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Note

CATALYTIC GASIFICATION OF ACTIVATED CARBON BY CO_2

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INTRODUCTION

Carbon monoxide, generated by the endothermic Boudouard reaction, is the reducing agent for most metal oxides. Carbonaceous materials may also be gasified by steam for the production of synthetic gas. Furthermore, the manufacture of activated carbons usually involves a carbonization and a partial gasification stage. Although numerous papers have been published on the effect of catalysts on the gasification of many types of carbon, most studies have dealt with the alkali and alkaline earth elements [1–5]. The influences of the transition metals [6,7] and mineral matter [8,9] have been investigated, but at present the mechanisms of catalysis are not entirely clear.

Activated carbon used for the adsorption of gold from slurries is contaminated by inorganic and organic species, and should be regenerated thermally by steam or CO_2 [10]. Catalysis of such gasification reactions may occur, although no work has been published in this regard. In this note the influence of selected contaminants on the gasification of activated carbon by CO_2 is investigated by thermogravimetry.

EXPERIMENTAL

A coconut shell carbon (Le Carbone G210 AS) with an apparent density of 890 kg m^{-3}, BET surface area of 1024 m^2 g^{-1} and particle size of 0.5–1.0 mm was used. Samples of carbon were impregnated by agitation in separate solutions of $NiSO_4$, $CoSO_4$, $Al(NO_3)_3$, $CuSO_4$, $MnSO_4$, $FeSO_4$ and $MgSO_4$ for 10–20 h until the carbon contained 1–2% of the metal. One of the samples was impregnated by mixing with a slurry of submicron SiO_2 particles.

The impregnated carbon was then treated in an atmosphere of nitrogen at 1000 °C for 1 h whereafter a constant mass was attained. In this way volatile

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components on the carbon could be removed, and the impregnated species were decomposed to yield mostly the metal oxides.

Gasification experiments were conducted in a thermobalance [11] at constant temperatures of 760, 900, 1090 and 1290 ° C, using 1.0 g of carbon in a small recrystallized-alumina crucible. Purified CO_2 was flushed through the furnace at a constant flow rate of 2.0 l min^{-1}.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate thermogravimetric results at 760 ° C. Similar results were obtained at other temperatures. The initial slopes of these curves were used in the logarithmic form of the Arrhenius equation to estimate the activation energies for the gasification reaction. These values are summarized in Table 1.

All gasification curves revealed a rapid initial phase, followed by a very slow approach to equilibrium. This rapid phase was more intense if the temperature of pretreatment was lower. The catalysts did not increase the rate significantly during the initial stage, but enhanced the duration thereof and the final conversion attained. The catalysts $NiSO_4$, $CoSO_4$, $Al(NO_3)_3$ and $CuSO_4$ in Fig. 1 exerted a more pronounced influence than SiO_2, $MnSO_4$, $FeSO_4$ and $MgSO_4$ in Fig. 2.

Very little comparable work has been published on the effects of SiO_2 and Al_2O_3, which enhanced the CO_2 gasification of graphite only marginally

