TEMPERATURE PROGRAMMED REACTION STUDIES OF POTASSIUM/CARBON INTERACTIONS AND CATALYST LOSS

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INTRODUCTION

The catalytic effect of alkali metals on the gasification rate of carbonaceous materials has been the subject of a number of studies in recent years (1-16). 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 (12). In addition, the rate of catalyst loss from the surface is directly influenced by the reduced form it takes. The present study provides insight into this subject by examining the reduction of potassium carbonate on the surface of a pure carbon substrate and the accompanying phenomenon of catalyst loss.

EXPERIMENTAL

An uncoated graphitized carbon from Supelco, 60/80 Carbopack B (180-250 μm), 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 utilizing an electronic microbalance and a quartz downtube reactor which enclosed the platinum sample tray as shown in Figure 1. 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. Ultra high purity (UHP) N_2 was used as the purge gas. The product gases were analyzed by an on-line gas chromatograph and nondispersive infrared CO and CO_2 analyzers.

To prepare a run, 20-30 mg of sample were loaded onto the microbalance tray and the reactor was placed in position. The system was purged with UHP N_2 to remove the oxygen and the furnace was raised to enclose the reactor. Two heat-up procedures were used: a linear 5°C/min rate and a rapid one step process where the furnace was preheated to 800°C and then raised to enclose to reactor.

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 2 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). For clarity in describing the various processes which occur during the transient heat-up period, the results are divided into five separate stages.

Stage I occurs below 250°C and represents the physical desorption of gases such as CO_2 and H_2O from the surface. Stage II (250-700°C) corresponds to the evolution of very small amounts of CO_2 due to the partial decomposition of the catalyst and possibly reactions with chemisorbed oxygen. This is followed by Stage III (700-800°C) where the catalyst is reduced through interaction with the carbon surface and large amounts of CO are generated. Stage IV represents an isothermal heat treatment period where the sample is exposed to UHP N_2 at 800°C. Although no measurable amounts of CO or CO_2 are observed during this stage, a steady weight loss occurs. Finally, Stage V represents the gasification of the carbon sample at 800°C.

When a freshly impregnated sample is heated to 250°C (Stage I), both CO_2 and H_2O are desorbed. The amount of CO_2 generated, normalized with respect to the initial amount of carbon present, is given in Figure 3 as a function of the initial potassium level, $(K/C)_o$. A linear response is observed where one mole of CO_2 is desorbed for every two moles of potassium present. This linearity clearly indicates that the potassium strongly influences the amount of CO_2 adsorbed and the stoichiometry suggests that each mole of potassium carbonate interacts with one mole of CO_2. The amount of CO_2 desorbed 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 amount of CO_2 adsorbed.

As the sample temperature approaches 700°C, CO begins to evolve as the catalyst is reduced on the carbon surface (Stage III). The total amount of CO generation is shown in Figure 4 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:

$$K_2CO_3 + 2\,C = 2\,\text{'KC'} + 3CO \qquad 1)$$

where 'KC' represents the reduced form. The nature of this reduced form is not clearly known but one possibility is a complex involving K, C and possibly O. This unknown complex readily decomposes in the 700-800°C temperature range under reducing conditions and releases alkali metal vapor to the gas phase. The total amount of CO generated during this stage was the same whether the sample was heated at a moderate rate or in one rapid step directly from room temperature to 800°C. For the samples with an initial catalyst concentration high enough to saturate the surface, the rate of CO generation reached a maximum independent of the initial loading and remained constant until the

reduction was nearly complete at which time a normal first order decay profile was observed. In other words, by doubling the initial catalyst concentration, the time for complete catalyst reduction would also be doubled. This phenomenon suggests that the rate is limited by the available surface area.

To analyze the kinetics of catalyst loss by vaporization, the change in the potassium content of several samples undergoing heat treatment was determined both by direct analysis of the samples after quenching and by indirect determination by weight loss measurements. A typical overall temporal profile of catalyst loss when a sample impregnated with potassium carbonate is gradually heated to 800°C in a reducing atmosphere is shown in Figure 5. For comparison, a sample impregnated with potassium hydroxide is also given. The results indicate that a large fraction of the catalyst is lost in a narrow temperature range around 800°C, denoted by Stage III in Figure 2.

