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The Catalyzed Graphite–Water Vapor Reaction—Isotopic Studies using $Ba^{13}CO_3$

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The mechanism of the catalytic effect of barium carbonate on the steam gasification of carbon was investigated by adding $Ba^{13}CO_3$ to pure graphite and measuring the kinetics and products of the reaction with water vapor as functions of temperature. The onset of the catalyzed reaction at around 800°C was accompanied by the appearance of ^{13}CO and $^{13}CO_2$ in the gas phase. When $Ba^{13}CO_3$ and graphite were heated together in an inert atmosphere, small amounts of $^{13}CO_2$ were evolved above 600°C and copious amounts of ^{13}CO and $^{13}CO_2$ above 900°C. Graphite catalyzed the decomposition of the $BaCO_3$ at low temperatures as the dissociation of pure $BaCO_3$ was very slow below 1000°C. The catalytic effect of the salt in the gasification reaction could be interpreted in terms of a sequential series of reaction steps involving decomposition of the carbonate to oxide, followed by regeneration of the carbonate phase by reaction with the gaseous environment.

INTRODUCTION

The carbonates and oxides of the alkali and alkaline earth metals are well known as active catalysts for the steam gasification of carbonaceous materials (*1*, *2*). The extensive literature includes well-documented reports of the catalytic effects of alkalies in the gasification of coal (*3*, *4*), char (*5*, *6*), graphite (*7*, *8*), wood (*9*), and even urban refuse (*10*). This subject is obviously of considerable current interest for the production of useful energy both from fossil fuels and solid wastes. However, the role played by the alkali additives in accelerating the formation of gaseous products or in reducing the temperature required for a given rate of conversion is not clearly understood. Recent detailed studies of the catalytic behavior of salts of the Group IA alkali metals (*6*) and the Group IIA alkaline earths (*7*) suggest that the inorganic additive passes through a series of sequential transformations with oxide or hydroxide being formed as an active intermediate during the gasification reaction. However, evidence for the exact pathways involved in the catalytic processes remains somewhat indirect and most proposed reaction schemes have been based on thermodynamic reasoning.

In the present investigation, an attempt has been made to unravel the steps of the catalyzed steam gasification reaction, using pure [^{12}C]graphite doped with a ^{13}C-labeled barium carbonate catalyst. It was hoped that analyses of the isotopic composition of the product gases during the reaction would provide useful information on the elementary steps involved in the catalytic process.

EXPERIMENTAL

The high-purity graphite powder used in

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this study was obtained from the Ultra Carbon Corporation (325 mesh, type UCP-2) and contained only trace amounts (<5 ppm) of Si and Mg impurities. This material had an initial surface area of 7.5 $m^2 \cdot g^{-1}$, as determined by nitrogen adsorption at −195°C, using a flow-type surface area analyzer (Micromeritics model 2100D). The ^{13}C-labeled barium carbonate used as a catalyst was obtained from Bio-Rad Laboratories, Richmond, Calif. and contained 58.25 at.% ^{13}C. Samples of this salt, subsequently referred to as $Ba^{12,13}CO_3$, were finely ground in an agate mortar and then thoroughly mixed with weighed amounts of the graphite in a Fisher minimill.

Measurements of the kinetics of the gasification reaction and analyses of the gaseous products were made in an automatically recording thermobalance (Mettler thermoanalyzer TA-2), coupled to a mass spectrometer sampling system, as shown schematically in Fig. 1. In a typical experiment, 200 mg of the $Ba^{12,13}CO_3$-doped graphite was placed in a thin-walled alumina crucible which was then mounted in contact with the Pt/Pt–10% Rh measuring thermocouple of the balance. A constant flow of helium (Linde, ultrahigh-purity grade) was passed through a bubbler containing distilled water at 25°C to give a partial pressure of water vapor in the gas stream of 23 Torr (3.1 kPa) and then into the quartz furnace surrounding the crucible and contents. The balance case was filled with a positive pressure of pure dry helium throughout the experiments. During gasification, weight losses of the doped graphite sample were continuously recorded with an accuracy of ±20 μg as a function of sample temperature. The latter was either increased linearly at a rate of 10°C · min^{-1} or held at a series of constant temperatures between 700 and 1100°C. In all cases, the total weight loss of the sample was kept below 10%, to minimize the effects of changing surface area and catalyst concentration.

