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Carbon Dioxide Gasification of Carbon Black: Isotope Study of Carbonate Catalysis

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Temperature-programmed reaction was used with labeled isotopes (^{13}C and ^{18}O) to study interactions between carbon black and potassium carbonate in pure He and 10% CO_2/90% He atmospheres. Catalytic gasification precursor complexes were observed. Carbon and oxygen-bearing carbon surface groups interacted with the carbonate above 500 K to form surface complexes. Between 500 and 950 K, and in the presence of gaseous CO_2, the complexes participated in C and O exchange with the gas phase while oxygen atoms within the complexes also exchanged wtih those on the carbon surface. As the temperature rose, the complexes decomposed, with CO_2 the initial product. Decomposition started around 500 K in pure He, and around 950 K in CO_2/He. Catalytic gasification began only after decomposition of significant portions of the complexes. Elemental potassium formed, and the active catalyst appears to alternate between being potassium metal and a potassium–oxygen–carbon complex. Potassium carbonate is not part of the catalytic cycle.

INTRODUCTION

Alkali-metal carbonates are effective catalysts for both steam and carbon dioxide gasification of carbon (e.g. (*1, 2*)). The mechanisms of these catalytic reactions are not well understood, but there are indications that the reactions proceed through oxygen-transfer processes. The catalysts appear to undergo cyclical, but simultaneous, reduction–oxidation reactions on the carbon surface (e.g. (*3*)). To test this idea of oxygen transfer, the interactions of carbon black and isotopically labeled potassium carbonates were studied in helium and in helium/carbon dioxide atmospheres. By labeling the carbon and oxygen of the carbonate in separate experiments, the reaction pathways of each can be followed. Temperature-programmed reaction (TPR) (*4*) with mass-spectrometric detection was used to separate the reaction steps in time (and temperature). In our experiments, mixtures of carbon and potassium carbonate were heated to about 1250 K at a rate of 1 K/s. This work is an extension and elaboration of some preliminary studies (*5, 6*).

The CO_2–carbon reaction was chosen because it is an important reaction in combustion processes, steam gasification, and many other areas. It exhibits effects probably typical of other catalyzed carbon-gasification reactions. In addition, it has the advantages of having no side reactions and allowing simple control of the experimental system. Carbon black was chosen as a model for coal char; similar catalytic gasification rates have been observed on chars and carbon blacks (*10*).

EXPERIMENTAL METHODS

Several reaction systems were studied, but the setup and technique were similar for all. In most runs, 10 mg of 60–80 mesh potassium carbonate, containing either ^{13}C or ^{18}O, were intimately mixed with 100 mg carbon black. The mixture was supported on a fritted quartz disk in an 8-mm-o.d. quartz downflow reactor. The sample was outgassed for 30 min at 4 Pa and 500 K. After

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cooling to 300 K, either pure He or 10% CO_2/90% He was passed through the mixture at 80 cm^3/min. While the gas was flowing, the reactor was heated with an electric furnace at 1 K/s to about 1250 K and later cooled to 300 K. In one experiment, carbon black with no carbonate added was heated in 10% CO_2/90% He to study the uncatalyzed reaction.

A quadrupole mass spectrometer, located immediately downstream from the reactor, continuously analyzed the reactor effluent. A micro-minicomputer system recorded five mass peaks and the temperature simultaneously. The carbonate was depleted of isotopic tracer during a single TPR experiment, and only one experiment was carried out on an individual sample. Devitrification (crystallization) of the quartz, an indication of the presence of an elemental alkali metal (*7*), was observed in most runs. As a result, the reactor walls became brittle, and a new reactor was used for each experiment.

The experimental apparatus was similar to one described in the literature (*4*). A special reactor and furnace were used to obtain the high temperatures needed in this study. A temperature programmer used the voltage signal from a 0.25-mm-diameter thermocouple, whose tip was centered in the reaction mixture, to control the furnace temperature. A Tylan mass flow controller maintained constant gas flow rates. The UTI mass spectrometer was located in a UHV chamber that was pumped by a turbomolecular pump. The mass spectrometer was calibrated daily by injecting CO and CO_2 pulses into the gas stream. The carbon dioxide cracking fraction at mass 28 and the concentrations of naturally occurring isotopes were subtracted from the appropriate signals in all data presented.