Many investigators have suggested that alkali metal catalyzed gasification involves a process where the catalyst continually undergoes an oxidation/reduction cycle (7,13). 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. (1,5) have described this process with a simple two step reaction sequence:

$$\text{'KC'} + CO_2 = \text{'KCO'} + CO \qquad 2)$$
$$\text{'KCO'} + C = \text{'KC'} + CO \qquad 3)$$

where 'KC' represents the reduced form and 'KCO' 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.

Regardless of the exact chemical form of the catalyst following Stage III, it seems that the formation of the reduced catalyst is a prerequisite for the observed rapid weight loss of catalyst around 800°C. In fact, the rapid weight loss does not seem to be directly related to the melting point of K_2CO_3 (891°C). Rather, it is due to the fact that at this temperature the catalyst is rapidly converted to its reduced form which is readily vaporized. This speculation is supported by the results obtained from samples impregnated with KOH. As shown in Figure 5, the KOH sample shows the same rapid loss of catalyst around 800°C even though KOH has a melting point of only 380°C.

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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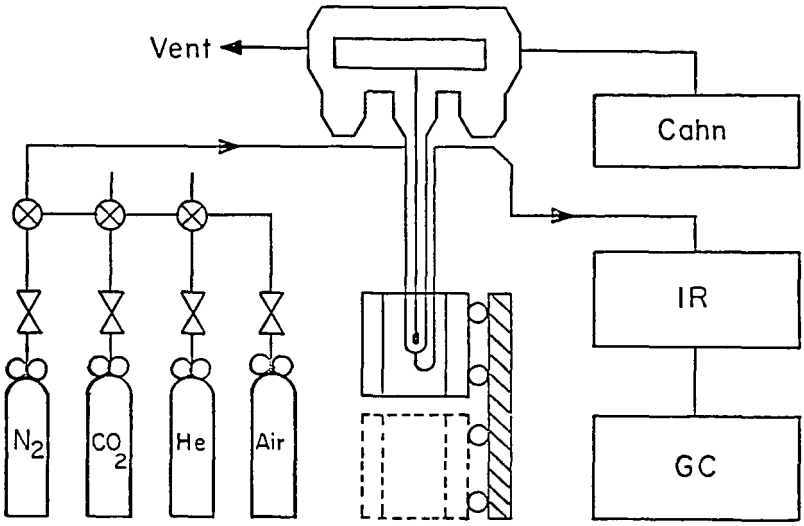

Figure 1. Schematic diagram of the Cahn microbalance system.

