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CATALYSIS BY ALKALI AND ALKALINE EARTH METALS OF THE GASIFICATION IN CO_2 AND IN STEAM OF CHARS FROM A BITUMINOUS COAL WITH HIGH INORGANIC MATTER CONTENT

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ABSTRACT

Several compounds of alkali and alkaline earth metals have been tested as catalysts for the gasification in carbon dioxide and in steam, under isothermic conditions, of chars from a bituminous coal with high inorganic matter content from Peñarroya (Córdoba, Spain).

The results show that some catalysts, and especially the alkali metal hydroxides, produce a deactivation for char gasification in both atmospheres. Such a deactivating effect is only observed when very low catalyst concentration is used. Char reactivity varies with the catalyst concentration and depends on the catalyst type (alkali or alkaline earth metal compound). NaAc and NaOH bring about a large increase of char reactivity at higher catalyst concentrations. By contrast, $CaAc_2$ and $CaCl_2$ produce a more substantial increase of char reactivity at comparatively lower catalyst concentrations. At high catalyst concentration and gasification temperature, the order of catalytic activity found is $CaCl_2 > NaAc > CaAc_2 > NaOH >$ NaCl for gasification in steam and $NaAc > NaOH > CaAc_2 > CaCl_2 >$ NaCl for gasification in carbon dioxide.

INTRODUCTION

Inherent mineral matter in coals and coal chars can adversely affect the catalysed gasification of such materials. Thus earlier workers [1–3] had noted a lesser efficiency of some alkali metal catalysts, and the behaviour was attributed to the reaction between the catalyst and mineral matter in the coal. Valenzuela-Calahorro and co-workers [4–6], when investigating the catalysed gasification reaction of chars produced from coals with high mineral matter content, found that some catalysts (and more generally when they are supported in relatively small amounts on the coal surface), bring about a char deactivation for its gasification in carbon dioxide, steam and air.

As it is expected that both coal rank and experimental conditions affect the catalysed gasification of coal chars, we studied the gasification in carbon dioxide and in steam, under isothermic conditions, of chars from a bituminous coal with high inorganic matter content from Peñarroya (Córdoba, Spain). The influence on char reactivity of catalyst concentration, gasification temperature, anion type and cation type was investigated.

EXPERIMENTAL

This coal was classified in a previous paper [7] (by following ASTM Standard D 338) as high volatile bituminous coal. The as-received coal was first ground and sized, and the particle size range 0.15–0.20 mm chosen for subsequent studies. Data relating to the chemical analysis of the starting coal and of its ash, as well as to the calorific value, have been reported elsewhere [7].

The catalysts were supported on the raw coal by following the method of impregnation: the support was wetted with an aqueous solution (5 g of sample per 10 ml of solution) containing a chloride, acetate or hydroxide of an alkali or alkaline earth metal (all reagent grade chemicals), and the mixture was then occasionally stirred until complete solvent evaporation and oven drying at 283 K for 24 h. The catalyst concentration (Table 1) was expressed as mmoles of catalyst per gram of dry coal.

A Mettler TA-3000 thermogravimetric unit was used for measuring weight changes taking place during the gasification reaction. About 10 mg of sample (raw coal or catalyst-impregnated coal) were placed in a platinum pan and then heated at a rate of 50 °C min^{-1} from room temperature to the

TABLE 1

Codes and preparation of samples

Catalyst	Catalyst concentrations [a]		
NaCl	0.16	0.80	1.60
NaAc	0.16	0.80	1.60
NaOH	0.16	0.80	1.60
KCl	0.11		
KAc	0.11		
KOH	0.11		
$MgCl_2$	0.25		
$MgAc_2$	0.25		
$Mg(OH)_2$	0.25		
$CaCl_2$	0.18	0.89	1.78
$CaAc_2$	0.18	0.89	1.78
$Ca(OH)_2$	0.18		

[a] Catalyst concentrations in mmol (g dry coal)$^{-1}$.

treatment temperature (900 or 950 °C). The heat treatment was carried out in an inert atmosphere of N_2 (at atmospheric pressure, $\phi = 200$ ml min^{-1}). Samples were held at the treatment temperature for 7 min, then N_2 was replaced by a flow ($\phi = 200$ ml min^{-1}) of CO_2 or of H_2O/N_2 (N_2 saturated with water vapour), which was obtained by bubbling N_2 (purity > 99.998 vol%) through deaerated distilled water at 25 °C.