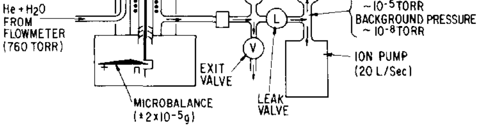

FIG. 1. Schematic diagram of thermal analysis–mass spectroscopy apparatus used for kinetic measurements.

During the course of the reaction, exit gases from the furnace were passed via a flexible bellows coupling to an ultrahigh-vacuum system, comprising an ion pump, capacitance manometer, and quadrupole mass spectrometer. Initial evacuation of the system was achieved with a zeolite trap cooled in liquid nitrogen. Subsequent pumping by the ion pump effectively reduced the background pressure to 10^{-8} Torr in the sampling system. After passage through a variable leak valve, the gas products were analyzed with the mass spectrometer. The complete scan of mass peaks 2–55 amu required about 1 min. Drifts in the sensitivity of the mass spectrometer were avoided by using a Faraday cup collector rather than an ion multiplier. The delay time required for passage of the 50 $cm^3 \cdot min^{-1}$ gas stream from furnace to mass spectrometer was approximately 2 min.

Typical mass spectra of product gases during gasification of the $Ba^{12,13}CO_3$-doped graphite, and an analysis of the flowing gas stream before the onset of the reaction, are illustrated in Fig. 2. Peaks arising from ^{13}C species of CO and CO_2 (amu = 29,45) could be clearly distinguished. However, because of the variable sensitivity of the mass spectrometer to peaks of different mass and the low pumping efficiency of the ion pump for helium, no attempt was made to calibrate individual peaks to the partial pressures of the components. Rather, spectra were normalized with respect to the helium (amu = 4) peak and changes in the normalized amplitudes of the other mass peaks were compared as the furnace temperature was

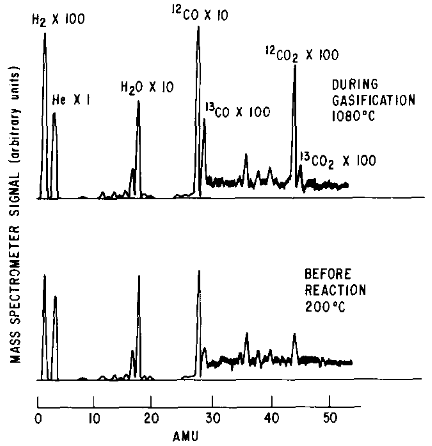

FIG. 2. Typical mass spectra of gas-phase composition from TGA apparatus before and during the catalyzed gasification reaction.

increased at a linear rate. This qualitative procedure gave good reproducibility in duplicate experiments. Also, because of the ubiquitous occurrence of the shift equilibrium ($H_2O + CO \rightleftharpoons H_2 + CO_2$) at elevated temperatures, measurable amounts of CO_2 were always found in the product gases when water vapor was present.

RESULTS

In order to assess the magnitude of the catalytic effects resulting from the addition of barium carbonate to graphite, measurements of overall gasification rate in water vapor ($P_{H_2O} = 23$ Torr, $50\ cm^3 \cdot min^{-1}$) were made at a series of constant temperatures between 700 and 1100°C, both with pure graphite and with graphite doped with 10% by weight $Ba^{12,13}CO_3$. Figure 3 shows Arrhenius plots of weight loss rate ($mg \cdot min^{-1}$) versus reciprocal temperature for these two materials. Data for two separate experiments involving different samples are included in each series of measurements and the reproducibility of the kinetic parameters was generally very satisfactory. The weight loss rates were observed to be accurately constant with time for periods of at least 20 min at each temperature and reproducible on successive thermal cycles. Hence, these data represent the steady-state kinetics of the catalyzed gasification of the graphite rather than irreversible weight changes resulting from salt decomposition or equilibration. Addition of the salt to the graphite resulted in a reduction in apparent activation energy from 68.3 to 46.9 $kcal \cdot mole^{-1}$ and, at a typical temperature of 900°C, the presence of the salt increased the overall gasification rate by nearly two orders of magnitude.