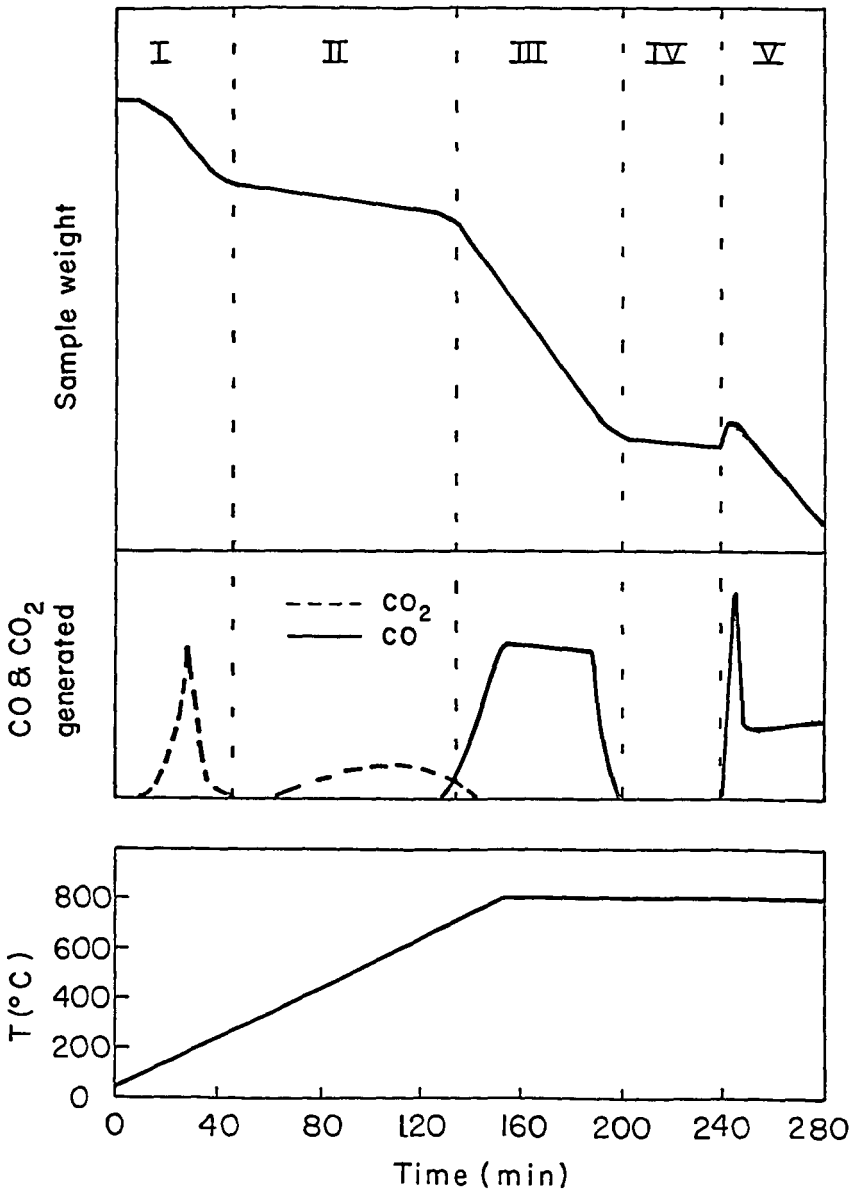

Figure 2. Characteristic stages during a typical TPR experiment.

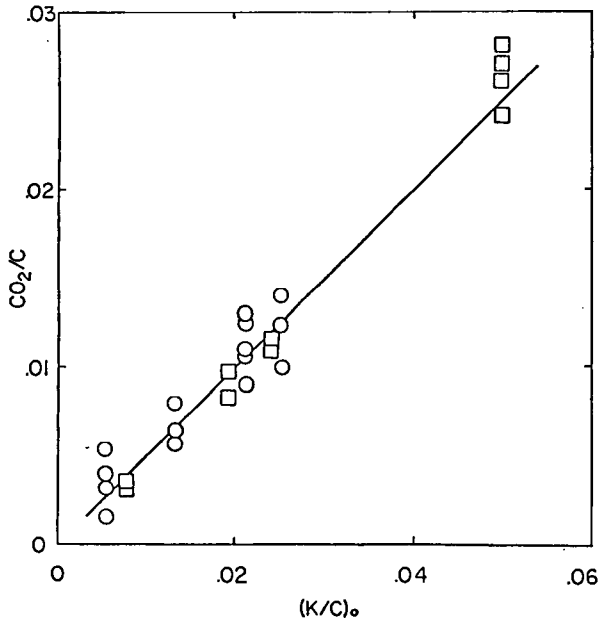

Figure 3. Dependence of low temperature CO_2 desorption on the initial catalyst loading; (○) K_2CO_3, (□) KOH.

