

THERMAL BEHAVIOUR IN STEAM OF A BITUMINOUS COAL DOPED WITH ALKALI AND ALKALINE EARTH METALS

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ABSTRACT

Various alkali and alkaline earth metal compounds have been tested as catalysts for the gasification in steam, under dynamic conditions, of a bituminous coal from Bélmez (Córdoba, Spain).

Most catalysts, at the lowest concentration studied, show a deactivation effect on the gasification reaction. Such an effect is sometimes enhanced with increasing catalyst concentration in the case of alkaline earth metal salts only. Amongst Na catalysts, NaOH gives rise to the largest increase in char reactivity with catalyst concentration at the smallest degree of conversion, while NaAc has proved to be the more active catalyst at the greatest degree of conversion. For K catalysts, the order of catalytic activity, whatever the degree of conversion, is $K_2CO_3 > KOH > KAc > KCl$ at high catalyst concentrations. The alkaline earth metals, in general, do not catalyse the gasification reaction of this coal. Either Na or K are the best catalysts, depending on the composition of the catalyst.

INTRODUCTION

Increasing interest in coal gasification processes has brought about a need to investigate the behaviour of local coal sources for these processes. The carbon–steam reaction has assumed unique importance since the major products of this reaction (CO and H_2) can be used not only as a medium-heating value gas but also as precursors for the catalytic synthesis of a wide range of products [1]. On the other hand, the alkali metal carbonates are particularly active catalysts for this reaction [2,3]. It has been reported [4] that a considerable part of potassium is deactivated by reaction with mineral matter in coal. Since most Spanish coals possess, as the main chemical characteristic, a high mineral matter content [5], it was thought of interest to study the gasification reaction of one of these coals in steam, in the presence of catalytic agents. This paper describes the effect of such variables as anion type, metal type, catalyst concentration and gasification temperature on the gasification in steam of a coal from the mine of S. Antonio (Bélmez, Córdoba).

EXPERIMENTAL

The starting coal was classified according to the ASTM norms as high volatile A bituminous [6]. The coal was first ground and sized, and the particle size 0.15–0.20 mm chosen for subsequent studies.

Ultimate analysis data (C, H, N, S) of the parent coal (Table 1) were obtained in a Perkin-Elmer (model 240 C) elemental analyser, while the percentage of oxygen was estimated by difference. Proximate analysis data (also in Table 1) were achieved using a Mettler TA-3000 thermogravimetric system [7]. Ashes (Table 2) were analysed following analytical methods described in the literature [8]. Results in Table 2 indicate that silica and alumina are the major ash components.

Catalyst-supported coal samples were prepared according to the method of impregnation; the support was wetted with a solution containing an acetate, carbonate, hydroxide or chloride of an alkali or alkaline earth metal (all reagent grade chemicals) (5 g of coal in 10 ml of aqueous solution); the mixture was occasionally stirred until complete solvent evaporation, and oven dried at 283 K for 24 h. Catalyst concentrations used were 1, 5 and 10 wt%, expressed, for a better comparison, as grams of "oxide" (that is only a reference basis for comparison) per 100 grams of coal (dry) basis.

The thermal behaviour in steam of char samples was measured thermogravimetrically (Mettler TA-3000 thermobalance) in the range 900–950°C. About 10 mg of sample, placed in a platinum crucible, were heated in flowing nitrogen (99.998 vol%, flow rate = 200 ml min⁻¹) at 50°C min⁻¹ to 950°C and held at that temperature until a constant weight was attained. The temperature of the sample was then changed to the initial reaction temperature and nitrogen gas exchanged for N₂/H₂O reactant gas prepared

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
		S	1.9
Ash	52.9	O _{diff}	9.0

TABLE 2

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

Coal	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	K ₂ O	Na ₂ O	SO ₃
SAO	58.4	28.7	3.2	1.1	1.7	0.02	5.7	1.3	0.6

