Mechanism of Potassium-Catalyzed Carbon/CO_2 Reaction

The mechanism of potassium-catalyzed C/CO_2 reaction is studied by a temperature and concentration programmed reaction (TCPR) technique. The proposed redox mechanism contains three surface complexes: $-CO_2K$, $-COK$, and $-CK$. The oxide groups are the intermediates during C/CO_2 gasification. The completely reduced form, $-CK$, is the end product of catalyst reduction and is the precursor for K loss. The stoichiometries of these surface groups are confirmed by oxygen and potassium balances.

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SCOPE

The gasification of coal and other carbonaceous materials by means of alkali metal catalysis has attracted a great deal of attention in recent years. However, despite many investigations the mechanism of catalytic gasification is still in debate. The knowledge of the reaction mechanism is of primary significance in understanding how alkali metal catalysis works and how it can be improved and utilized for process applications.

The primary objective of this work was to use a series of experiments under transient but programmed conditions to probe the subtle features of the overall gasification reaction. The C/H_2O reaction, another important gasification reaction, is similar in many ways to the C/CO_2 reaction.

Previously published results indicate that the overall reaction involves a series of oxidation/reduction steps involving reaction intermediates. Therefore, the key to the reaction mechanism is the direct or indirect determination of the nature of these intermediate compounds. The programmed transient experiments have the potential for separation of the oxidation from the reduction reactions and for indirect determination of the reaction steps and intermediate compounds.

CONCLUSIONS AND SIGNIFICANCE

The experimental observations on the potassium-catalyzed carbon/CO_2 gasification reaction can be explained by a redox mechanism. Under gasification conditions, the oxidation and the reduction reactions occur concurrently and cannot be isolated. However, using a temperature and concentration programmed reaction (TCPR) technique, the reactions can be separated and analyzed.

The catalyzed reduction involves a series of reactions in which the catalyst is progressively reduced by the carbon. During this process, potassium-oxygen-carbon complexes with different oxygen stoichiometries are formed. The results specifically indicate the formation of three groups: $-CO_2K$ (possibly a carboxylic structure), $-COK$ (a phenolic structure), and $-CK$. The completely reduced group $-CK$ is readily decomposed to free potassium metal, which is easily vaporized at gasification temperatures. This explains the mechanism of catalyst loss and its significance under reducing conditions.

The gaseous product during catalyst reduction was primarily CO formed above 700°C. At low temperatures CO_2 was desorbed, which was due to the decomposition of potassium bicarbonate to carbonate. The formation of CO_2 at high temperatures was not significant in this study. However, the proposed mechanism sug-

gests that CO_2 can also be a product of catalyst reduction, depending on the nature of the carbonaceous substrate.

The reduced forms of catalyst, $-CK$, and $-COK$, are readily oxidized to $-CO_2K$ when they are exposed at high temperatures to an oxidizing gas such as CO_2. During the gasification process, the catalyst cycles between $-COK$ and $-CO_2K$; the reduction occurs by carbon and the oxidation by CO_2. However, the rate-limiting step is the reduction by carbon. The free potassium metal, the reduced complex $-CK$, or the potassium carbonate are not reaction intermediates during the gasification process.

There are various inconsistencies in the literature on the stoichiometry of the reaction intermediates and the overall oxygen and catalyst balance. In this study, the proposed mechanism is supported by a complete oxygen balance. For example, complete reduction of the catalyst gives three CO molecules for two potassium atoms initially present, consistent with the K_2CO_3 stoichiometry and the formation of $-CK$, while the oxidation of $-CK$ to $-CO_2K$ is confirmed by the oxygen uptake of two oxygen atoms for each potassium atom present. The catalyst loss, usually neglected in previous studies, is shown to be significant and is included in the determination of potassium concentration.

