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THERMAL BEHAVIOUR IN AIR OF A BITUMINOUS COAL WITH HIGH MINERAL MATTER CONTENT DOPED WITH COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS

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ABSTRACT

A study has been made of the catalytic behaviour of a number of compounds of alkali and alkaline earth metals on the gasification in air, in dynamic conditions, of chars from a bituminous coal with high mineral matter content provided in the mine of Bélmez (Córdoba, Spain).

Some catalysts at a low catalyst concentration show a deactivation effect of the gasification reaction. Such an effect, however, takes place for a lesser number of catalysts and to a shorter extent than when the gasification of the same material is effected in steam at higher temperatures. In general, the hydroxides, acetates and carbonates do not show a substantial difference in their catalytic activity; the chlorides seem to be less efficient catalysts. The alkali metals are much more active catalysts than the alkaline earth metals.

INTRODUCTION

It is a well known fact that some compounds of alkali and alkaline earth metals can exert catalytic effects on the reactions of coals with oxygen, carbon dioxide, hydrogen and steam [1–3]. This catalysis increases the rate of gasification and lowers the processing temperature. Investigations in recent years, however, have shown that a considerable part of these catalysts can be inactivated by reaction with the indigenous mineral matter of coals [4–7]. Now, as most Spanish coals possess a high mineral matter content [8], it was thought of interest to determine the extent of catalyst inactivation in the gasification of materials with such chemical characteristics. Previous studies of gasification [9,10] carried out in carbon dioxide and in steam at relatively high gasification temperatures, in isothermic and dynamic conditions, have shown that such an inactivation effect takes place, and sometimes significantly, in the case of some catalysts. This paper deals with the influence of the catalyst concentration, anion type and metal type on the gasification in air of chars from a coal with high mineral matter content from the mine of S. Antonio (Bélmez, Córdoba).

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TABLE 1

Chemical analysis of the coal

Proximate (wt.%)		Ultimate (wt.%, daf basis)	
Moisture	1.8	C	80.9
Volatile matter	19.9	H	6.7
Fixed carbon	25.4	N	1.5
Ash	52.9	S	1.9
		O_{diff}	9.0

EXPERIMENTAL

The coal under study was classified by following the ASTM norms as high volatile A bituminous [11]. The starting coal was first ground and sized, and the particle size between 0.15 and 0.20 mm chosen for subsequent studies.

The chemical composition of the starting coal is given in Table 1. Ultimate analysis data (C, H, N, S) were obtained in a Perkin-Elmer, model 240 C, elemental analyser, while the oxygen percentage was estimated by difference. Proximate analysis data (moisture, volatile matter, fixed carbon, ash) were gained using a Mettler TA-3000 thermogravimetric system [12]. Ash composition (Table 2) was obtained by following analytical methods described in the literature [13]. Silica and alumina are the major ash components.

Coal samples containing the catalyst were prepared by the method of impregnation: the coal support was wetted with an aqueous solution (10 cm^3 of solution per 5 g of coal) of the acetate, carbonate, hydroxide or chloride of Na, K, Mg or Ca (all reagent grade chemicals); the mixture was then occasionally stirred until complete solvent evaporation and was oven dried at 283 K for 24 h. The concentrations of catalyst used were 1, 5 and 10%, expressed, for a better comparison, as grams of "oxide" (that is only a reference basis) per 100 g of coal (dry) basis.

The thermal behaviour in air of char samples was measured thermogravimetrically (with a Mettler TA-3000 thermobalance) in the temperature range 300–700 °C. About 10 mg of sample was placed in a platinum crucible and then heated in flowing nitrogen (99.998 vol%, flow rate = 200 cm^3 min^{-1}) at 50 °C min^{-1} to 950 °C and held at that temperature until a constant weight

TABLE 2

Ash chemical analysis (expressed as oxides) for the parent coal

Coal	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	SO_3
SAO	58.4	28.7	3.2	1.1	1.7	0.02	5.7	1.3	0.6