As it was conceivable that the results shown in Fig. 3 might reflect some decomposition of the salt phase at the higher temperatures, a study was made of the thermal stability and gaseous decomposition products evolved from the $Ba^{12,13}CO_3$ salt on heating in water vapor as a function of time and temperature. Figure 4 summarizes the results of a series of measurements of weight loss rates and analyses of the gaseous species formed on heating a 100-mg sample of $Ba^{12,13}CO_3$ in the helium–water vapor steam during a programmed temperature rise of $10°C \cdot min^{-1}$. The total weight of the salt in this case was five times that used in the subsequent catalysis experiments. Figure 4 shows the mass spectrometer signal produced by the four species,

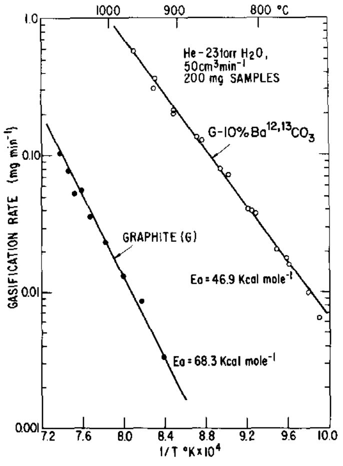

FIG. 3. Effects of barium carbonate catalyst on reactivity of graphite. Gasification rates in water vapor vs $1/T$°K for pure graphite and graphite–10% $Ba^{12,13}CO_3$.

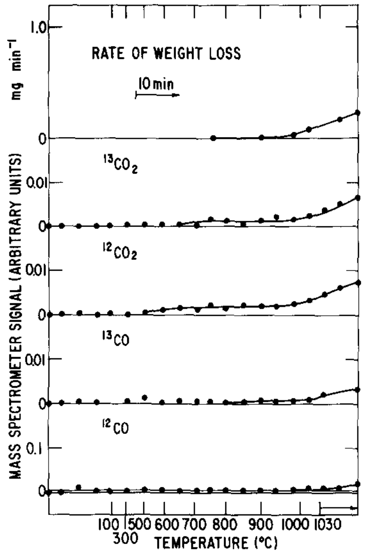

FIG. 4. Rate of weight loss and gas product distribution on heating 100 mg $Ba^{12,13}CO_3$ in water vapor at 10°C · min^{-1}.

^{12}CO, ^{13}CO, $^{12}CO_2$, and $^{13}CO_2$ and the corresponding rate of weight loss of the salt as a function of temperature. Below 950°C decomposition of the salt was barely detectable by weight loss, but minor amounts of $^{12}CO_2$ and $^{13}CO_2$ were identified in the gas stream at temperatures as low as 700°C. Above 950°C, the salt began to lose weight at a measurable rate. These losses were due primarily to dissociation of the carbonate rather than vaporization, as shown by the increasing amounts of CO_2 which appeared in the gas phase. Roughly equal concentrations of $^{13}CO_2$ and $^{12}CO_2$ were produced at these higher temperatures, as expected from the isotopic ratio of $^{13}C/^{12}C$ (~ 1.4) in the labeled salt. Only very small amounts of ^{13}CO and ^{12}CO were detected in the products at the highest temperature attained (1030°C) and the CO products may have been due to a CO^+ fragment produced from CO_2 in the mass spectrometer ion source. The course of the decomposition reaction of the salt may therefore by assumed to be,

$$Ba^{12}CO_3 = BaO + {}^{12}CO_2$$

and

$$Ba^{13}CO_3 = BaO + {}^{13}CO_2.$$

However, the overall rate of decomposition of the salt was very small (0.1% · min^{-1} at 1000°C).

The results of a typical experiment on the catalyzed gasification of graphite are summarized in Fig. 5. In this case, the sample was graphite doped with 10 wt% $Ba^{12,13}CO_3$, heated at an increasing temperature of 10°C · min^{-1} in the He–H_2O stream. Three distinct temperature regimes could be distinguished. Below 600°C, no weight loss of the sample nor gaseous products could be detected and the gasification reaction was apparently immeasurably slow in this range. Between 600 and 900°C, a slow weight loss occurred, accompanied by the appearance of small quantities of gasification products (H_2 and $^{12}CO_2$). A slight decomposition of the salt must have been taking place in this temperature range, as evidenced by the appearance of minor amount of $^{13}CO_2$. Above 900°C, the catalyzed gasification reaction occurred at a rate which increased rapidly with increas-

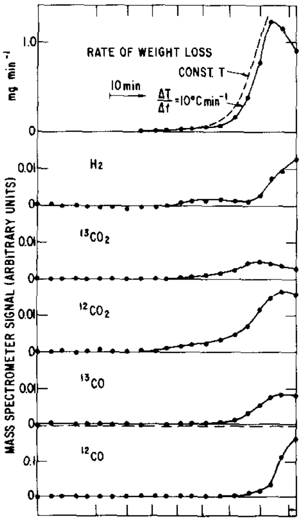

FIG. 5. Rate of weight loss and gas product distribution on heating 200 mg graphite + 20 mg $Ba^{12,13}CO_3$ in water vapor at 10°C · min^{-1}.