Introduction

The mechanism of carbon gasification catalyzed by alkali metals has been the subject of numerous studies in recent years. Reviews by Wen (1980), Wood and Sancier (1984), and Pullen (1984) have summarized most of the work which has appeared in the literature through June, 1984. The majority of the proposed mechanisms can be classified into one of several broad groups: oxygen transfer, electrochemical or electron transfer, and a third group involving intermediates such as charge transfer complexes, electron donor acceptor complexes, and intercalate or lamellar compounds. Of these groups, a consensus is emerging that oxygen transfer can adequately describe the experimental observations. This mechanism involves an oxidation/reduction (redox) cycle where the active catalyst continuously cycles between the oxidized and the reduced forms. The reduced form is thought to be a highly reactive compound that acts as an oxygen carrier. It splits the gaseous reactant and transfers the oxygen atom to the carbon surface where it reacts with the carbon substrate to form CO. The subsequent release of CO reduces the catalyst compound and completes the cycle.

The existence of an oxygen transfer mechanism was suggested in general form as early as the 1930's by Kroger (1939) and Fox and White (1931), and later advanced by other investigators including McKee and Chatterji (1975, 1978) and Veraa and Bell (1978). In McKee and Chatterji's mechanism, the alkali metal carbonate undergoes carbothermal reduction to the metal followed by oxidation due to steam or CO_2, which reforms the carbonate. They based their reaction schemes on thermodynamic considerations and concluded that the reactive intermediates are the free alkali metals and alkali metal hydroxides for steam gasification; for CO_2 gasification the active intermediates are the free alkali metals and the metal oxides. For CO_2 gasification, they suggest the following reaction mechanism:

$$K_2CO_3 + 2C = 2K + 3CO \tag{1}$$

$$2K + CO_2 = K_2O + CO \tag{2}$$

$$K_2O + CO_2 = K_2CO_3 \tag{3}$$

$$\overline{\qquad\qquad\qquad\qquad}$$

$$2(C + CO_2 = 2CO) \tag{4}$$

Veraa and Bell's mechanism is similar and also allows for the reformation of the carbonate during the gasification process.

In recent years, researchers have more closely examined the nature and the role of the reactive intermediate in an oxygen transfer mechanism and have concluded that metallic K is not an important intermediate species during gasification; rather, the catalytic cycle involves oxide groups (Moulijn et al. 1984). Mims and Pabst (1981, 1983) were among the first to propose surface complexes and demonstrated the presence of oxygen-containing groups on the carbon surface. They observed a direct correlation between the surface concentration of these groups and the gasification rate. A linear relationship between the catalyst concentration and the gasification rate has been previously established (Mims and Pabst, 1980a,b; Spiro et al., 1983; Sams and Shadman, 1983; Hamilton et al., 1984). Utilizing Fourier-transform infrared (FTIR) techniques, Freriks et al. (1981) and Yuh and Wolf (1984) also observed the presence of surface groups.

In summary, the characterization and study of the intermediate groups remains the key to determining the mechanism and the fundamental kinetics of the alkali-catalyzed CO_2/carbon reaction. In this study, a series of experiments under transient conditions was conducted in which the temperature and the gas concentrations were varied in a programmed manner. This provided the opportunity to resolve and isolate various reaction steps and study the active intermediates qualitatively and quantitatively.

Experimental

Apparatus

A 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 carbonate by an incipient wetness technique, then dried at room temperature in air and stored under vacuum.

The experiments were conducted in a thermogravimetric reactor system utilizing an electronic microbalance and a quartz downtube reactor that enclosed the sample tray as shown in Figure 1. The reactor was heated by a movable electric furnace with a PID controller. The reactor system also included a gas prepa-

