Effect of Alkaline Hydroxides in the Carbonization of Coals

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Introduction

Carbonaceous materials heat-treated in presence of potassium hydroxide give charcoals with high surface area (1,2). The objective of the present paper is to investigate the role of potassium hydroxide in the carbonization mechanism and to determine why potassium is so effective in the development of the porosity of the resultant charcoal.

Experimental

A low rank coal (Menouna, Algeria) with an ash content of 3.6 % by weight has been sieved to a particle size between 0.5 and 1 mm in diameter. Coal sample (10 g) were impregnated with KOH or NaOH in a solution of ethanol which was then evaporated at 310 K under flowing argon. Alkaline hydroxide content ranges from 0 to 70 % by weight in the impregnated sample. Untreated and alkaline treated coal samples were then carbonized in the argon stream at a heating rate of 5 K/min up to 1200 K. Evolution of CO_2 and CO was recorded using infra-red cells. After carbonization the alkaline salt was removed by refluxing in diluted HCl and the char was then washed with distilled water. Adsorption isotherm of CO_2 was carried out at 273 K and the micropore volume was determined by the Dubinin equation.

Results and Discussion

The change in micropore volume of the charcoal after treatment at 1070 K is shown in Figure 1 as a function of the hydroxide content. It is seen that the micropore volume first decreases by addition of hydroxide and thereafter increases again. In the case of KOH however, W_o is considerably larger than for NaOH. For a KOH content of 66 % by weight, a highly activated carbon is obtained since its equivalent surface area is about 1600 m^2/g as measured by CO_2 adsorption.

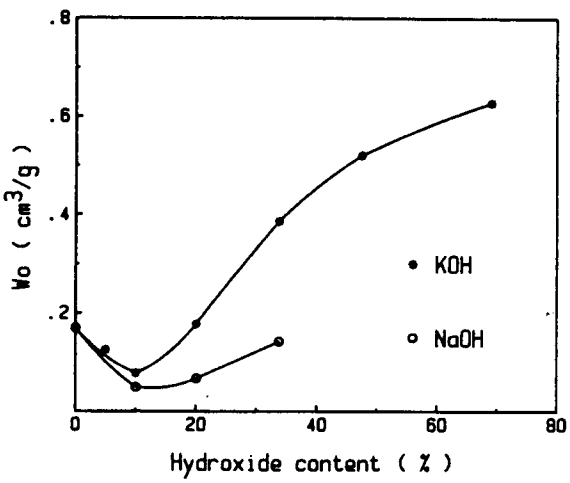

Figure 1. Change in micropore volume W_o of the charcoal as a function of hydroxide content.

The total weight loss of the coal after carbonization at 1220 K is indicated in Table 1. The weight losses corresponding to CO_2 and CO evolution are also shown. It is interesting to note that the total coal weight loss is almost the same in presence or absence of hydroxide. The weight losses as CO_2 and as CO are however far higher in the presence of hydroxide. It was also observed that CO_2 is evolved at rather low temperature (570-1070 K) whereas CO starts only at 920 K. These results clearly suggest that the formation of CO_2 and CO occurs through different reaction steps. The reaction with an alkaline hydroxide may

Table 1. Coal Weight Loss during Carbonization.

Coal	weight loss (%)		
	as CO_2	as CO	total
non treated	0.8	<0.1	29
NaOH treated	1.0	20.4	28
KOH treated	3.5	11.0	30

take place. The first step is the formation of carbonate and the evolution of H_2 (3).

$$4\ MeOH + = CH_2 \rightarrow Me_2CO_3 + Me_2O + 3\ H_2 \qquad (1)$$
$$Me = K,\ Na$$

In fact, carbonate formation and hydrogen evolution were detected with our samples in the temperature range 470-1220 K. It has also to be noted that H_2 evolution is detected at much higher temperature in the absence of hydroxide (T > 770 K).

In a second step the alkaline carbonate partly decomposes on the carbonaceous material giving CO_2 and a surface salt complex as shown by Mims et al. (4) in the case of K_2CO_3. Therefore CO_2 would originate from a partial decomposition of carbonate.

The formation of CO occurs at higher temperature and is directly related to the amount of hydroxide initially present. For hydroxide content less than 10 %, no CO evolution was observed. For higher content of hydroxide, the formation of CO represents a significant fraction of the total weight loss. A possible reaction for CO formation would therefore be :

$$Me_2CO_3 + 2\ C \rightarrow 3\ CO + 2\ Me \qquad (2)$$

The presence of alkaline metal was indirectly detected in carbonized sample. In fact these samples partially burn when rapidly contacted with air at room temperature.

These results clearly show that in presence of MeOH carbonization and partial gasification simultaneously occur. Although the precise mechanism of activation is not fully understood, it appears that the increase of microporosity is related to the extent of decomposition of the carbonate into CO_2 in the temperature range 570-1070 K. It has already been mentioned that in this temperature interval K_2CO_3 decomposes on carbon into CO_2 and a surface salt complex (4). A higher number of surface salt complexes would therefore initiate a higher number of sites where gasification occurs. Hence the pronounced development of micropore volume with KOH would result from a higher degree of dispersion of the potassium salt through the coal particle during the heat treatment as compared to the sodium salt.

Conclusion

Carbonization and gasification simultaneously occur during pyrolysis of a low rank coal in presence of alkaline hydroxide. The results suggest that the development of microporosity in the case of KOH is due to a high degree of dispersion of the potassium salt on the carbonaceous material. The micropore characteristics of the resultant charcoal are described in another paper (5).

References

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