It was previously established that 15 min was enough time to reach the maximum rate of weight loss and so to enable us to determine the maximum reactivity.

EXPERIMENTAL RESULTS

The reactivity of the chars produced from the raw coal and from the samples containing catalyst was estimated by using the equation [8]

$$R_M = \frac{1}{W_0} \frac{dW}{dt}$$

where R_M is the reactivity (mg h^{-1} mg^{-1}), W_0 is the weight of char (mg) (dry ash free basis) at the gasification temperature and dW/dt represents the maximum weight loss (mg min^{-1}).

The reactivity values for the gasification in steam at 900 and 950 °C of chars which were produced from the starting coal and from resultant samples when using the lowest catalyst concentration are plotted in Figs. 1 and 2, respectively. It can be seen that samples containing KAc, KOH, NaOH, $MgCl_2$ or $MgAc_2$ catalysts show a reactivity lower than that of the pure coal char, which indicates that the presence of these compounds on the char surface brings about a char deactivation for its gasification under such

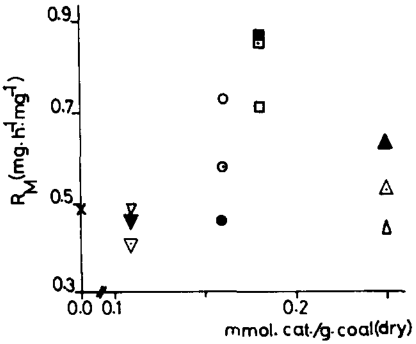

Fig. 1. Reactivity in steam at 900 °C of chars from raw coal, ×, and from coal samples containing catalyst: ○, NaCl; ⊙, NaAc; ●, NaOH; □, $CaCl_2$; ⊡, $CaAc_2$; ■, $Ca(OH)_2$; ▽, KCl, ▽, KAc; ▼, KOH; △, $MgCl_2$; △, $MgAc_2$; ▲, $Mg(OH)_2$.

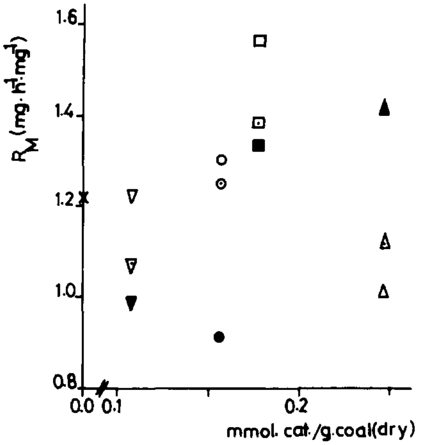

Fig. 2. Reactivity in steam at 950 °C of chars from raw coal, ×, and from coal samples containing catalyst: ○, NaCl; ⊙, NaAc; ●, NaOH; □, $CaCl_2$; ⊡, $CaAc_2$; ■, $Ca(OH)_2$; ▽, KCl; ▽, KAc, ▼, KOH; △, $MgCl_2$; △, $MgAc_2$; ▲, $Mg(OH)_2$.

conditions. The rest of the catalysts increase char reactivity in relation to the starting coal char. On the other hand, Figs. 3 and 4 depict the variation of char reactivity with increasing catalyst concentrations for chars supporting Na and Ca catalysts. It is induced that Ca catalysts, in general, show a higher catalytic activity than Na catalysts. Moreover, the reactivity follows a variation with catalyst concentration which depends on the catalyst type (alkali or alkaline earth metal compound). Thus for Na compounds the reactivity at both gasification temperatures studied first varies irregularly in accordance with the catalyst and then always increases. For Ca catalysts,

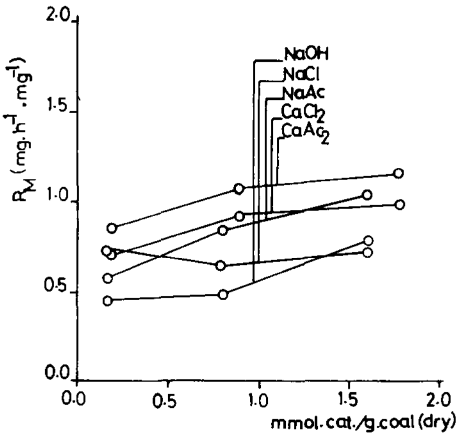

Fig. 3. Gasification in steam at 900 °C. Variation of the reactivity with catalyst concentration.