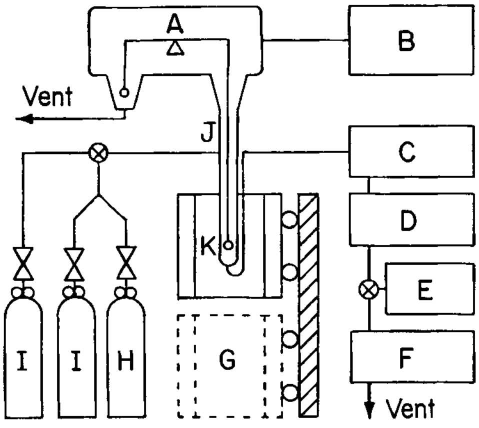

Figure 1. Schematic of the reactor system.
A, electronic microbalance; B, microbalance controller and monitor; C, D, CO/CO_2 infrared analyzers; E, gas chromatograph; F, flow meter; G, electric furnace with PID controller; H, carbon dioxide; I, nitrogen; J, quartz reactor; K, sample tray.

ration section for mixing and metering the feed gas at the desired compositions and flow rates. The reactant gas was a mixture of 15% CO_2/85% N_2. Ultrahigh-purity (UHP) N_2 was used as the purge gas. Typical sample sizes were 20–30 mg. The product gases were analyzed by an on-line gas chromatograph and nondispersive infrared CO and CO_2 analyzers.

The potassium content of the carbon samples was determined by digesting the samples in a mixture of 3HF:1HNO_3:1HCl before analysis by flame emission spectroscopy. The powder x-ray diffraction analysis was conducted utilizing a Siemens D500 unit with a Cu K_α radiation source (λ = 1.57 Å [0.157 nm]). Further details of the experimental equipment are given elsewhere (Talverdian, 1984; Sams et al., 1985).

Procedure

The reaction of potassium carbonate with carbon in a reducing environment was studied in a series of temperature and concentration programmed reaction (TCPR) experiments. In these experiments, the temperature and the reacting gas concentration were varied in such a way as to resolve various stages of the process and especially to separate the catalyst reduction and oxidation steps. To accomplish this, two schedules of heating and reaction were adopted.

Schedule 1 incorporated a gradual increase in temperature (5°C/min) under pure nitrogen with an isothermal period at 800°C prior to gasification. Gasification was begun by switching the feed gas from N_2 to CO_2 following the isothermal period. The purpose of this procedure was to determine the temperature dependence of the desorption reactions.

Schedule 2 involved a rapid, one-step procedure in which the furnace was preheated to 800°C, then raised to enclose it in a pure nitrogen atmosphere. Following complete reduction of the catalyst, the reaction environment was changed by switching the feed gas from pure N_2 to a mixture containing 15% CO_2. The objective of this procedure was to monitor the oxidation and reduction processes isothermally.

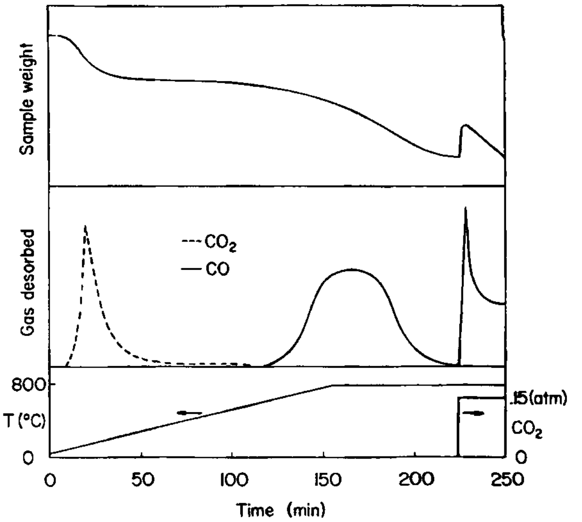

Figure 2. Typical profiles during experiments with slow heating of the sample, schedule 1.
SI conversion: kPa-atm × 101.325.

Results and Discussion

The typical profiles obtained in a TCPR experiment under schedule 1 are shown in Figure 2. This figure gives weight loss and the CO and CO_2 profiles when a sample containing 10.7 wt. % K_2CO_3 was heated to 800°C using schedule 1. At low temperatures (below 200°C), a large CO_2 peak, some water vapor, and a weight loss were observed. Between 200 and 700°C, very little CO, CO_2, or weight loss was detected. At higher temperatures, however, significant amounts of CO were observed. Following the CO peak, the CO_2 reactant mixture was introduced to initiate the gasification process and two important features were observed: a CO overshoot and a weight gain.