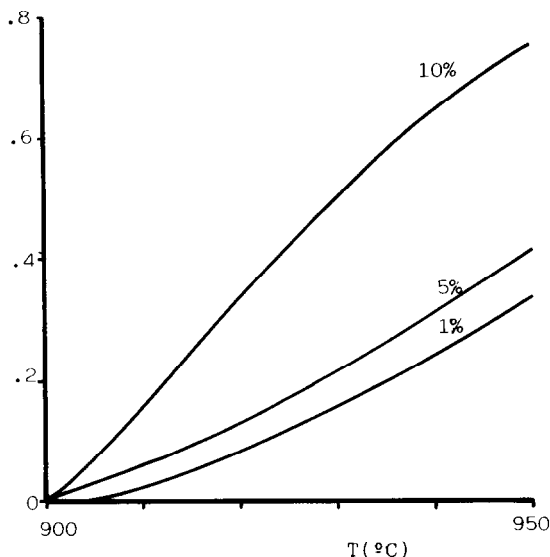


Fig. 1. α vs. T for char gasification using Na acetate catalysts.

by bubbling N_2 (flow rate = 200 ml min^{-1}) through water at 30°C . Gasification experiments were carried out at a heating rate of 1°C min^{-1} . The weight loss during gasification was monitored continuously on the thermobalance and the results were then suitably converted to be plotted as α vs. T ; resultant plots are similar to that shown, as an example, in Fig. 1.

EXPERIMENTAL RESULTS AND DISCUSSION

The reactivity was calculated by the equation [9]

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

where R = reactivity of the char; α = degree of conversion, referred to the char sample at the initial gasification temperature (dry ash free basis); $d\alpha/dt$ = variation of the degree of conversion with time (min^{-1}). Reactivity values obtained in this way, together with gasification temperatures and degrees of conversion, are given in Figs. 2–8.

The above results first show that the behaviour of the alkali and alkaline earth metal compounds studied in the gasification reaction in steam of a coal char with high inorganic matter content depends on the metal (alkali or alkaline earth) type and on the concentration. For the alkali metals, at the lower concentrations studied, whatever the degree of conversion, char deactivation occurs for its gasification in steam, i.e., the catalyst-supported samples are less reactive than the char samples without catalyst (SAO). At

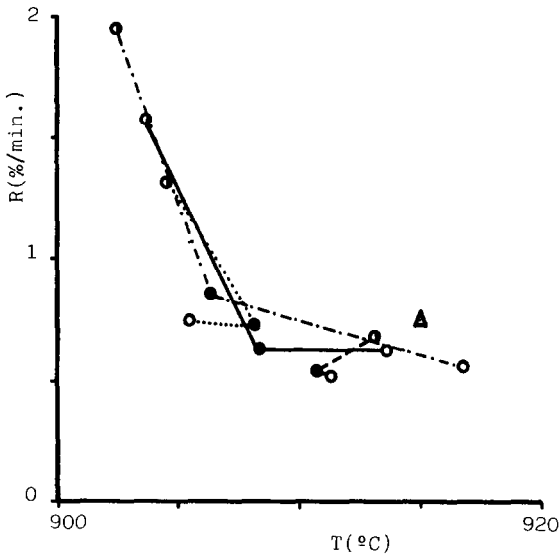


Fig. 2. Reactivity at $\alpha = 0.05$ of char samples doped with Na compounds: (○) 1%; (●) 5%; (◐) 10%; (—) acetate; (·····) carbonate; (- - -) hydroxide; (- · - ·) chloride and (Δ) SAO.

higher catalyst concentrations, however, char reactivity increases, though to an extent depending on the catalyst, in relation to the raw coal char reactivity. As an illustration of this, the reactivity at $\alpha = 0.05$ and 0.25 has been plotted against gasification temperature for Na catalysts in Figs. 2 and 3, respectively. At $\alpha = 0.05$ and at low catalyst concentrations (Fig. 2) all catalyst-containing samples present a smaller reactivity than SAO; however, some differences can be observed amongst the catalysts. While for NaAc, Na_2CO_3 and NaCl such reactivity values are reached at gasification temperatures lower than for SAO, when NaOH is used as catalyst the reactivity value is obtained at a higher temperature, indicative of a poorer char gasification. NaOH is the Na catalyst with the lowest melting point (NaOH, 318°C ; Na_2CO_3 , 851°C ; NaCl, 801°C) and, therefore, the catalyst-char contact time, with the catalyst in the molten state, before the beginning of char gasification will be longer than for any other Na catalyst. Thus, diffusion of the catalyst in char pores and reactions between the catalyst and the mineral matter would take place to a larger extent than for other Na catalysts. In this way, the results suggest that catalyst-mineral matter reactions could be responsible for the char deactivation and gasification. In this respect, earlier workers [4,9,10] attributed the lower efficiency of alkali metal catalysts to their reaction with indigeneous mineral matter in coals. Valenzuela et al. [11] suggested that char deactivation could be due to the deactivation of the catalyst by reaction with mineral matter and formation of reaction products which would prevent the gasification reaction. It can be