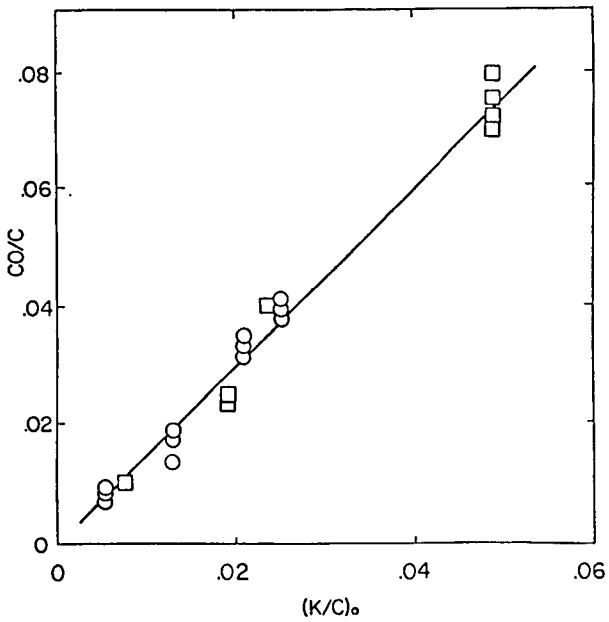

Figure 4. Dependence of high temperature CO generation on the initial catalyst loading; (○) K_2CO_3, (□) KOH.

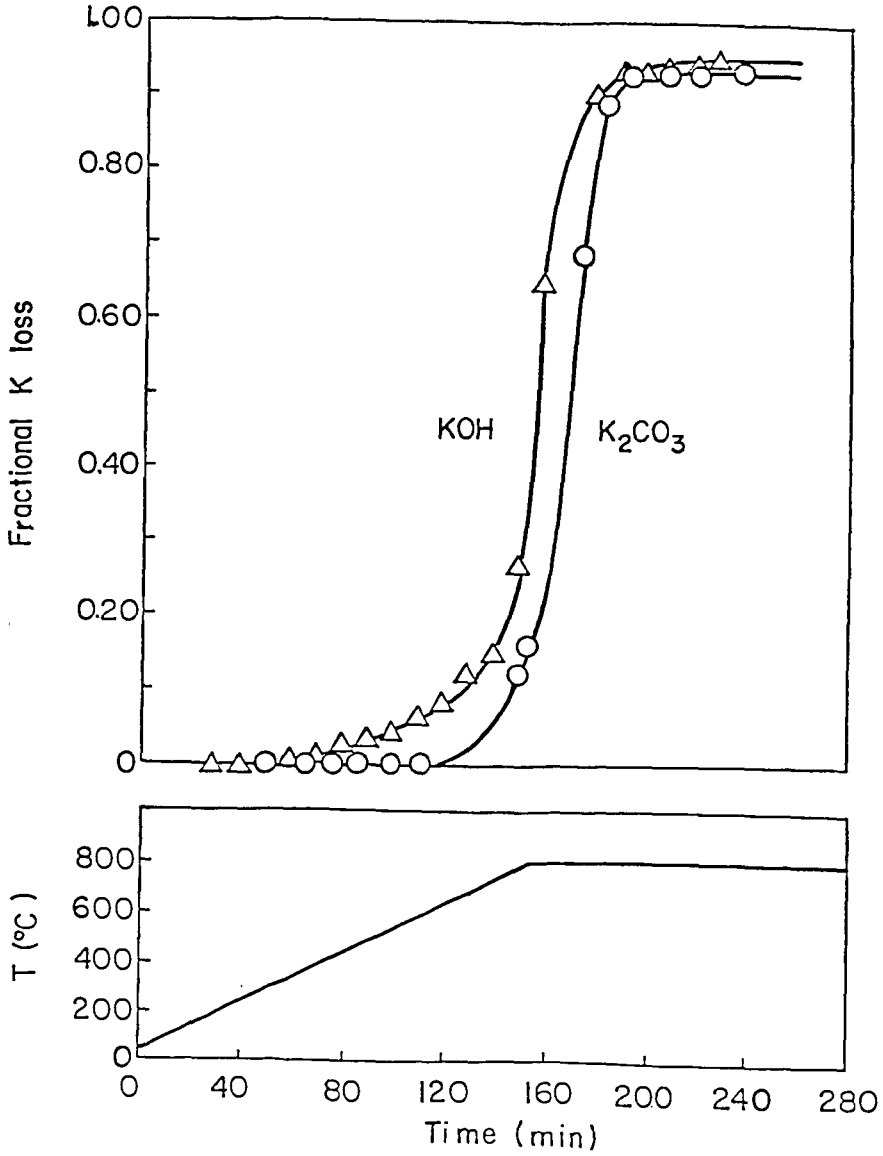

Figure 5. Catalyst loss profiles during a typical TPR experiment.