Typical results for schedule 2 are given in Figure 3, where the weight loss and the CO and CO_2 profiles are shown for a sample containing 10.7 wt % K_2CO_3. During the initial transient heat-up period, a rapid weight loss was observed that resulted from the desorption of CO_2 and some water vapor. At higher temperatures, CO was the primary product. The CO peak rapidly reached a plateau where the CO generation rate was nearly con-

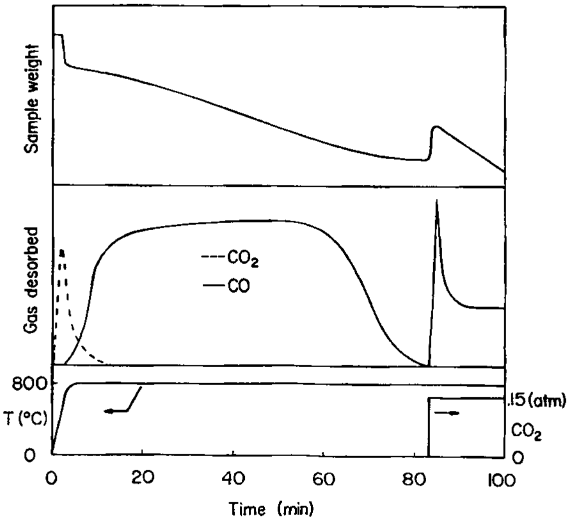

Figure 3. Typical profiles during experiments with rapid heating of the sample, schedule 2.
SI conversion: kPa-atm × 101.325.

stant, and then dropped sharply when the reaction was completed. A CO overshoot and weight gain were also observed at the onset of gasification.

The total amounts of CO and CO_2 obtained during catalyst reduction were independent of the heating schedule. This indicates that the heating method only infuences the rate of desorption and that the amounts of CO and CO_2 desorbed ultimately depend on the initial catalyst concentration.

Mechanism of catalyst reduction

A number of temperature-programmed desorption (TPD) and/or thermogravimetric analysis (TGA) studies have been conducted in recent years to investigate the reduction of alkali metal catalysts on carbon substrates and determine its possible relationship to the reactivity of the carbon substrate. In each study, the catalyzed samples were heated in an inert atmosphere and the desorbed gases and/or the weight changes were continuously monitored as a function of temperature.

The TPD results indicate that various amounts of CO and CO_2 were formed due to the catalyst/carbon interaction. However, no agreement on the location, separation, or relative amounts of CO_2 has been reached. For example, the CO_2 peak has been observed at temperatures below 200°C (Wood et al., 1984), in the 225–800°C range (Kapteijn et al., 1984; Wigmans et al., 1983), and at temperatures above 625°C (Saber et al. 1983, 1984); yet others did not see any significant CO_2 evolution (McKee and Chatterji, 1975, 1978). In one study (Yuh and Wolf, 1984), CO_2 was observed for one substrate but not for another. The common observation from these studies is CO evolution at temperatures above 700°C. Most of these studies were qualitative and none provided a complete oxygen balance.

The present study shows that the first event in the reduction process is the evolution of CO_2 and H_2O below 200°C. Molar quantities of CO_2 and H_2O desorbed during this stage were proportional to the initial catalyst concentration as shown in Figure 4. The amount of CO_2 was calculated by integrating the CO_2 peak. The amount of water was determined by the weight loss results assuming that the weight loss at this temperature was only due to CO_2 and H_2O. The results indicate that for every mole of initial carbonate, one mole of CO_2 and one mole of H_2O are generated.