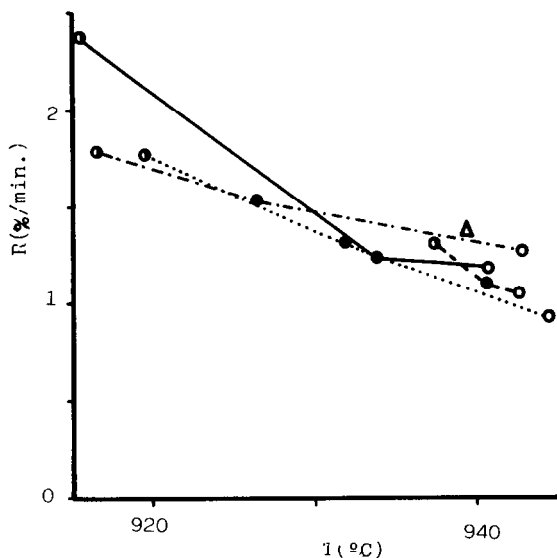


Fig. 3. Reactivity at $\alpha = 0.25$ of char samples doped with Na compounds: (○) 1%; (●) 5%; (◐) 10%; (—) acetate; (·····) carbonate; (- - -) hydroxide; (- · - · -) chloride; and (Δ) SAO.

also noted that at $\alpha = 0.25$, such reactivity values for most Na catalyst samples are reached at a higher temperature than for SAO, which suggests that char deactivation is enhanced, though not substantially, by increasing the gasification temperature. For K catalyst samples (Figs. 4 and 5), how-

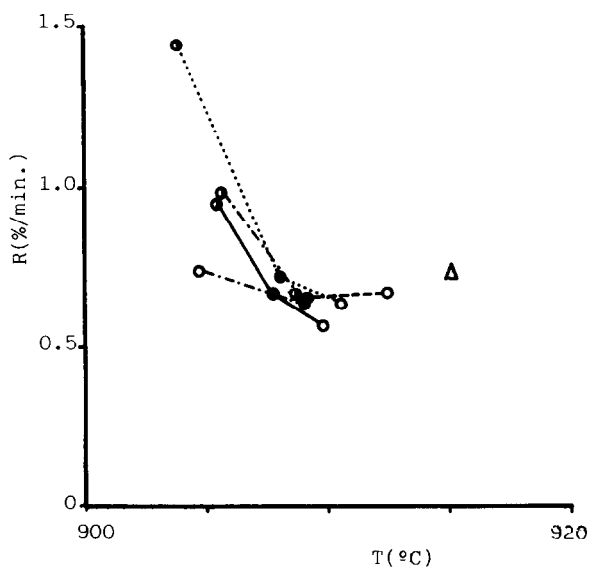


Fig. 4. Reactivity at $\alpha = 0.05$ of char samples doped with K compounds: (○) 1%; (●) 5%; (◐) 10%; (—) acetate; (·····) carbonate; (- - -) hydroxide; (- · - · -) chloride.

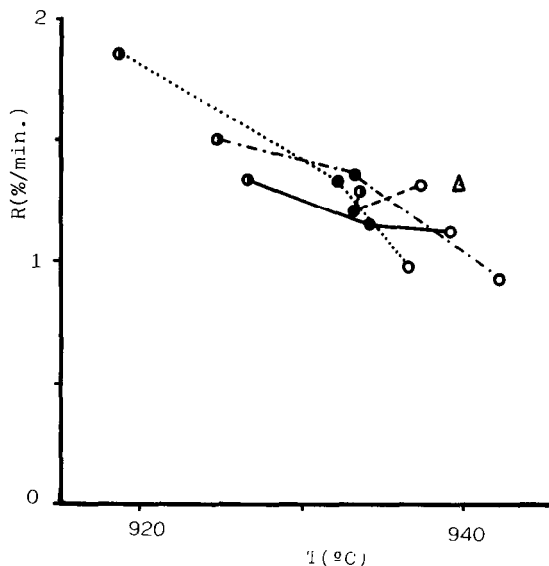


Fig. 5. Reactivity at $\alpha = 0.25$ of char samples doped with K compounds: (○) 1%; (●) 5%; (◐) 10%; (—) acetate; (·····) carbonate; (-·-·-) hydroxide; (- - - -) chloride; and (Δ) SAO.

ever, the observed effect for NaOH catalyst at $\alpha = 0.05$ and 0.25 appears only at the highest degree of conversion and not at the lowest one, which seems to be an abnormal result. On the other hand, the increase in char reactivity at high catalyst concentrations must be the result of the catalytic effect of the catalyst remaining from reaction with the mineral matter.

