Interactions Between Carbon and Alkali Metals During Catalytic Carbon Gasification

by

F. Shadman and D.A. Sams
Department of Chemical Engineering
University of Arizona
Tucson AZ 85721

Introduction

The catalytic effect of alkali metals on the gasification rate of carbonaceous materials has been the subject of a number of studies. Despite these efforts, the active form of the catalyst during gasification and the effects of catalyst loss remain unclear. The understanding of the reduction of alkali metal catalysts from its initial oxidized form and the identification of the reduced form are necessary requisites for determining the reaction mechanism. Experimental observations from this laboratory clearly indicate that catalyst loss occurs simultaneously with the reduction (1).

Experimental

An uncoated graphitized carbon from Supelco, with a surface area of approximately 100 m^2/g was used as the substrate in this study. The samples were impregnated with potassium by an incipient wetting technique, then dried at room temperature and stored under vacuum.

The data in this study was generated in a thermogravimetric reactor system. The other major components were a movable electric furnace, a temperature controller and an auxiliary type K thermocouple. The system also included a gas preparation section for mixing and metering the feed gas at the desired compositions and flow rates. The reactant gas was a mixture of 15% CO_2 and 85% N_2. The product gases were analyzed by an on-line gas chromatograph and nondispersive infrared CO and CO_2 analyzers.

Results and Discussion

To examine the interaction of the potassium catalyst with the carbon surface, a series of temperature programmed reaction experiments were conducted where the sample mass and the reaction products were continually monitored. Figure 1 shows typical temporal profiles for the CO and CO_2 peaks when the sample is heated to 800°C in a reducing atmosphere at a moderate rate (5°C/min).

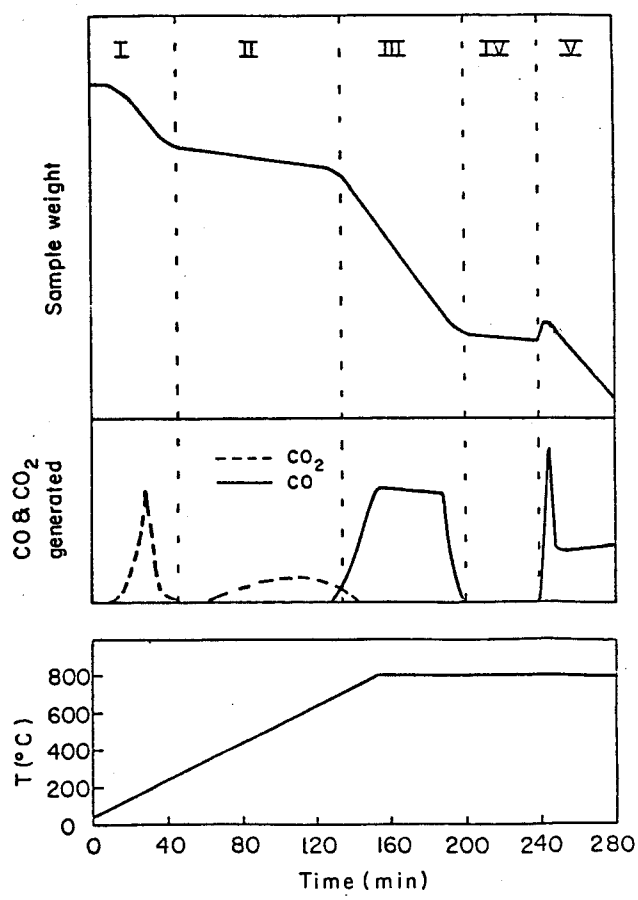

Figure 1. Typical CO_2 and CO profiles during a TPR experiment.

When a freshly impregnated sample is heated to 250°C, both CO_2 and H_2O are detected. The amount of CO_2 generated, normalized with respect to the initial amount of carbon present, is given in Figure 2 as a function of the initial potassium level, $(K/C)_o$. A linear response is observed where one mole of CO_2 is generated for every two moles of potassium present. This

