

Eutectic Salt Catalysts for Graphite and Coal Char Gasification

D.W. McKee, C.L. Spiro, P.G. Kosky and E.J. Lamby

General Electric Corporate Research and Development
Schenectady, New York 12301

INTRODUCTION

The reactivity of carbonaceous materials, such as graphite and coal char, towards carbon dioxide and steam is strongly enhanced by the presence of many alkali metal salts (1,2). Interest in this subject has been stimulated recently by the development of new processes for the catalyzed gasification of coal (3,4). For a catalyst to function satisfactorily, a three-phase interface must be maintained between the carbonaceous substrate, the catalyst phase and the gaseous oxidant. Whatever the detailed mechanism of the catalytic process, overall rates of gasification should be enhanced by improving the contact between catalyst and carbon, for example by melting of the catalyst phase. However, if the carbon surface becomes coated with a film of molten salt, kinetics are likely to be limited by diffusion of the gaseous reactant through the salt film and the overall rates will be reduced. In this study, the behavior of binary and ternary eutectic salt catalysts in the gasification reactions of graphite and coal char with CO_2 and steam was investigated.

EXPERIMENTAL

Pure graphite powder and chars prepared from ground Illinois #6 HvB and Pittsburgh HvA coals were used in this study. Binary and ternary eutectic catalysts were prepared by fusion of finely ground salt mixtures having compositions corresponding to the eutectic melting temperatures. Weighed amounts of the finely ground eutectic catalysts were intimately mixed with the powdered graphite and char samples to give an initial catalyst concentration of 10 weight %.

Measurements of gasification kinetics in flowing CO_2 (400 ml/min) or steam (23 mm. H_2O in helium) were performed in an automatically recording controlled atmosphere thermobalance. The balance was usually operated in the isothermal mode with weight changes being recorded as a function of time at a series of temperatures in the range 650-950°C. The total weight loss of each sample was kept below 20 wt.% to minimize the effects of changing surface area and catalyst concentration during the experiments. Fresh samples of char or graphite were used for the study of each catalyst system. However, with each sample of char or graphite plus catalyst, kinetic measurements of gasification rate were made at a series of increasing temperatures, followed by cooling to room temperature in the flowing gas stream. Such a cycle was repeated

several times for each sample to check on the reproducibility of the measurements.

RESULTS AND DISCUSSION

Gasification rates in 1 atm.(0.1MPa) CO_2 as a function of temperature are shown in Figure 1 for a sample of Illinois #6 char to which had been added 10 wt.% of the pre-melted eutectic NaCl -60mole.% Na_2CO_3 (m.p.640°C, Na/C=2.7 Atom.%). Included on the figure are the Arrhenius plots for the uncatalyzed char and for char samples with 10 wt.% NaCl (Na/C=2.5 Atom.%) and Na_2CO_3 (Na/C=2.8 Atom.%) catalysts. The results of kinetic measurements during four successive thermal cycles are shown,

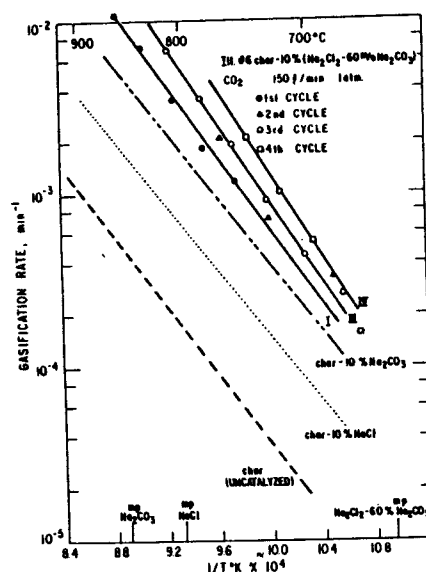


Figure 1 Illinois #6 coal char gasification in CO_2 . Effect of NaCl (Na/C=2.5 Atom.%), Na_2CO_3 (Na/C=2.8 Atom.%) and NaCl - Na_2CO_3 (Na/C=2.7 Atom.%) eutectic catalyst. Rates vs. $1/T$.

the sample being cooled to room temperature at the end of each series of measurements. It is evident that

the eutectic catalyst was more active than the sum of the individual salt components, both on a weight basis and when compared at equal Na/C atom ratios. It was also observed that the catalytic activity increased steadily on repeated cycling, probably because the molten catalyst phase continued to spread over the char surface, attaining a more effective dispersion with each successive cycle. Similar results were obtained with graphite as the substrate and in this case again a progressive increase in catalytic activity was observed on successive gasification cycles, the overall activity of the eutectic catalyst being greater than that of the sum of the individual components at the same concentration.