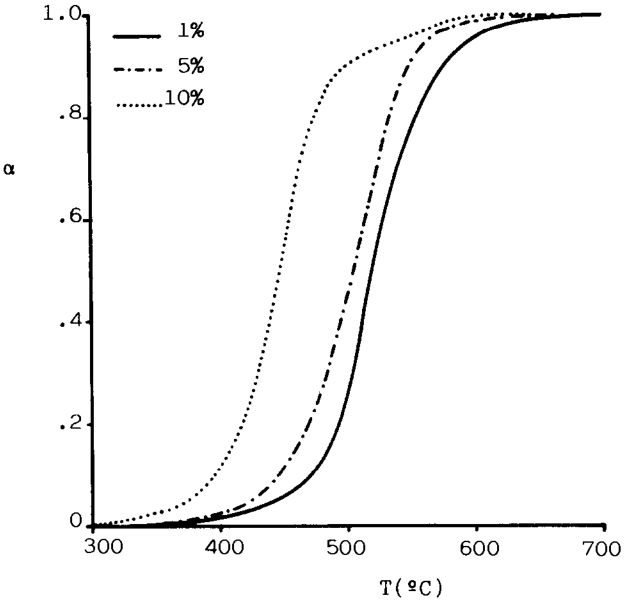

Fig. 1. Variation of α versus T for the gasification of chars with NaAc.

was attained. The sample was then cooled down to the initial reaction temperature and nitrogen gas exchanged for dry air. Gasification experiments were carried out at a heating rate of 2° C min^{-1}. The weight loss during gasification was continuously monitored on the thermobalance and the results were suitably transformed to be plotted as α versus T; resultant plots are similar to that shown, as an illustrative example, in Fig. 1.

EXPERIMENTAL RESULTS AND DISCUSSION

The reactivity of the pure char and of chars impregnated with the catalysts was calculated by using the equation [5]

$$R = \frac{1}{1-\alpha}\frac{d\alpha}{dt} \qquad (1)$$

where R = reactivity of the char; α = degree of conversion referred to the char sample (dry ash free) at the initial gasification temperature; $d\alpha/dt$ = variation of the degree of conversion with time (min^{-1}). Some resultant reactivity data, those of more significance, have been plotted against gasification temperature in Figs. 2–8 or are given in Table 3.

The results of the present study first indicate that the catalytic activity of the compounds of the alkali and alkaline earth metals tested as catalysts for the gasification in air of chars from a bituminous coal with high mineral matter content depends on the catalyst concentration. As shown in Fig. 2,

TABLE 3

Reactivity and gasification temperature of char samples doped with acetates of alkali and alkaline earth metals

Catalyst	α	T (°C)			R (% min^{-1})		
		1%	5%	10%	1%	5%	10%
NaAc	0.3	503	484	429	2.88	2.28	2.67
	0.7	539	524	462	5.43	6.56	6.98
KAc	0.3	505	466	404	3.23	2.60	2.26
	0.7	539	498	441	5.41	8.04	5.72
$MgAc_2$	0.3	505	503	492	3.12	2.87	2.85
	0.7	537	538	524	5.98	6.20	7.53
$CaAc_2$	0.3	502	501	500	2.92	2.74	2.83
	0.7	537	540	538	5.48	5.39	5.15

where the reactivities of samples at a relatively small degree of conversion are compared, at a low catalyst concentration some catalysts, such as the hydroxides of Na and K, give rise to a decrease in the reactivity and/or to an increase in the gasification temperature in relation to the pure char. As a

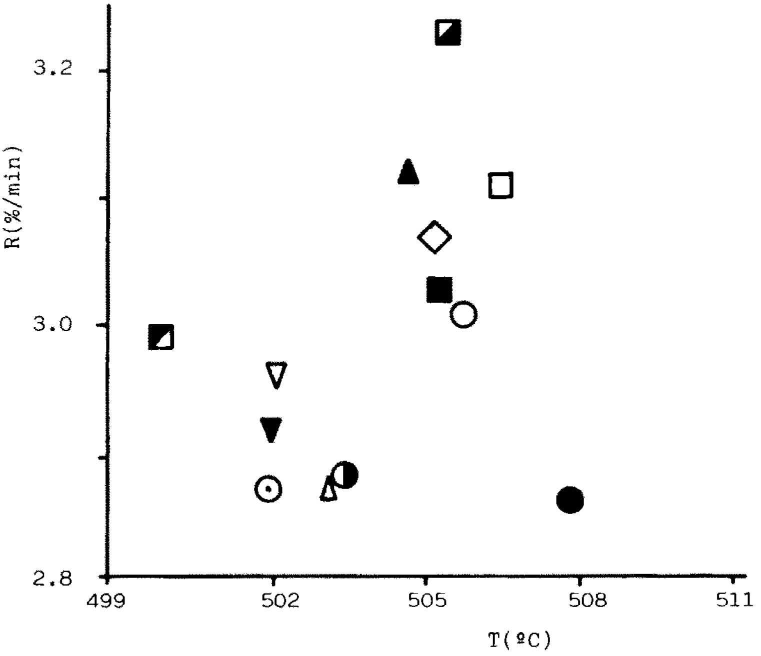

Fig. 2. Reactivity at $\alpha = 0.3$ of the pure char, ◇, and char samples from the coal doped with 1% of catalyst: ○, NaOH; ⊙, NaCl; ◑, NaAc; ●, Na_2CO_3; □, KOH; ◩, KCl; ◪, KAc; ■, K_2CO_3; △, $MgCl_2$; ▲, $MgAc_2$; ▽, $CaCl_2$; ▼, $CaAc_2$.