Materials

Sterling RX-76 carbon black (Cabot Corporation), an oil-based black, was specified as containing 0.5% ash, 1.5% sulfur, 0.5–1.0% oxygen, and ppm of heavy metal (*8*). Research-grade, isotopically labeled potassium carbonates (Prochem) were used; according to the supplier, 90% of the carbon in the $K_2{}^{13}CO_3$ was ^{13}C and 71.5% of the oxygen in the $K_2C^{18}O_3$ was ^{18}O.

The helium was UHP grade from Scientific Gas Products (99.999%) and was purified further by a Hydrox purifier and a 4A sieve trap in liquid nitrogen. The 10% CO_2/90% He was a mixture of UHP gases (Scientific Gas Products) and the composition was verified. The carbon dioxide calibration gas was UHP grade (99.995%, Scientific Gas Products). Carbon monoxide calibration gas was CP grade (99.5%, Matheson).

RESULTS

Whenever a carbon or oxygen is mentioned without the isotopic prefix, it refers to ^{12}C or ^{16}O, e.g., K_2CO_3 means potassium carbonate containing only ^{12}C and ^{16}O. Only when desirable for clarity are the normal isotopes identified. When the labeled isotopes appear, they are specified as such, i.e., ^{13}C and ^{18}O.

Potassium Carbonate and Carbon in Helium

When a mixture of 10 mg $K_2{}^{13}CO_3$ and 100 mg carbon black was heated in pure helium, carbonate decomposition began

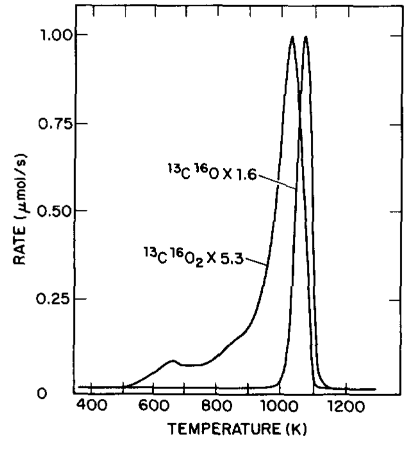

FIG. 1. ^{13}C TPR spectra for a mixture of $K_2{}^{13}C^{16}O_3$ and carbon black in pure-He flow.

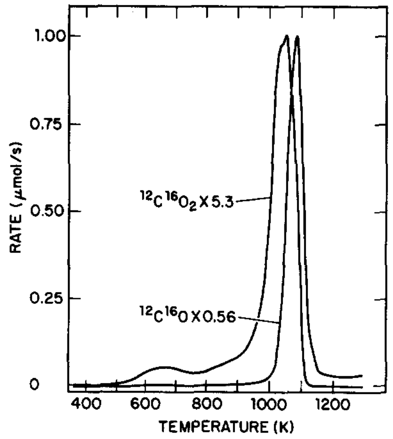

FIG. 2. ^{12}C TPR spectra for a mixture of $K_2{}^{13}C^{16}O_3$ and carbon black in pure-He flow.

near 500 K (Fig. 1). Not only did the carbonate decompose to emit $^{13}CO_2$, but almost as much $^{12}CO_2$ was produced as $^{13}CO_2$ (Figs. 1 and 2 and Table 1). The $^{12}CO_2$ had to originate from the carbon black; Fig. 2 was corrected for the 10% ^{12}C component in the carbonate. At 1000 K carbon gasification began. This consumed the carbon dioxide being produced and yielded ^{12}CO and ^{13}CO in a 3 : 1 ratio. Of the ^{13}C in the carbonate, 92% was observed as ^{13}CO or $^{13}CO_2$. The gaseous oxide products had 63 μmol of atomic oxygen beyond the total oxygen available in the 60 μmol of carbonate that decomposed. This corresponds to an oxygen amount in the carbon black of 1.0%, which is within the range stated by the manufacturer. These observations mean that some of the oxides originally within the carbon black were converted to gaseous CO_2.

TABLE 1

Temperatures and Amounts ($K_2{}^{13}CO_3$ and C in He)

Product	Peak temperature (K)	Amount (μmol)
$^{13}CO_2$	1029	25
$^{12}CO_2$	1055	22
^{13}CO	1071	35
^{12}CO	1086	114

This experiment shows that potassium carbonate, in the presence of carbon but in the absence of gaseous carbon dioxide, decomposes to emit CO_2 at temperatures above 500 K. Simultaneously, carbon dioxide containing carbon from the carbon substrate also appears.