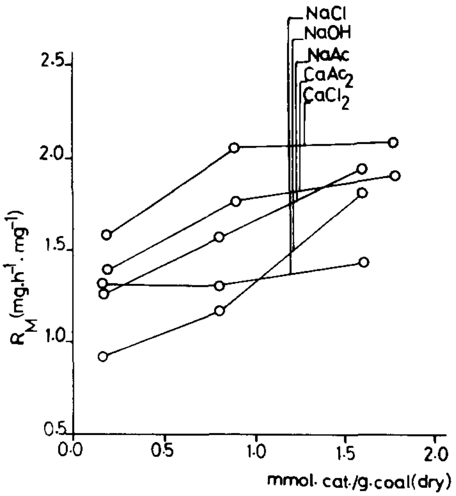

Fig. 4. Gasification in steam at 950 ° C. Variation of the reactivity with catalyst concentration.

however, the reactivity first augments and later remains almost steady. Hippo et al. [9] and Linares-Solano et al. [10], when investigating the activity of Ca for lignite char gasification, found a rectilinear increase in char gasification rate over a certain range of Ca loadings. This indicates that catalyst dispersion is independent of loading.

In relation to the gasification in carbon dioxide at 900 and 950 ° C, from Figs. 5 and 6 it can be inferred that char deactivation effects also occur in this case at both gasification temperatures for a certain number of catalysts, when these are present in a relatively small amount on the char surface. The effect takes place to a small extent for NaCl, NaAc and NaOH at the lower

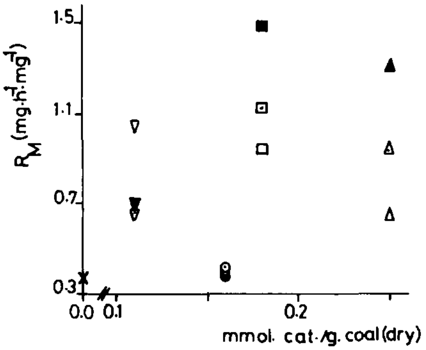

Fig. 5. Reactivity in carbon dioxide at 900 ° C of chars from raw coal, ×, and from coal samples containing catalyst: ○, NaCl; ⊙, NaAc; ●, NaOH; □, $CaCl_2$; ⊡, $CaAc_2$; ■, $Ca(OH)_2$; ▽, KCl; ▿, KAc; ▼, KOH; △, $MgCl_2$; ◬, $MgAc_2$; ▲, $Mg(OH)_2$.

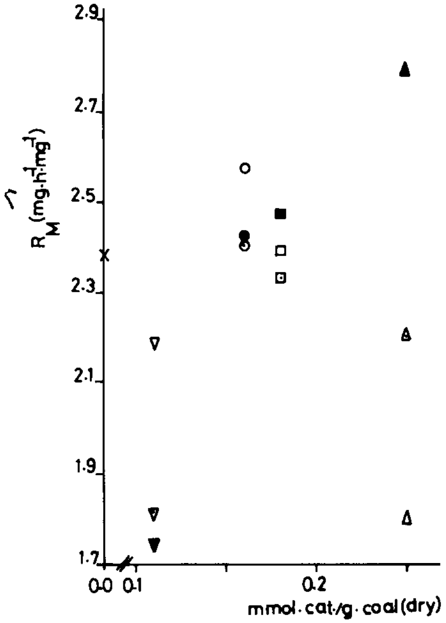

Fig. 6. Reactivity in carbon dioxide at 950 °C of chars from raw coal, ×, and from coal samples containing catalyst: ○, NaCl; ⊙, NaAc; ●, NaOH; □, CaCl$_2$; ⊡, CaAc$_2$; ■, Ca(OH)$_2$; ▽, KCl; ▽, KAc; ▼, KOH; △, MgCl$_2$; △, MgAc$_2$; ▲, Mg(OH)$_2$.