possible explanation of these results, earlier workers [4–6] have observed a lesser efficiency of the alkali metal catalysts as a result of their reaction with the inherent mineral matter of coals. In this respect, Valenzuela et al. [9–10] have suggested that the char deactivation could be due to the inactivation of the catalyst by reaction with mineral matter and subsequent formation of reaction products which would prevent the gasification reaction. Also, it must be noted that at high degrees of conversion such an effect is much less frequently observed. Moreover, when the above results are compared with those obtained in the gasification in steam of the same samples [10], one finds that in the latter case the deactivation effect takes place for a higher number of catalysts and also to a larger extent. It suggests that the gasificant agent also influences the char deactivation, maybe as a result of the difference in the gasification temperature.

With increasing catalyst concentration, the catalytic activity follows a variation which depends on whether the catalyst is a compound of an alkali metal or of an alkaline earth metal. In the former case, the catalytic activity, with only the exception of some catalysts, such as the carbonates at high degrees of conversion, as will be seen below, augments with catalyst con-

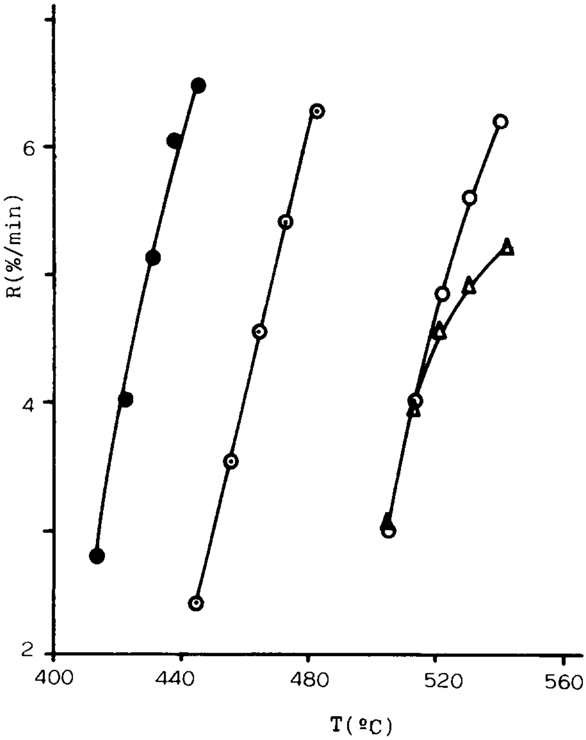

Fig. 3. Variation of the reactivity with gasification temperature for the pure char, △, and char samples from the coal doped with NaOH: ○, 1%; ⊙, 5%; ●, 10%.

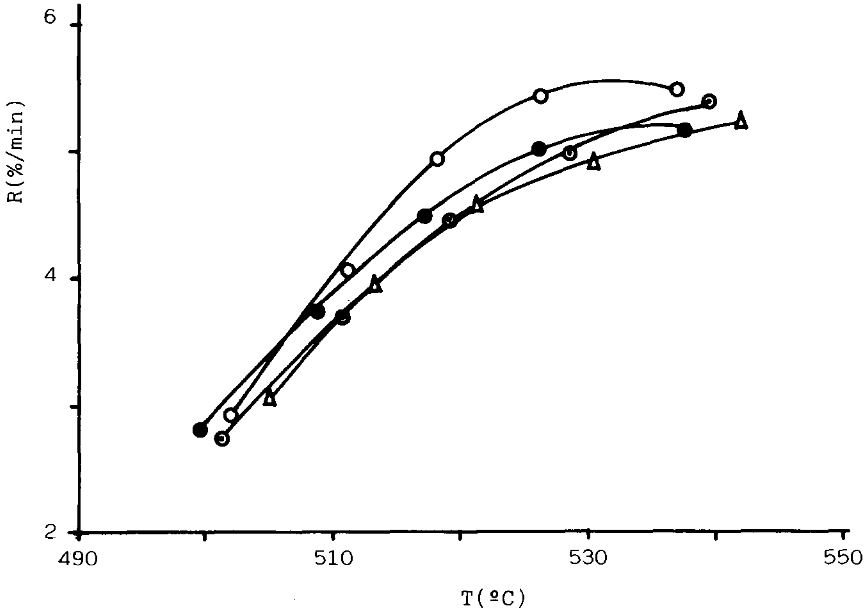

Fig. 4. Variation of the reactivity with gasification temperature for pure char, △, and char samples from the coal doped with $CaAc_2$: ○, 1%; ⊙, 5%; ●, 10%.