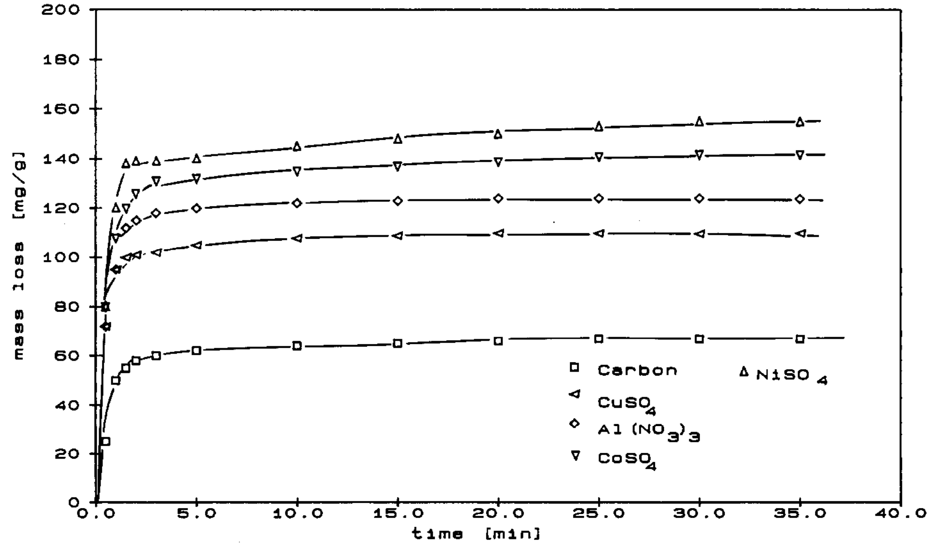

Fig. 1. The influence of $NiSO_4$, $CoSO_4$, $Al(NO_3)_3$ and $CuSO_4$ on the gasification of activated carbon by CO_2 at 760 ° C.

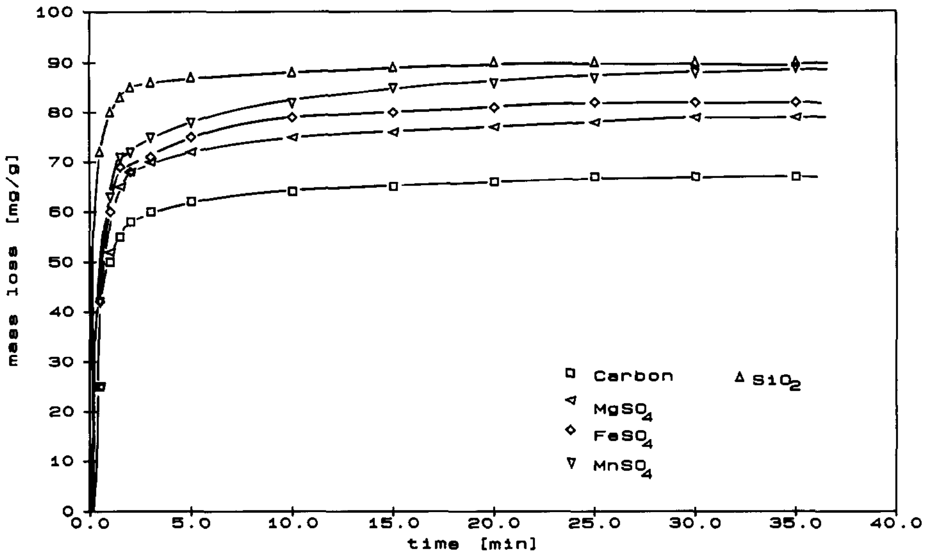

Fig. 2. The influence of $MnSO_4$, $FeSO_4$, $MgSO_4$ and SiO_2 on the gasification of activated carbon by CO_2 at 760 °C.

[11]. While McKee [3] surmised that stable oxides such as Al_2O_3 or MgO would not show catalytic activity, MgO was found to be active [4,12]. Too little is known about the mechanisms of catalysis for a detailed analysis of the data in Figs. 1 and 2.

The activation energies in Table 1 are very low, and imply control by pore diffusion rather than chemical reaction. The catalysts did not affect the activation energy markedly; this is in agreement with the results of Kapteijn et al. [4]. This suggests that the catalyst increased only the number of active sites [4].

TABLE 1

Activation energies of gasification reaction catalyzed by different species

Catalyst	Activation energy (kJ mol^{-1})
Carbon only	51
$NiSO_4$	35
$CoSO_4$	43
$Al(NO_3)_3$	38
$CuSO_4$	47
SiO_2	36
$MnSO_4$	39
$FeSO_4$	39
$MgSO_4$	46

CONCLUSIONS

Activated carbon was impregnated with $NiSO_4$, $CoSO_4$, $Al(NO_3)_3$, $CuSO_4$, $MnSO_4$, $FeSO_4$, $MgSO_4$ or SiO_2, and was then heated in N_2 at 1000°C. All these additives revealed some catalytic activity during the gasification of carbon in CO_2, but did not decrease the activation energy markedly.

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