk of CD1073oxiCa.

The higher radical concentration of CD1073oxiCa compared to CD1073oxi (Table 6; ungasified samples) may be explained either by quinone reduction into semi-quinone during the Ca acetate solution exchange step, or by a Ca⁺⁺ catalysed adsorption or absorption of O₂ by the demineralized coal (CD). The higher oxygen wt % of CD1073oxiCa compared to CD1073oxi (Table 1) would favour the second hypothesis.

The physico-chemical state of Ca in CD1073oxiCa1073 may not be inferred accurately from the present work ; in particular, no calcium compound could be identified by XRD analysis. The literature data suggest the formation of CaO during the final pyrolysis step at 1073 K, according to Barthe et al. (5).

Reactivity in gasification

The Arrhenius plots for the air gasification reaction of the 4 samples studied are reported in Fig.2. The apparent activation energy is the same, 120 kJ.mol⁻¹, in agreement with literature data, Khan (7), Linares-Solano et al (8). The preexponential factor is strongly increased in presence of Ca. A main observation lies in the very similar behaviour of CD1073oxiCa and of CD1073oxiCa1073. Since the evolution of CO, CO₂ from CD1073oxiCa is catalyzed by Ca, already at about 723 K, the Ca carboxylate² species should not have to be decomposed into CaO to be catalytically active. The similar catalytic effect of Ca in CD1073oxiCa1073, presumed to consist of CaO/C, indicates the role of the "CaO"/C interface as already mentioned, Linares-Solano et al. (8). It should be considered that the formation of "C-O-Ca" complexes at that interface occurs during the gasification experiment itself. Those active sites composing complexes should be similar to those arising from the Ca carboxylate species of CD1073oxiCa in course of its gasification. Hence a similar reactivity of the Ca exchanged sample and of its repyrolysed derivative; the nature of the Ca catalytically active complexes is not yet established.

Characterization of partially gasified samples

The Ca/C ratios at burn off 30 and 60 % of CD1073oxiCa (Table 3) strongly support the view that gasification takes place in the bulk as well as in the surface of this sample particles. A strongly preferential surface gasification would result in much more enrichment of Ca in the surface, at increased gasification ratios, than is experimentally observed.

It must be pointed out that the microporous volume and area (Table 5) exhibit a drastic decrease as the wt % gasification of CD1073oxiCa becomes equal or superior to 20 % ; this is not observed over the non Ca exchanged sample CD1073oxi. It is possible that the mesoporous area increases in compensation to the decrease of the microporous area, during the gasification of CD1073oxiCa, but it has still to be confirmed.

An increase of the radical concentration was observed following partial gasification of both CD1073oxi and CD1073oxiCa (Table 6). Since the difference

observed between the two samples decreased as the temperature (and therefore the degree of gasification) increased, it may be supposed that kinetic limitations predominate in coal oxidation in the vicinity of room temperature, to be replaced by thermal equilibrium limitations at the higher temperatures of gasification.

CONCLUSION

It is suggested that even at room temperature the calcium exchanged carboxylic groups of coal catalyse the adsorption or absorption of ambient oxygen.

It was shown that thermal decomposition of the Ca carboxylate species into CaO is not a prerequisite to observe a catalytic effect of Ca in the low temperature gasification of C by air.

Partially gasified samples (low temperature air gasification ; Ca carboxylate species as catalyst precursors) show interesting microtextural properties when compared to the blank samples.

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Table 1 : Ultimate analysis of the initial samples

Samples	wt (%)					
	C	H	N	O	S	Ca
CD	72.2	4.33	1.46	19.63	0.69	0.04
CD1073	90.4	1.30	1.19	7.04	0.80	0.08
CD1073oxi	73.6	1.80	1.54	24.02	0.56	
CD1073oxiCa	64.0	1.65	1.41	26.10	0.54	3.40

Table 2 : Microporous structure of the initial samples

Samples	Volume (cm ³ /g)	Surface (m ² /g)	Diameter (nm)
CD	0.042	90	1.9
CD1073	0.208	370	2.2
CD1073oxi	0.163	329	2.0
CD1073oxiCa	0.131	289	1.8

Table 3 : Atomic ratio Ca/C obtained by ESCA measurements and by ultimate analysis at different conversions of the CD1073 oxi Ca sample

δ (%)	Ca/C (ESCA)	Ca/C (Ultimate Analysis)	$\frac{(\text{Ca/C}) \text{ ESCA}}{(\text{Ca/C}) \text{ Ul. An.}}$
0	0.0196	0.0159	1.23
30	0.0212	0.0215	0.99
60	0.0904	0.0397	2.28

Table 4 : Selectivity of CO versus
CO + CO₂ during gasification

Samples	Selectivity of CO
CD1073	0.24 - 0.26
CD1073oxi	0.11 - 0.13
CD1073oxiCa	0.03 - 0.04

Table 5 : Micropore structure at different conversions
of char-air reaction

τ (%)	CD1073oxi			CD1073oxiCa		
	V(cm ³ /g)	S(m ² /g)	\bar{D} (nm)	V(cm ³ /g)	S(m ² /g)	\bar{D} (nm)
0	0.163	329	2.0	0.131	289	1.8
5	0.206	376	2.2	0.136	304	1.8
15	0.218	395	2.2	0.129	283	1.8
20	0.227	410	2.2	0.140	297	1.9
40	0.213	373	2.3	0.045	82	2.2
60	0.198	349	2.3	0.035	29	2.3

Table 6 : ESR measurements at different conversions of the char-air
reaction

τ (%)	CD1073oxi		CD1073oxiCa	
	Hpp(gauss)	R'(spins/g)	Hpp(gauss)	R'(spins/g)
0	3.4	6.5×10^{16}	11.0 and 3.8	1.7×10^{18}
15	3.4	11.0×10^{18}	3.8	8.8×10^{18}
60	4.2	2.4×10^{18}	3.7	12.7×10^{18}