centration, as shown in Fig. 3 for the NaOH catalysts. In the latter case, however, the catalytic activity, frequently, increases (Fig. 4) up to a certain value of catalyst concentration and decreases for higher concentrations. Valenzuela et al. [10], when investigating the catalytic effect of the acetates of Mg and Ca on the gasification in steam of this bituminous coal (as it is expected that in the gasification conditions such compounds are found in solid state as oxides) have suggested that the reduction in the catalytic activity from a catalyst concentration could be due to the prevention by the catalyst of the diffusion of the reactant gas in char pores. A deeper analysis of the results now shows that such an effect can also take place when the chlorides of the alkaline earth metals are used as catalysts.

On the other hand, the results also indicate that the same compounds of Na and K present a similar catalytic behaviour. Thus, as shown in Figs. 5 and 6, as an example, for the carbonates, at each degree of conversion the reactivity varies similarly to gasification temperature and catalyst concentration. The observed drop in char reactivity at high degrees of conversion and catalyst concentrations must be due to the depletion of the gasifiable coal mass (the larger the catalyst concentration, the smaller the proportion of coal per mass unit of sample and, therefore, it will become totally gasified at a lower degree of conversion).

The anion of the salts and hydroxides exerts an influence on the activity of the catalysts. From Fig. 7 (for Na catalysts, $\alpha = 0.3$) and Fig. 8 (K

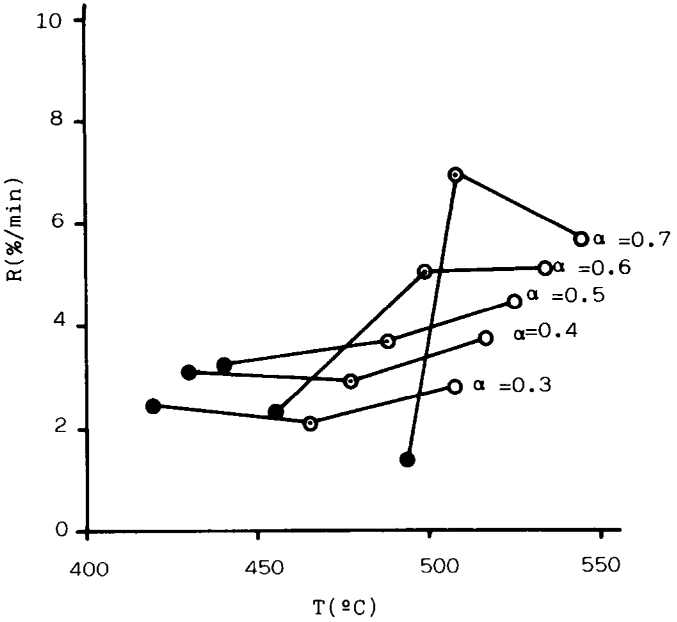

Fig. 5. Variation of the reactivity with gasification temperature for char samples from the coal doped with Na_2CO_3: ○, 1%; ⊙, 5%; ●, 10%.

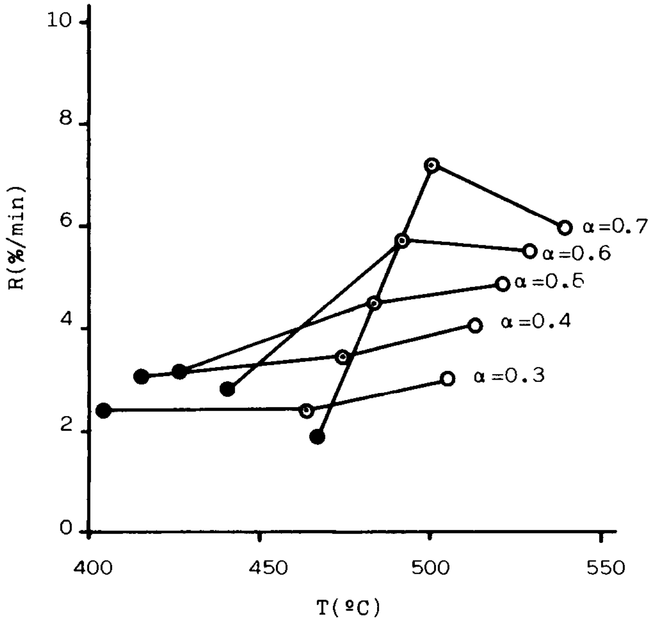

Fig. 6. Variation of the reactivity with gasification temperature for char samples from the coal doped with K_2CO_3: ○, 1%; ⊙, 5%; ●, 10%.