ing temperature. The broken curve in Fig. 5 shows the rate of weight loss measured at constant temperatures in the experiments used to deduce the Arrhenius behavior (Fig. 3). The agreement between the temperature-programmed experiment of Fig. 5 and the steady-state kinetic experiments of Fig. 3 is satisfactory, and indicates that transient salt decomposition and equilibration during heating was insignificant compared with graphite gasification above 900°C. In this temperature range, species arising from the graphite (^{12}CO, $^{12}CO_2$) were evolved together with labeled species (^{13}CO, $^{13}CO_2$) from the salt phase, but much of the CO_2 and some of the H_2 probably originated from the shift reaction between the initially formed CO and water vapor. As expected, ^{12}CO was the major gaseous product formed during the gasification of the graphite. At the highest temperatures (>1000°C), the overall rate of the reaction and the ^{13}C products diminished as the graphite substrate gasified and lost physical contact with the salt particles. This pattern of behavior was repeated in several duplicate experiments with different $BaCO_3$-doped graphite samples; in no case were methane or other hydrocarbons detected in the gaseous products of the catalyzed reaction with water vapor.

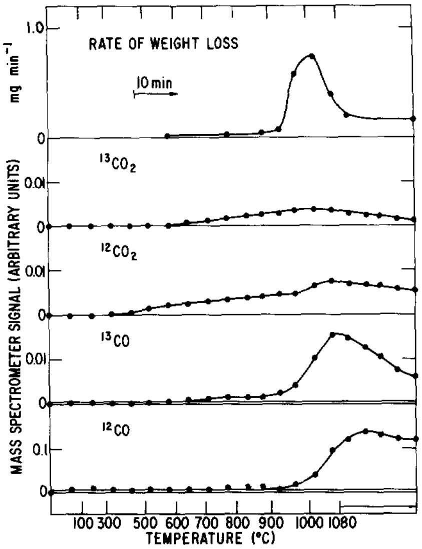

FIG. 6. Rate of weight loss and gas product distribution on heating 200 mg graphite + 20 mg $Ba^{12,13}CO_3$ in dry helium at 10°C · min^{-1}.

The occurrence of solid-state reactions between $BaCO_3$ and the graphite was investigated by heating the two phases together in a stream of dry helium. Figure 6 shows the distribution of gaseous reaction products and weight loss data for the case of a sample of graphite doped with 10% $Ba^{12,13}CO_3$ and heated at an increasing temperature of 10°C · min^{-1} in this inert atmosphere. Analysis of the evolved gases showed that between 600 and 900°C, both $^{13}CO_2$ and $^{12}CO_2$ were formed. By comparison with the results obtained with pure $BaCO_3$ (Fig. 4) and allowing for the fivefold ratio in mass of the $BaCO_3$ used in the two experiments, the rate of evolution of CO_2 was approximately ten times greater in the presence of graphite. At temperatures of 900°C and above, a rapid weight loss was observed and simultaneously ^{12}CO and ^{13}CO appeared in the gas phase. It is likely that some gasification of the graphite occurred as a result of reaction with CO_2 produced from the graphite-catalyzed salt decomposition,

$$^{12}CO_2 + {}^{12}C\text{ (graphite)} = 2\ {}^{12}CO$$

and

$$^{13}CO_2 + {}^{12}C\text{(graphite)} = {}^{12}CO + {}^{13}CO.$$

However, because of the absence of water vapor and the secondary shift reaction, the CO_2 content of the gas phase remained small compared to the results shown in Fig. 5 and CO was the major gaseous product at temperatures of 1000°C and above. The approximately equal amounts of $^{12}CO_2$ and $^{13}CO_2$ produced at these temperatures suggest that, as in Fig. 4, most of the CO_2 was formed from the decomposition of the salt,

$$Ba^{12}CO_3 = BaO + {}^{12}CO_2$$

and

$$Ba^{13}CO_3 = BaO + {}^{13}CO_2.$$

However, the concentrations of CO_2 produced per unit weight of $BaCO_3$ near 1000°C were larger than for pure $BaCO_3$ by a factor of 10–20, indicating that the presence of the graphite had accelerated the decomposition of the salt. This was confirmed by the observation that at 1000°C, the rate of fractional weight loss was about 40 times greater for the $BaCO_3$–graphite mixture than for pure $BaCO_3$. The total weight loss (11.6 mg) during the experiment shown in Fig. 6 was greater than expected for the reactions,

$$BaCO_3 + C = BaO + 2CO \ (5.6 \text{ mg})$$

and

$$BaCO_3 = BaO + CO_2 \ (4.4 \text{ mg})$$

probably because some graphite was gasified by CO_2 evolved from the decomposing salt.