gasification temperature (Fig. 5), and in general to a larger degree for KCl, KAc, KOH, CaAc$_2$, MgCl$_2$ and MgAc$_2$ at the higher temperature (Fig. 6). On the other hand, Figs. 7 and 8 indicate that the order of catalytic activity for the Na and Ca compounds studied depends on the gasification temperature and on the catalyst concentration. At 900 °C, though to an extent according to the catalyst type and the catalyst concentration, the chars containing Ca compounds show a reactivity higher than those with Na compounds. At 950 °C, however, Na catalysts, with the exception of NaCl,

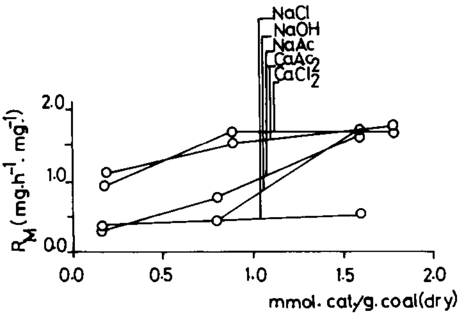

Fig. 7. Gasification in carbon dioxide at 900 °C. Variation of the reactivity with catalyst concentration.

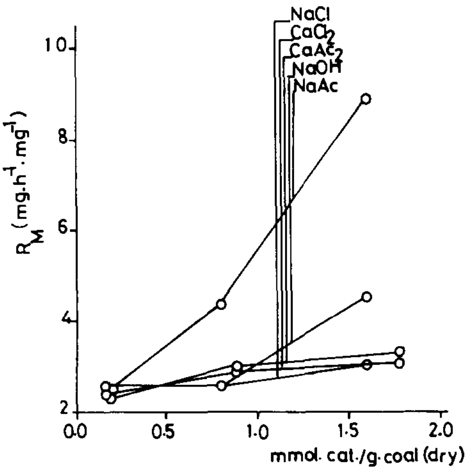

Fig. 8. Gasification in carbon dioxide at 950 °C. Variation of the reactivity with catalyst concentration.

bring about a large enhancement of char reactivity when increasing the catalyst concentration. As a result of this, Ca compounds are more efficient catalysts than Na compounds at lower catalyst concentrations, while the opposite behaviour is observed at higher concentrations. Moreover, in a similar way to observations in the gasification in steam, char reactivity follows a variation with catalyst concentration that depends on whether the catalyst is a Na or a Ca compound. In the former case, except for NaCl, char reactivity suffers a considerable increase above a certain catalyst concentration. However, when a Ca compound is used as catalyst, char reactivity first augments, and then either increases only slightly or remains steady.

DISCUSSION

As has been mentioned, a certain number of catalysts when present in small amounts on the support surface, produce a deactivation of the char for its gasification both in steam and in carbon dioxide. In this respect, earlier workers [1–3] have observed a lesser efficiency of alkali metal catalysts as a result of their reaction with inherent mineral matter of the coals. Hüttinger and Minges [11], when studying the influence of the catalyst precursor anion in catalysis of water vapour gasification of carbon by potassium, under thermodynamic and kinetic considerations, have demonstrated that potassium carbonate is drastically deactivated by reaction with deliberately added silica. Valenzuela-Calahorro and co-workers [4–6], when investigating the catalysed gasification in different media of chars from a semi-anthracite coal and from a bituminous coal, have found that not only does the catalyst deactivation take place by reaction with mineral matter but also, as a result of this, the char deactivation for its gasification. These workers have suggested that such a deactivating effect could be due to the reaction of the catalyst with mineral matter and subsequent formation of reaction products which would prevent char gasification reactions. Note (see Figs. 1, 2, 5, 6) that, in general, the char deactivation takes place to a larger extent when the alkali metal hydroxides are used as catalysts. As these compounds possess relatively low melting points (318.4°C, NaOH; 360.4°C, KOH), it is expected that during the heat treatment such compounds remain in the molten state longer, and thus in contact with the carbon support. Therefore, the diffusion of these catalysts in char pores (and hence the catalyst dispersion and the reaction with mineral matter on the coal surface), as well as the deactivation of both the catalyst and the char, may take place to a larger extent than for other alkali and alkaline earth metal compounds with higher melting points. On the other hand, such an effect is not observed when the char supporting NaOH is gasified in carbon dioxide at 950°C, which could be an abnormal result, as was found in a previous work [5] when studying the gasification in steam, at a comparatively lower gasification temperature, of a char containing KOH.