For the alkaline earth metal compounds, at low and, in some cases, even at high concentrations (Fig. 6), char reactivity decreases in relation to SAO reactivity. The alkaline earth metal acetates, at a certain temperature below the gasification temperature, first transform to the respective carbonates, which then decompose (decomposition temperature: 400°C , MgCO_3 ; 780°C , CaCO_3) to oxides (melting points: 2800°C , MgO ; 2580°C , CaO). Thus at the gasification temperatures the supposed catalysts would be found in the solid state and it is expected that their reaction with the mineral matter takes place to a lesser extent than in the case of the alkali metal catalysts. This fact, together with the decrease in char reactivity with concentration, suggest that in the case of the alkaline earth metal acetates char deactivation could be due not only to its reaction with the mineral matter but also to the prevention, by the supposed catalyst in the solid state, of the diffusion of the reactant gas in char pores.

The results in Figs. 2 and 3 indicate that the order of catalytic activity for the Na catalysts depends on both the degree of conversion and the catalyst concentration. At $\alpha = 0.05$ and 0.25 and at the lowest catalyst concentration, all Na catalysts deactivate the gasification reaction. At the highest

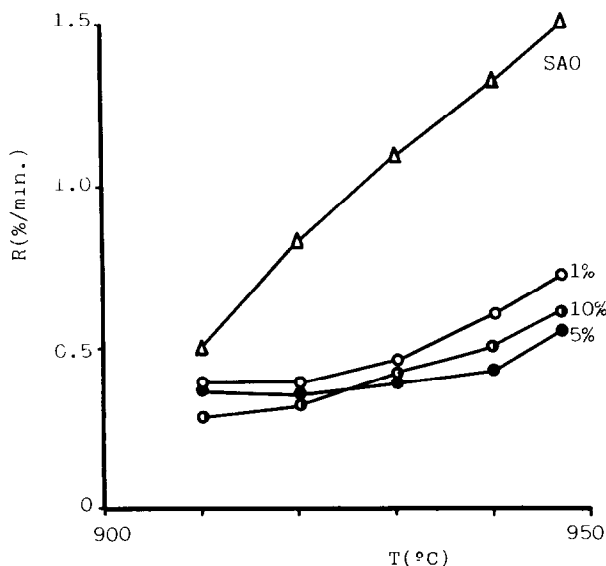


Fig. 6. Variation of the reactivity with temperature for the raw coal char, SAO and Ca acetate doped samples.

catalyst concentration, the order of catalytic activity is $\text{NaOH} > \text{NaAc} > \text{Na}_2\text{CO}_3 > \text{NaCl}$ at $\alpha = 0.05$ and $\text{NaAc} > \text{NaOH} > \text{Na}_2\text{CO}_3 > \text{NaCl}$ at $\alpha = 0.25$. It can be observed that NaOH is the Na catalyst which brings about the largest increase in char reactivity (Fig. 2) with catalyst concentration at $\alpha = 0.05$. At such a degree of conversion and at the intermediate and the highest catalyst concentrations, it can be also noted that the reactivity values are obtained at gasification temperatures lower than in the case of other Na catalysts. Therefore, it can be concluded that, in general, at low degrees of conversion, NaOH is the best Na catalyst for the gasification in steam of the char from this coal with high mineral matter content. Similar results were found by Valenzuela et al. [11] when investigating a coal of similar rank and chemical characteristics. These workers explained the results in terms of the possible influence on char reactivity of such factors as interactions between the catalyst and mineral matter, the diffusion of the catalyst in char pores and the formation of active species during the catalysed gasification reaction. On the other hand, the observed order of catalytic activity at the largest studied degree of conversion must be the result of the greater char gasification at smaller degrees of conversion in the case of the NaOH-char sample than for the NaAc-char sample.