As shown in Table 1, the peak temperatures were always in the order

$$^{13}CO_2 < {}^{12}CO_2 < {}^{13}CO < {}^{12}CO$$

Peak temperatures were reproducible to ±18 K and differences between products were reproducible within ±7 K.

Extreme devitrification of the quartz reactors occurred during the experiments, indicating the presence of elemental potassium. Devitrification was greater for this reaction system (K_2CO_3/C/He) than with any other.

Uncatalyzed Carbon Gasification in CO_2

For comparison with the catalyzed reaction, 100 mg of carbon black, without carbonate, were heated to 1273 K in 10% CO_2/90% He. Gasification began near 1050 K and the rate was still rising when the run ended at 1273 K. At this point the rate was 1.2 μmol/s. As shown in Fig. 3, when the CO signal increased, the CO_2 signal decreased half as fast, as expected for CO_2 gasification. To see these effects Fig. 3 is shown with an expanded rate scale relative

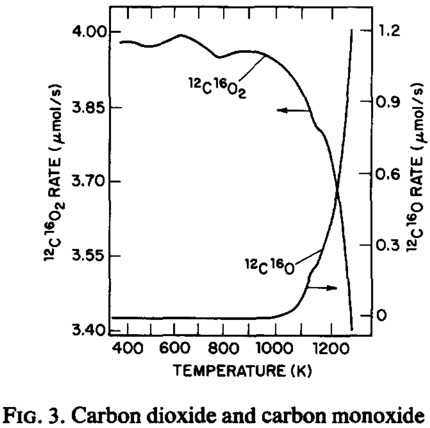

FIG. 3. Carbon dioxide and carbon monoxide signals for uncatalyzed CO_2 gasification of 100 mg carbon black.

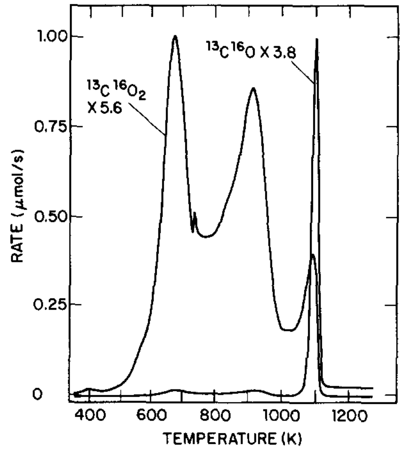

FIG. 4. ^{13}C TPR spectra for a mixture of $K_2{}^{13}CO_3$ and carbon black heated in CO_2/He flow.

to the figures for catalyzed gasification in the next two sections.

$K_2{}^{13}CO_3$ and Carbon in CO_2

When 100 mg of carbon black and 10 mg $K_2{}^{13}CO_3$ were heated in CO_2/He flow, production of $^{13}CO_2$ began near 500 K and continued with major peaks at 675, 910, and 1090 K (Fig. 4). Peak temperatures were reproducible to ±5 K and $^{13}CO_2$ curves from different runs were similar (Fig. 5). For carbon monoxide, most of the ^{13}CO formed in a peak at 1100 K. Of the total amount of ^{13}C in the carbonate, 80% was detected as $^{13}CO_2$ and 14% appeared as ^{13}CO.

As reported before (*5*, *6*), it is notable that the $^{12}CO_2$ gas-stream signal decreased as $^{13}CO_2$ formed. Changes in the $^{12}CO_2$ signal below 950 K (Fig. 6) were mirror images of the changes in the $^{13}CO_2$ signal (Fig. 4) when scale factors are considered. The $^{12}CO_2$ consumed was within ±15% of the $^{13}CO_2$ produced (35 μmol). This means that at temperatures between 500 and 950 K, in the presence of carbon and gaseous CO_2, potassium carbonate does not decompose but rather exchanges atoms or molecules with those in the gas phase.

Starting at 950 K, the $^{12}CO_2$ signal rose above the steady-flow value of the 10% CO_2/90% He gas stream (Fig. 6). Since there is no other source for $^{12}CO_2$, this must indicate decomposition at 950 K of the carbonate, now largely depleted of its ^{13}C. This behavior was quite reproducible, and was seen in experiments using both $K_2{}^{13}CO_3$ and $K_2C^{18}O_3$.