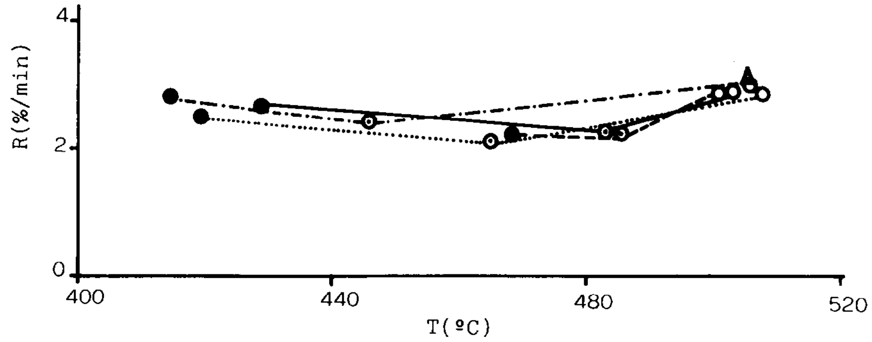

Fig. 7. Reactivity at $\alpha = 0.3$ of the pure char, △, and char samples from the coal doped with Na catalysts: ○, 1%; ⊙, 5%; ●, 10%; ———, acetate; ······, carbonate; –·–·–·, hydroxide; ------, chloride.

catalysts, $\alpha = 0.7$) it is inferred that even though, in general, at both degrees of conversion the hydroxides, acetates and carbonates do not show a great difference in their catalytic activity, it seems that at the higher degree of

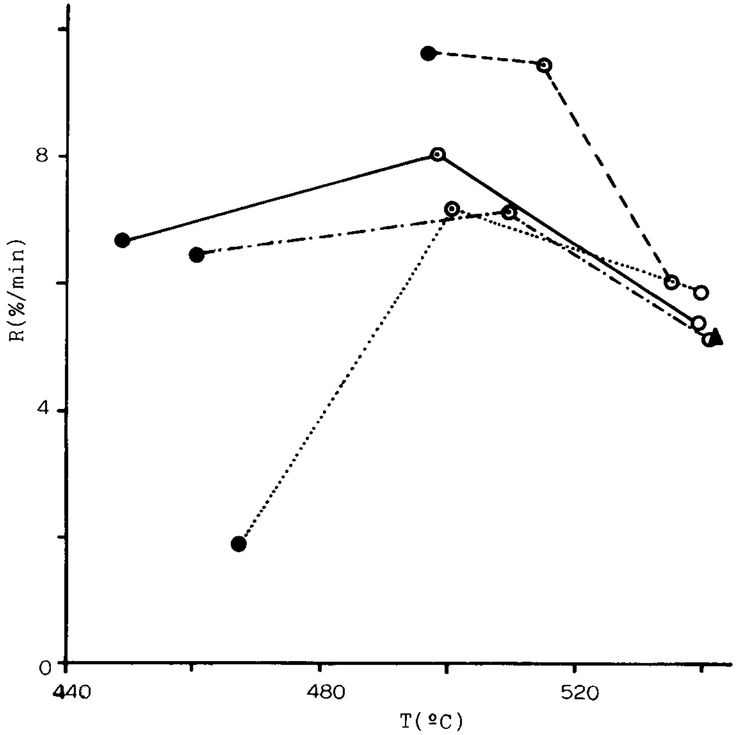

Fig. 8. Reactivity at $\alpha = 0.7$ of the pure char, △, and char samples from the coal doped with K catalysts: ○, 1%; ⊙, 5%; ●, 10%; ———, acetate; ······, carbonate; –·–·–·, hydroxide; ------, chloride.

conversion the first two are slightly more efficient catalysts; the chlorides, mainly at the lower degree of conversion, are much less active catalysts.

As could be expected, the type of metallic cation, whether alkali or alkaline earth, has a more marked influence on the catalytic activity of the studied compounds. Data in Table 3 indicate that, except for the lowest studied catalyst concentration, the order of catalytic activity is: K > Na ≫ Mg > Ca. The order found for K and Na is in agreement with the results of some earlier workers [14–17]. The differences in the catalytic activity of K and Na have been attributed by Wigmans et al. [18] to the better intercalating properties of potassium and to the higher activity of sodium on oxygen-rich surfaces.

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