The unique and stoichiometric dependence of CO_2 and H_2O on the catalyst concentration indicates that the CO_2 and H_2O desorbed were not physisorbed gases. An explanation for this low-temperature process is that the initial potassium carbonate is converted to potassium bicarbonate during the impregnation process and the observed CO_2 and H_2O are the result of the following bicarbonate decomposition reaction:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O \qquad (5)$$

Analysis of the unheated impregnated samples by powder x-ray diffraction confirmed the existence of potassium bicarbonate. The formation of bicarbonate may also explain the results of Wood et al. (1984), who observed CO_2 and H_2O desorption below 200°C.

The low-temperature decomposition of bicarbonate was followed by a stage (200–700°C) where only small amounts of CO_2 were desorbed. The next significant reaction stage is the high-temperature desorption of CO. The total amount of CO generated in this stage is shown in Figure 5, where the CO/C ratio is given as a function of the initial K/C ratio. For all catalyst loadings, three moles of CO were detected for each mole of potassium carbonate originally present, suggesting complete reduction of carbonate.

The overall stoichiometric ratio of three moles of CO for each mole of K_2CO_3 is in agreement with the results reported by McKee and Chatterji (1975, 1978) and Yuh and Wolf (1984). They reported this ratio for the alkali metal carbonate reduction on graphitic carbons and suggested the following carbothermal reduction reaction:

$$M_2CO_3 + 2C = 2M + 3CO \qquad (6)$$

In contrast, Wigmans et al. (1983) and Cerfontain and Moulijn (1983a) have reported separate CO and CO_2 peaks and

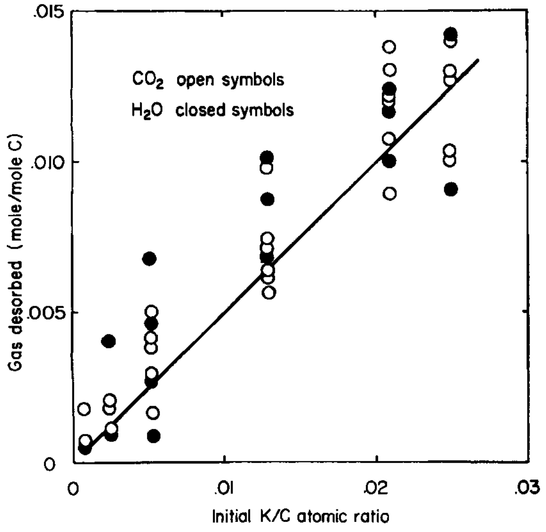

Figure 4. CO_2 and H_2O desorbed during the early stage of catalyst reduction.
—— $CO_2/K = H_2O/K = \frac{1}{2}$.

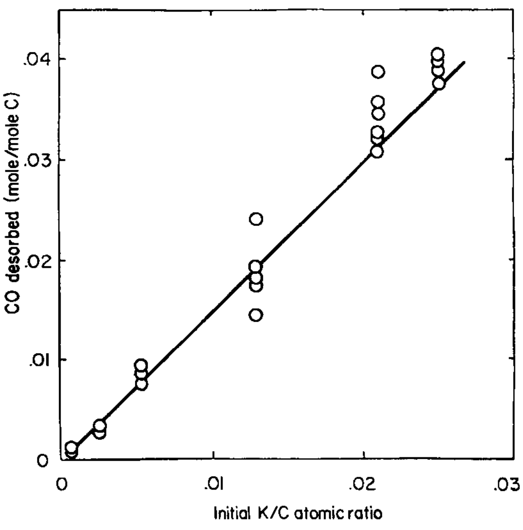

Figure 5. CO desorbed during complete reduction of the catalyst.
—— $CO/K = \frac{3}{2}$.

attributed them to a two-step reduction process:

$$M_2CO_3 = M_2O + CO_2 \qquad (7)$$

$$M_2O + C = 2M + CO \qquad (8)$$

It is interesting to note that in the above-cited studies those reporting primarily CO used graphitic substrates. This is in agreement with our data, which are also for a graphitic sample. The dependence of the product distribution on the substrate can be through various factors. For example, certain substrates may catalyze CO_2 generation. Another important factor is the amount and the nature of chemisorbed and/or indigenous oxygen in the initial samples, which could be the source of CO_2. Our uncatalyzed carbon samples did not give off significant amounts of CO or CO_2 when heated to high temperatures in an inert atmosphere, indicating they were free of chemisorbed oxygen.