Near 1050 K, catalyzed gasification began; the $^{12}CO_2$ signal decreased to zero and the ^{12}CO signal increased (Fig. 6). A peak was seen in the ^{12}CO signal above 1100 K. Although the initiation temperature of the catalyzed reaction appears to be about the

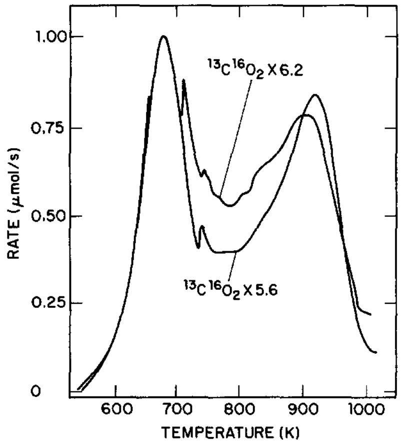

FIG. 5. $^{13}CO_2$ TPR spectra for two separate mixtures of $K_2{}^{13}CO_3$ and carbon black in CO_2/He flow.

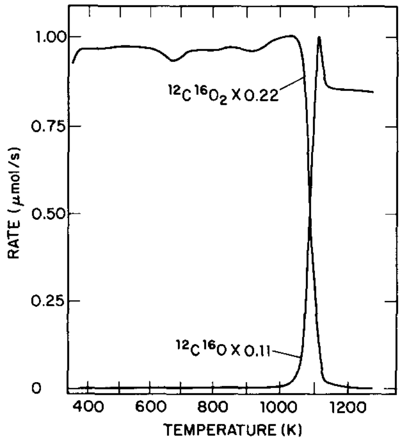

FIG. 6. ^{12}C TPR spectra for a mixture of $K_2{}^{13}CO_3$ and carbon in CO_2/He flow.

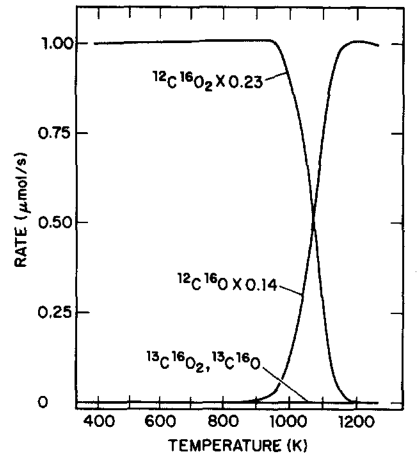

FIG. 7. TPR spectra for reheating a mixture of $K_2{}^{13}CO_3$ and carbon black in CO_2/He flow. Initial heating was to 1250 K.

same as that for the uncatalyzed reaction, the signal magnitude for ^{12}CO in Fig. 6 is about eight times that in Fig. 3, and all the CO_2 had reacted in the catalyzed system by 1200 K. With the catalyst, therefore, a much higher gasification rate was observed.

In one run, after heating to 1250 K, the reactor was cooled to room temperature and reheated to 1250 K, all in continuous CO_2/He flow. During the second heating, no K_2CO_3-decomposition peaks were seen in the ^{12}CO or $^{12}CO_2$ (Fig. 7). This implies that there was no carbonate in the system to decompose during the second heating; potassium carbonate did not reform when the system was cooled after the first heating. Gasification, indicated by the decrease in $^{12}CO_2$ and increase in ^{12}CO signals, started 100–150 K earlier in the second heating. The decrease in $^{12}CO_2$ and increase in ^{12}CO signals were more gradual than in the first heating. No ^{13}C products were detected during the second heating, and no decrease in the $^{12}CO_2$ signal due to exchange was observed.

Reactors devitrified in these experiments, but to a lesser extent than seen for C and K_2CO_3 in He flow.

$K_2C^{18}O_3$ and Carbon in CO_2

When 10 mg $K_2C^{18}O_3$ and 100 mg carbon black were heated in CO_2, $C^{18}O_2$, and $C^{18}O^{16}O$ were observed in a series of peaks between 500 and 1100 K (Fig. 8). The $C^{18}O^{16}O : C^{18}O_2$ ratio was 80 : 1 (40 : 1 based on ^{18}O), and 2–2.3 times as much $C^{18}O^{16}O$ was produced as $^{13}C^{16}O_2$ in the previously described experiment. This corresponds to the $^{18}O : {}^{13}C$ ratio in the two carbonates. However, unlike the $^{13}CO_2$ signals described in the previous section, $C^{18}O^{16}O$ had several peaks which were not so reproducible. Figure 9 shows $C^{18}O^{16}O$ traces from two experiments.