Low melting ternary eutectics were also found to be very active catalysts. Thus, Illinois #6 char doped with $\text{NaCl-Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4$ (m.p. 612°C), at a Na/C concentration of 2.4 Atom.%, showed gasification rates in CO_2 comparable to those of a char doped with K_2CO_3 at the same K/C concentration. K_2CO_3 is generally considered the most active catalyst for char gasification, whereas the individual sodium salts, NaCl , Na_2CO_3 and Na_2SO_4 are much less active.

The improved performance of eutectic salt catalysts was even more marked for gasification in steam than in CO_2 , especially at temperatures below 800°C . Figure 2 shows kinetic data for a char derived from Pittsburgh coal gasified in a stream of helium saturated with water vapor at 25°C (23 mm., 3.1 kPa H_2O). The sample containing the Li,Na,K carbonate eutectic catalyst was at least an order of magnitude more reactive than a sample containing the same concentration of K_2CO_3 alone.

It should be noted that during the course of the catalyzed gasification reactions other active intermediates, such as alkali metal, oxide or hydroxide may form on the carbon surface (1,2), so that the initial composition of the eutectic phase may not be maintained. Nevertheless, the enhancement of the low temperature gasification rates observed with eutectic catalysts substantiates the general conclusion that melting and spreading of the salt phase are important parameters in achieving high conversion rates. The influence of catalyst melting point and the formation of channels and pits by the mobile catalyst droplets (5), suggest that the catalytic process involves a localized interaction between the salt particles and the carbon substrate. The details of this interaction are however still controversial(6).

CONCLUSIONS

Gasification rates of coal char and graphite in CO_2 and steam in the temperature range $700\text{-}900^\circ\text{C}$ can be considerably increased by the addition of binary and ternary eutectic alkali salt catalysts. The reduced melting points of the eutectic phases result in enhanced catalytic activity at the lower gasification temperatures by achieving a better dispersion of the salt phases on the carbonaceous substrates.

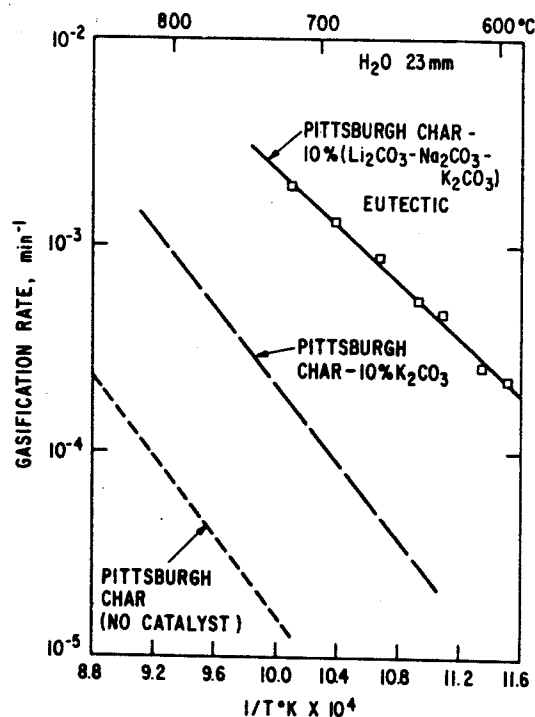


Figure 2 Pittsburgh coal char gasification in steam. Effect of K_2CO_3 (K/C=2.4 Atom.%) and $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (Li/C=1.4; Na/C=1.0; K/C=0.9 Atom.%) eutectic catalyst. Rates vs. $1/T$.

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