The catalytic effect of the carbonaceous phase on the decomposition of the salt was investigated further by measuring the decomposition pattern of a large (100 mg) sample of $Ba^{12,13}CO_3$ containing a small (10 mg) addition of graphite. Figure 7 shows the evolution of gaseous products and weight loss rates of this mixture on heating in water vapor. Comparison with Fig. 4 indicates that decomposition of the salt to give $^{12}CO_2$ and $^{13}CO_2$ in about equal amounts was much more rapid between 600 and 900°C in the presence of graphite than with pure $BaCO_3$. Thus, not only did the salt catalyze the gasification of the graphite between 600 and 900°C but the graphite catalyzed the decomposition of the salt in the same temperature range. Above 800°C, ^{12}CO, ^{13}CO, and H_2 became major components of the gas phase; in addition, the shift reaction contributed to increased CO_2 concentrations at the higher temperatures. The rate of weight loss and the evolution of CO and H_2 eventually diminished on heating at 1080°C as the graphite became depleted. In this case, the total weight loss (19.1 mg) was less than that expected for the reactions,

$$BaCO_3 + C = BaO + 2CO \ (28 \text{ mg})$$

and

$$BaCO_3 = BaO + CO_2 \ (22 \text{ mg}).$$

Hence, decomposition of the salt and gasification of the graphite were not completed in the duration of the experiment.

It appears unlikely that appreciable amounts of ^{12}CO were evolved from the reactor surfaces during these experiments, as in the absence of graphite very little CO was produced (Fig. 4). The preponderance of ^{12}CO in Figs. 6 and 7 must be due to the presence of ^{12}C(graphite) in each case. Processes such as,

$$^{12}C(\text{graphite}) + {}^{13}CO = {}^{13}C(\text{graphite}) + {}^{12}CO$$

and

$$^{12}C(\text{graphite}) + {}^{13}CO_2 = {}^{13}CO + {}^{12}CO$$

may help to augment the proportion of ^{12}CO in these experiments.

DISCUSSION

Many alkaline earth salts, as exemplified in the present case by barium carbonate,

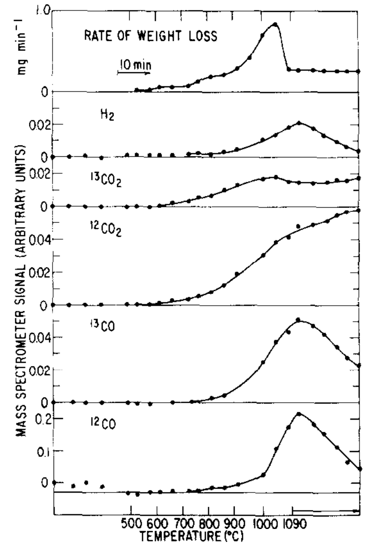

FIG. 7. Rate of weight loss and gas product distribution on heating 100 mg $Ba^{12,13}CO_3$ + 10 mg graphite in water vapor at 10°C · min^{-1}.

are active catalysts for the carbon–H_2O reaction. This experimental study has shown that the salt particles not only provide sites for enhanced reactivity on the carbon surface, but also actively participate in the gasification process by undergoing a series of sequential reactions with the carbon substrate and with the components of the gaseous environment. The net effect (Fig. 3) of the salt addition is a dramatic acceleration in the overall rate and a lowering of the apparent activation energy of the reaction.

Comparison of the observed rates for the catalyzed graphite–H_2O and graphite–CO_2 reactions (*11*) shows that whereas the reaction of pure graphite with water vapor is faster than the reaction with CO_2 by a factor of about 5, in the presence of added $BaCO_3$ the rates are very similar for the two catalyzed reactions, suggesting that the same rate-determining step is operating in each case.

The initial step in the sequence appears to be the reaction of the carbonate phase with the graphite substrate,

$$BaCO_3 + C = BaO + 2CO. \qquad (1)$$

The present study, using $BaCO_3$ additive labeled with ^{13}C, has demonstrated that ^{13}CO from the carbonate is formed during the catalyzed gasification reaction at 900°C and above, whereas in the absence of graphite, decomposition of the salt by direct dissociation,

$$BaCO_3 = BaO + CO_2 \qquad (2)$$

is very slight at these temperatures.