The above results (Figs. 1, 2, 5, 6) also indicate that the alkaline earth metal hydroxides, when supported in small concentrations on the char surface, frequently give rise to the largest enhancement of char reactivity. This means that, even though their catalytic activity can be to a certain extent reduced by reaction with mineral matter, the deactivating effect of the catalyst takes place to a lesser degree than for the other catalysts. Alkaline earth metal hydroxides decompose at relatively low temperatures (350°C, $Mg(OH)_2$; 580°C, $Ca(OH)_2$) to give water and the respective oxides, which are rather inert and thermally very stable compounds that melt at high temperatures (> 2500°C). As it is probable that the catalyst, in equilibrium with other products, is found in the solid state during the heat pretreatment and also during char gasification, the catalyst diffusion in char pores and also the reaction with mineral matter must take place in more unfavourable conditions than for the alkali metal hydroxides; hence the lesser catalyst deactivation.

As has been mentioned, the catalytic activity of most of the alkali metal compounds studied increases substantially beyond a certain catalyst concentration. The increase in char reactivity probably results from the creation of active sites on the coal surface by the catalyst remaining from the reaction with mineral matter. (It seems that a fraction of the catalyst is deactivated by reaction with mineral matter and the rest must exert the catalytic action.) On the other hand, some differences are observed in relation to the catalytic behaviour of NaAc and NaOH. NaAc is a more efficient catalyst than NaOH, and also the increase in char reactivity generally starts at a lower catalyst concentration in the former case. NaAc thermally decomposes to Na_2CO_3, which melts at 851° C; NaOH, however, melts at a much lower temperature (318.4° C). Therefore, the diffusion of the catalyst in char pores, the reaction of the catalyst with mineral matter and the catalyst deactivation will take place to a lesser degree in the former case. Hence the higher catalytic activity of NaAc.

$CaAc_2$ is a more active catalyst than the Na compounds, mainly in the steam atmosphere and at low catalyst concentration and gasification temperature. $CaAc_2$ must be in the solid state, as oxide, before and during gasification conditions. Therefore, as the catalyst probably does not reach most of the internal surface area of the support (and also the catalyst–mineral matter reactions will take place mostly in a solid–liquid heterogeneous phase), a lesser catalyst deactivation than for Na compounds can be assumed, which explains the higher char reactivity. The results also indicate that above a certain catalyst concentration char reactivity either increases slightly or remains steady. The relative decrease of char reactivity could be due to the prevention by the catalyst (which must be closing pore entrances) of diffusion of the gasificant agents. Hippo et al. [9], when investigating the enhancement of lignite char reactivity to steam by cation addition, found that differences in reactivity between the calcium exchanged and raw lignite chars became less as reaction temperature was increased. The results were attributed to increasing mass transport control of the reaction and possibly enhanced catalyst deactivation due to particle agglomeration and sintering.

NaCl and $CaCl_2$ present abnormal behaviour from the standpoint of the above discussion. That is, NaCl, which melts at a temperature (801° C) lower than the gasification temperature, does not substantially affect char reactivity by increasing catalyst concentration, though in some cases it first decreases slightly and then increases. However, $CaCl_2$, which also melts at a temperature (782° C) lower than the gasification temperature, presents similar behaviour to $CaAc_2$ as catalyst. These results, at least in principle, suggest that such compounds interact with mineral matter and/or perhaps participate in the catalysis mechanism in a different manner from that of the other Na and Ca compounds. On the other hand, $CaCl_2$ shows a higher catalytic activity than NaCl in both atmospheres. The explanation of these results is not straightforward. Nevertheless some differences between the properties of these compounds in the molten state are observed. Numerous metals are soluble in their halide melts and thus form extremely reducing solutions. The solubility varies with the nature of the metal. In particular, Na in all proportions (total miscibility) is soluble in its chloride at temperatures close to 1000° C and Ca presents a solubility of 16 mol% [12]. Therefore, NaCl deactivation may be due to dissolution in the catalyst melt of Na formed in the catalysis reaction and subsequent reaction of the mixture (Na plus NaCl melt) with mineral matter. This deactivating effect may take place to a lesser extent for $CaCl_2$. It must be noted, however, that it has been reported that alkaline earth metal chlorides present higher [4] or lower [5,6] catalytic activity than alkali metal chlorides depending on the coal being studied and on the gasification conditions, which suggests that other factors, such as coal composition, must contribute to the catalyst deactivation.

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