Based on our results, the following mechanism is suggested for the reduction of the carbonate on the surface:

$$K_2CO_3 \overset{C}{=} (\text{—}CO_2K) + (\text{—}COK) \qquad (9)$$

$$(\text{—}CO_2K) + C = (\text{—}CK) + CO_2 \qquad (10)$$

$$(\text{—}CO_2K) + C = (\text{—}COK) + CO \qquad (11)$$

$$(\text{—}COK) + C = (\text{—}CK) + CO \qquad (12)$$

$$(\text{—}CK)_{(s)} = K_{(g)} \qquad (13)$$

where —CO_2K, —COK, and —CK represent the fully oxidized, the partially reduced, and the completely reduced surface groups, respectively. In reaction 9, carbonate decomposes on carbon sites to form surface oxides. These oxides are believed to be the carboxylic $(\text{—}C\lesssim^{O}_{OK})$ and phenolic (—C—OK) groups observed in most IR studies.

This mechanism is obviously different from that given by reaction 6. However, it gives the same overall CO to K_2CO_3 ratio, which is in agreement with our data and those of McKee and Chatterji (1975, 1978) and Yuh and Wolf's study (1984), which utilized a graphitic substrate. The first reaction may proceed at temperatures as low as 250°C and can be completed before any significant reduction of catalyst or CO evolution takes place. Reaction 10 was negligible in our experiments, probably due to the graphitic sample but other substrates may catalyze this reaction as previously discussed. Reaction 13 is given to represent the vaporization of the potassium from the carbon surface. This is in agreement with the observation that catalyst reduction is necessary before rapid loss by vaporization (Shadman et al., 1984; Sams et al., 1985).

An important observation shown in Figure 3 is the region where the CO generation rate is almost constant for the samples with a catalyst concentration high enough to saturate the surface. These samples exhibited CO production rates independent of the initial K/C ratios. This plateau phenomenon suggests that catalyst reduction requires intimate contact with the surface and that the rate of catalyst reduction is limited by the available surface area.

Mechanism of catalyst oxidation

After complete reduction, the catalyst is in the completely reduced form, —CK. Introduction of CO_2 oxidizes the catalyst and initiates the gasification process. As shown in Figures 2 and 3, two important features were observed at the onset of gasification: a weight gain and a CO overshoot. The weight gain is a result of the rapid oxygen uptake due to the catalyst/CO_2 interaction. The excess CO, which produces the overshoot, is the by-product of the initial oxidation of the —CK surface groups. The results indicate that catalyst oxidation is much faster than the gasification rate that takes place simultaneously. That is why the initial system response can be used to analyze the catalyst oxidation as the primary process.

The oxygen uptake for the oxidation of the completely reduced groups, —CK, can be evaluated both from the total area of the CO overshoot peak and from the weight gain observed shortly after the introduction of CO_2 feed. By comparing the oxygen uptake with the amount of catalyst present at the onset of gasification, the stoichiometry of catalyst oxidation can be determined. However, unlike the CO_2 or CO generation steps during catalyst reduction, which are related to the initial catalyst concentration, the size of the weight gain and CO overshoot are directly related to the catalyst concentration at the onset of the gasification stage. This concentration is different from the initial loading because of catalyst loss during the reduction stage. The results are shown in Figure 6, where the oxygen uptake per atom of carbon is plotted as a function of the corresponding K/C ratio. The results show a good agreement between the oxygen calculated for the CO overshoot and that from the weight gain. Moreover, the slope of the line in Figure 6 indicates that the oxygen to potassium atomic ratio is 2 in the fully oxidized form of surface complex.