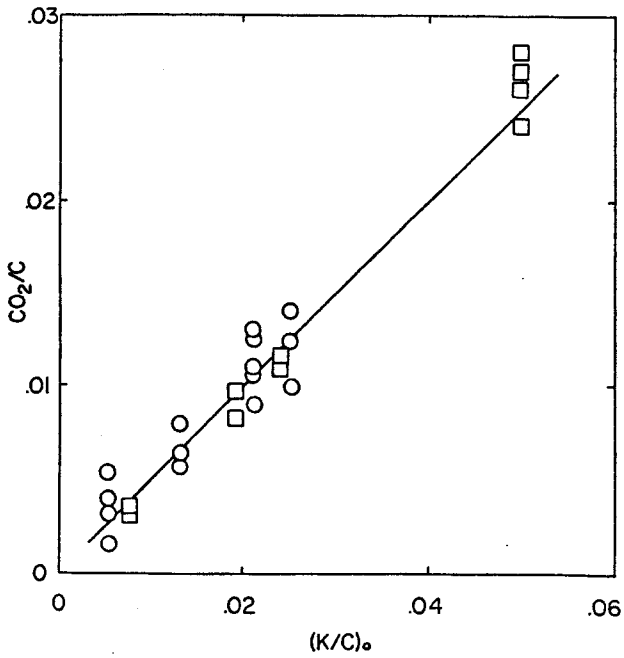

Figure 2. Dependence of low temperature CO_2 on the initial catalyst loading; (O)K_2CO_3, (□) KOH.

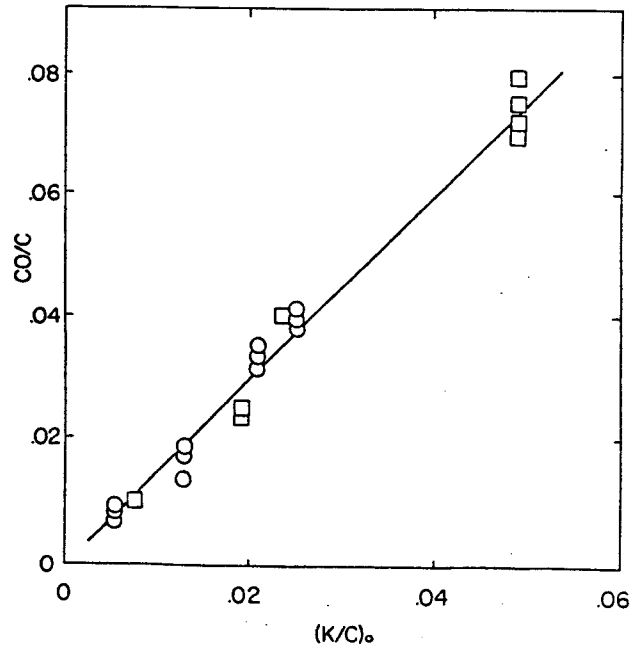

Figure 3. Dependence of high temperature CO on the initial catalyst loading; (O)K_2CO_3, (□) KOH.

linearity clearly indicates that the potassium strongly influences the amount of CO_2 uptake and the stoichiometry suggests that each mole of potassium carbonate interacts with one mole of CO_2. The amount of CO_2 detected was independent of the rate at which the sample was heated to 250°C. The scatter in the data implies that other factors may influence the total amount of CO_2 generated.

As the sample temperature approaches 700°C, CO begins to evolve as the catalyst is reduced on the carbon surface. The total amount of CO generation is shown in Figure 3 where the CO/C ratio is given as a function of the initial K/C ratio. For each sample, three moles of CO were generated for each mole of potassium carbonate originally present indicating complete reduction of the carbonate:

$$K_2CO_3 + 2\ C = 2(-C-K) + 3CO \qquad (1)$$

where -C-K represents the reduced form.

Many investigators have suggested that alkali metal catalyzed gasification involves a process where the catalyst continually undergoes an oxidation/reduction cycle. The catalyst, after first being reduced during the transient start-up period, is oxidized upon the introduction of CO_2 and produces a CO profile characterized by an overshoot. The oxidized form then interacts with the carbon surface to liberate another CO thus returning to the reduced form completing the cycle. Moulijn et al. (2,3) have described this process with a simple two step reaction sequence:

$$K_xO_y + CO_2 = K_xO_{y+1} + CO \qquad (2)$$

$$K_xO_{y+1} + C = K_xO_y + CO \qquad (3)$$

where K_xO_y represents the reduced form and K_xO_{y+1} the oxidized form. A supporting observation for this type of mechanism is a slight weight gain which accompanies the CO overshoot at the onset of gasification due to the oxidation of the reduced form of the catalyst.

In conclusion, the process of catalyst reduction appears to be an activated one which requires intimate contact with active sites so that for samples which are initially saturated with catalyst, the rate of reduction is limited by the available surface area. The amount of CO generated during this process indicates that the catalyst is completely reduced. Furthermore, catalyst loss kinetics suggest that the formation of a reduced form of the catalyst is a prerequisite for rapid vaporization and escape to the gas phase.

Acknowledgments

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