For K catalysts at the lowest catalyst concentration, as for Na catalysts, char deactivation always takes place for its gasification (Figs. 4 and 5). At the highest catalyst concentration, however, whatever the degree of conversion, the order of catalytic activity is: $\text{K}_2\text{CO}_3 > \text{KOH} > \text{KAc} > \text{KCl}$. Now,

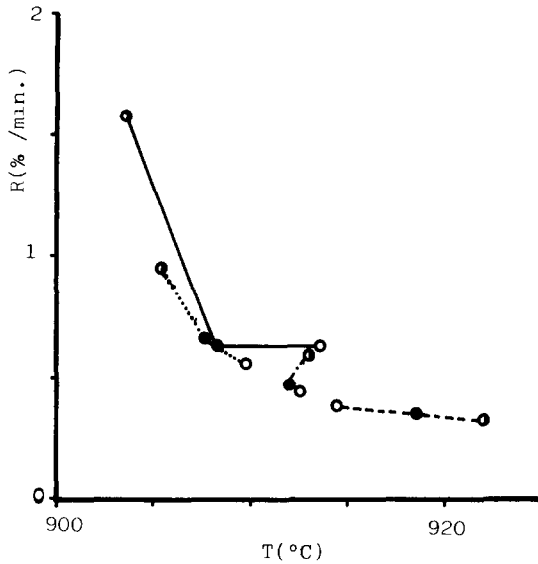


Fig. 7. Reactivity at $\alpha = 0.05$ of char samples doped with acetates of alkali and alkaline earth metals: (○) 1%; (●) 5%; (◐) 10%; (—) Na; (·····) K; (---) Mg; (- - - -) Ca.

unlike Na catalysts, the best catalyst at low degrees of conversion does not suffer from a reduction in its catalytic activity in relation to any other K catalyst at higher degrees of conversion and catalyst concentrations.

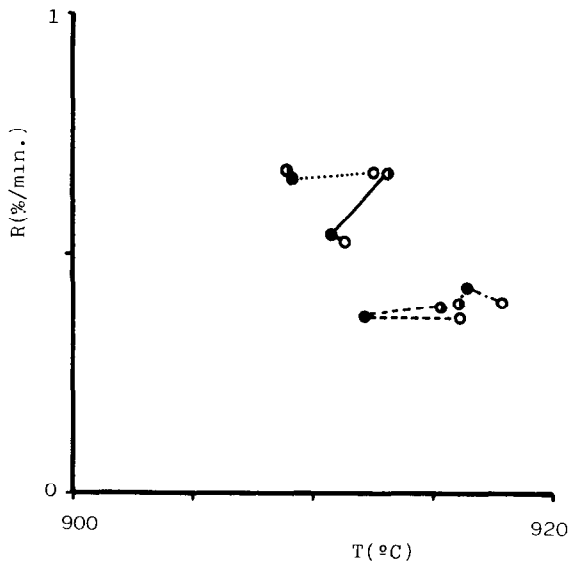


Fig. 8. Reactivity at $\alpha = 0.05$ of char samples doped with chlorides of alkali and alkaline earth metals: (○) 1%; (●) 5%; (◐) 10%; (—) Na; (·····) K; (---) Mg; (- - - -) Ca.

When comparing the reactivity of char samples containing the alkali and alkaline earth metal catalysts in the chemical form of either acetates (Fig. 7) or chlorides (Fig. 8), one finds that for the former, at any studied degree of conversion, the reactivity order is $\text{NaAc} > \text{KAc} > \text{Ac}_2\text{Mg} > \text{Ac}_2\text{Ca}$, while for the chlorides, this order is $\text{KCl} > \text{NaCl} > \text{MgCl}_2, \text{CaCl}_2$. The results first show that in both cases alkali metals are much more effective catalysts than alkaline earth metals for the gasification in steam of chars from coals with such chemical characteristics. Moreover, either Na or K is the best catalyst depending on the catalyst chemical form: NaAc or KCl when the catalysts are, respectively, added as acetates or chlorides. In this respect, some earlier workers [12–15], however, when investigating carbon gasification (in most cases on coal of similar rank but with different chemical characteristics), found that K is a more effective catalyst than Na. The differences in the catalytic activity of Na and K have been attributed by Wigmans et al. [16] to the higher activity of sodium on oxygen-rich surfaces and to the better intercalating properties of potassium.

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