Based on these results and the reactions suggested for the catalyst reduction, the following mechanism is suggested for the catalyst oxidation:

$$(\text{—}CK) + CO_2 = (\text{—}COK) + CO \qquad (14)$$

$$(\text{—}COK) + CO_2 = (\text{—}CO_2K) + CO \qquad (15)$$

The weight gain and CO overshoot indicate that these reactions are very fast compared to the reduction reactions, 11 and 12.

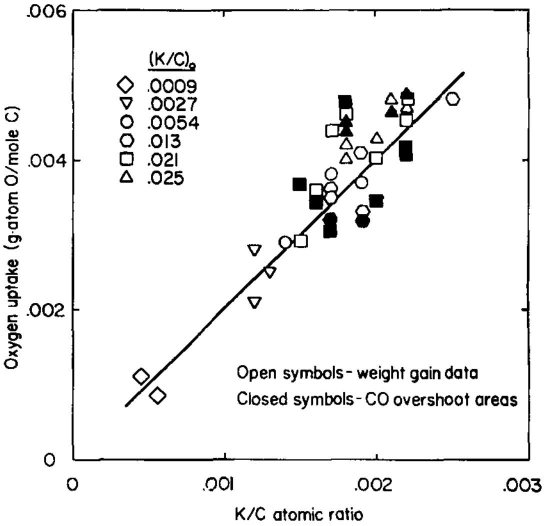

Figure 6. Oxygen uptake during the oxidation of the completely reduced catalyst.

—— O/K = 2.

This suggests that the fully oxidized form of the catalyst, $—CO_2K$, is dominant at 800°C.

Kapteijn and Moulijn (1983a,b), Cerfontain and Moulijn (1983b), and Moulijn et al. (1984) have studied the oxidation of the catalyst at the onset of gasification and report a weight gain and CO overshoot similar to ours. By integrating the area of CO overshoot, Cerfontain and Moulijn (1983b) report that the catalyst is oxidized to a degree such that $0.5 < CO/K < 1.0$. Qualitatively, these results are in general agreement with ours; however, quantitatively the agreement is poor. The discrepancy may be due to the fact that they neglected the catalyst loss in determining the potassium concentration at the onset of gasification. Our results indicate that the potassium loss especially during TPD experiments is significant and could be the source of many discrepancies in the literature data (Shadman et al., 1984; Sams et al. 1985).

Mechanism of catalytic gasification

The mechanism of catalytic carbon gasification by CO_2 can be explained by a redox mechanism involving a combination of the oxidation and the reduction reactions previously suggested. Therefore, the following sequence is suggested for the gasification process after the initial rapid transient stage is over:

$$(—CO_2K) + C = (—COK) + CO \qquad (11)$$

$$(—COK) + CO_2 = (—CO_2K) + CO \qquad (15)$$

The complete reduction of the catalyst to —CK by reactions 10 or 12 in an oxidizing atmosphere at 800°C is not likely. This is based on the fact that reactions 10 and 12 are much slower than reaction 14 and do not take place appreciably during gasification. The sharp overshoot peak supports the assumption that reaction 14 is very fast. Moreover, the fact that catalyst loss under oxidizing (gasification) conditions is much slower than that under reducing conditions (Shadman et al., 1984; Sams et al., 1985) supports the idea that the completely reduced form, —CK, is not present to an appreciable degree during gasification. The fast rate of oxidation also suggests that the rate-limiting step in the overall process is the reduction of the oxidized surface group, $—CO_2K$, via reaction 11.

It is well established that the presence of CO reduces the observed rate of gasification. This inhibition effect can be explained by reactions 11 and 15. As discussed before, reaction 15 is fast and approaches equilibrium while reaction 11 is the rate-limiting step. The presence of CO shifts the equilibrium of reaction 15 to the left and lowers the concentration of the oxidized surface sites, $—CO_2K$. This lowers the observed rate of the overall reaction.

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