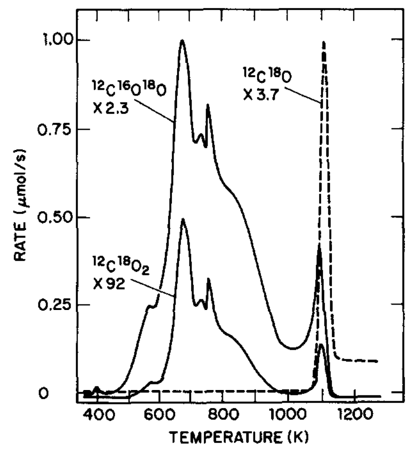

FIG. 8. TPR spectra for ^{18}O products for a mixture of $K_2C^{18}O_3$ and carbon black in CO_2 flow.

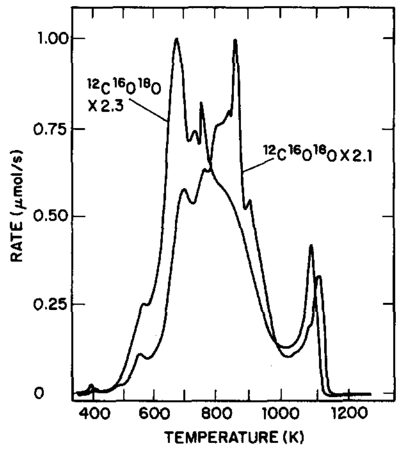

FIG. 9. $C^{16}O^{18}O$ TPR spectra for two separate mixtures of $K_2C^{18}O_3$ and carbon in CO_2/He flow.

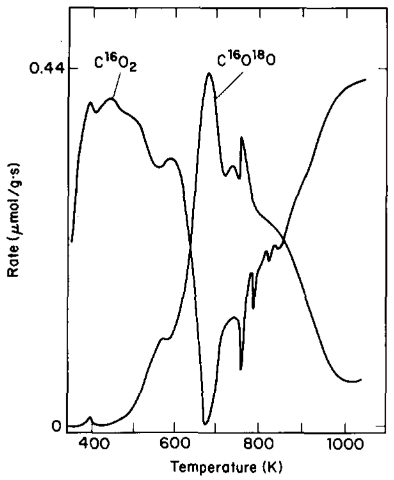

FIG. 10. $C^{16}O^{18}O$ and $C^{16}O_2$ signals for a mixture of $K_2C^{18}O_3$ and carbon black in CO_2/He flow below 1000 K.

The carbonate contained 152 μmol ^{18}O, and 132 μmol were observed in the products. Of the total ^{18}O detected in the effluent, 80% appeared below 1050 K.

The $^{12}C^{16}O_2$ and $^{12}C^{16}O$ signals were similar to those in the ^{13}C experiments. Below 950 K, the $^{12}C^{16}O_2$ signal changes were mirror images of the $C^{18}O^{16}O$ changes (see Fig. 10). The amount of $^{12}C^{16}O_2$ consumed was within 10% of the amount of $C^{16}O^{18}O$ formed. Changes in signal magnitudes also were within 10% of each other.

Above 950 K, the $^{12}C^{16}O_2$ signal merely repeated the behavior shown in Fig. 6 and is not illustrated. It showed decomposition of the carbonate at 950–1050 K. Above 1050 K, carbon gasification took place and produced a maximum $C^{16}O$ signal near 1120 K. A $C^{18}O$ peak also formed above 1100 K (Fig. 8).

DISCUSSION

Potassium Carbonate and Carbon in Helium

Pure potassium carbonate does not decompose noticeably under our experimental conditions (*6, 9*). In the presence of carbon, however, decomposition of the carbonate occurs. Not only our works, but other recent papers have reported low-temperature decomposition of potassium carbonate in the presence of carbon in an inert gas (*10, 11*).