The equilibrium stability regions of $BaCO_3$ and BaO as functions of P_{CO}, P_{CO_2}, and temperature are shown in Fig. 8, as calculated from the free energies of reactions (1) and (2). These curves, which were derived assuming unit activity of the solid phases, give only a qualitative indication of the phases likely to be present under a given set of conditions. Mutual solid solubility would broaden the stability boundaries and, as the free energies depend on particle size, with highly dispersed salt particles the reactions could occur at substantially lower temperatures than indicated from the bulk thermodynamic properties. Nevertheless, the solid curve of Fig. 8 indicates that reduction of $BaCO_3$ to BaO by reaction of carbon is possible over a wide range of P_{CO} and temperature and the experimental data shown in Figs. 5–7 confirm that appreciable amounts of ^{13}CO are evolved on heating $Ba^{13}CO_3$ with graphite at temperatures of 900°C and above. The broken curve of Fig. 8 indicates that the direct decomposition of $BaCO_3$ to give BaO via reaction (2) may on thermodynamic grounds occur only at substantially higher temperatures for a given gas-phase pressure of CO_2 identical to the CO pressure involved in the reaction of $BaCO_3$ and C. However, the production of CO_2 in the experiments shown in Figs. 6 and 7 suggests that the rate of decomposition of the $BaCO_3$ was accelerated catalytically by the presence of the graphite, even at temperatures as low as 700°C. It may be noted that a similar catalytic effect has recently been reported for the case of potassium carbonate (*12*). On heating in contact with coal, K_2CO_3 apparently decomposed, liberating CO_2 at temperatures in the range of 500–700°C, even though the pure salt is stable to

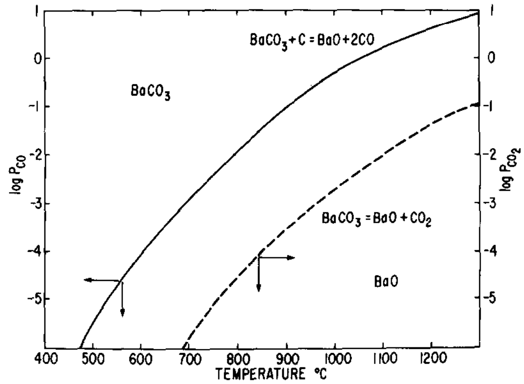

FIG. 8. Equilibrium stability regions of $BaCO_3$ and BaO corresponding to the reactions, $BaCO_3$ + C = BaO + 2CO (solid curve) and $BaCO_3$ = BaO + CO_2 (broken curve), as functions of P_{CO}, P_{CO_2} (atm) and temperature.

much higher temperatures. In the present series of experiments, it therefore appears probable that the active catalytic phase present on the graphite surface during the gasification reaction is BaO formed by both reaction (1) and the graphite-catalyzed reaction (2).

Previously reported thermogravimetric experiments (*7*) have shown that alkaline earth oxides, such as BaO or SrO, react readily with a gas mixture containing both H_2O and CO in the range 700–950°C, the most likely sequence of reactions being, for Ba,

$$BaO + H_2O = Ba(OH)_2 \qquad (3)$$

and

$$Ba(OH)_2 + CO = BaCO_3 + H_2. \qquad (4)$$

$Ba(OH)_2$ may have only a transitory existence at these temperatures but the surface of the BaO particles may provide sites for the dissociation of H_2O molecules adsorbed from the gas phase, the overall reaction resulting from the sequence of reactions (1) → (3) → (4) being,

$$C + H_2O = CO + H_2.$$

The graphite-catalyzed $BaCO_3$ decomposition reaction (2) also contributes some CO_2 to the gas products and the concentration of CO_2 is further enhanced by the shift reaction,

$$CO + H_2O = CO_2 + H_2$$

which probably approaches equilibrium under the conditions of these experiments. It may be noted that although potassium carbonate deposited on coal char has been claimed (*4*) to catalyze the methanation reaction, $2CO + 2H_2 = CH_4 + CO_2$, no methane or other hydrocarbons could be detected in the gaseous products in the present series of experiments. However, the equilibrium concentration of CH_4 would be very small under the conditions used in this study.

This work has demonstrated the effectiveness of thermogravimetry coupled with mass spectrometry and selective isotopic labeling for studying the nature of catalytic processes and solid-state reactions. Investigations of this type form a sound fundamental basis for future spectroscopic studies of reaction intermediates at the interface between solid phases which mutually interact chemically to yield favorable sites for gasification reactions.

ACKNOWLEDGMENT

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