Experimentally, the 10 mg $K_2{}^{13}CO_3$/100 mg C mixture, when heated in pure helium, exhibited carbonate decomposition beginning near 500 K. The carbonate decomposed almost completely between 500 and 1100 K (see Table 2). Carbon dioxide was the primary product below 1000 K, and it formed from both carbon black and carbonate. The $^{13}CO_2$ exhibited a trace moderately different from that of the $^{12}CO_2$, and this implies that two complexes formed which decompose at different rates. Since excess oxygen was observed in the decomposition products, the carbonate apparently bonded to the carbon through surface oxides, starting at 500 K. The surface of the substrate carbon was almost unquestionably covered by surface oxygen complexes at the start of the experiment, since it was not subjected to the rigorous conditions necessary for their removal (*12*).

The final stoichiometry of the potassium compound is difficult to determine because of oxygen from the carbon black. Some potassium atoms were present since the reactor devitrified (*7*). Wood *et al.* (*13*) have directly observed the presence of potassium atoms in the gas phase above carbon–carbonate mixtures.

TABLE 2

Carbonate Decomposition ($K_2{}^{13}CO_3$ and C in He)

Temperature (K)	Percent K_2CO_3 decomposed (%)
500	0.2
600	1.6
700	6.4
800	11.4
900	21.0
1000	47.6
1050	84.6
1100	99.6
1160	100

The potassium carbonate apparently weakens the carbon–carbon bonds in the carbon black since carbon from the black is seen in the gaseous products. Some of the $^{12}CO_2$ is seen at temperatures far below gasification, further showing how strong is the interaction between the two solids. Above 950 K, carbonate decomposition accelerated and carbon monoxide production began. The $^{12}CO : ^{13}CO$ ratio was 3 : 1 suggesting that both $^{13}CO_2$ from the carbonate and $^{12}CO_2$ from the carbon black gasified the black.

Huhn *et al.* (*11*) observed some results similar to those from our pure-He-flow experiments. They found that coke reacted with K_2CO_3, starting at 575 K, in an inert atmosphere, to release CO_2. They, too, obtained approximately equal amounts of $^{12}CO_2$ and $^{13}CO_2$, different $^{12}CO_2$ and $^{13}CO_2$ traces, and a higher temperature for the $^{12}CO_2$ trace. They proposed an isotopic exchange of ^{13}C in the carbonate with ^{12}C in the carbon substrate, followed by carbonate decomposition. Their proposal, however, gives no cause for the 1 : 1 ratio of $^{13}CO_2 : ^{12}CO_2$, and it incorrectly predicts the same peak temperature for the two signals. Their proposal also forecasts a 5 : 1 ratio of $^{13}CO : ^{12}CO$; we obtained a 3 : 1 ratio. Moreover, if half the ^{13}C originally in the carbonate exchanged with ^{12}C from the substrate, only half of the original ^{13}C should appear in the gas phase when carbonate decomposed. We observed 92% of the ^{13}C in gas-phase products.

All these results suggest that the carbonate will interact with surface oxides in the carbon substrate to form carbon–oxygen–carbonate complexes at low temperatures.

CO_2 Exchange Reactions below 1000 K

In the presence of carbon, decomposition of the carbonate did not occur below 950 K when 10% CO_2 was in the gas phase, though significant decomposition occurred in pure helium below 950 K. Though decomposition did not occur, both carbon and oxygen exchanged between the carbonate and gas-phase CO_2 between 500 and 1000 K, as reported earlier (*5*, *6*). Figure 10 shows the simultaneous and opposite changes in the CO_2 carrier gas and the $C^{16}O^{18}O$ from $K_2C^{18}O_3$. Eighty to ninety percent of the original carbon and oxygen isotopes in the carbonate exchanged below 1000 K, and the amount of labeled CO_2 produced was close to the amount of gas-phase CO_2 consumed; the stoichiometry of the mixture did not change.

Carbon is necessary for this exchange to take place; no exchange occurred when pure carbonate was heated in CO_2 (*6*). Carbon from the carbon black, however, did not *exchange* with carbon in the gas-phase CO_2. In experiments with $K_2{}^{12}CO_3$ and ^{13}C in the solid carbon, essentially no products containing ^{13}C appeared in the gas phase below 1000 K (*6*). This confirms the implications from the pure-helium experiments that carbon does not exchange between the carbonate and the carbon black.

Exchange with gas-phase CO_2 usually depleted the surface of ^{18}O at lower temperature than it depleted the surface of ^{13}C. Also, $^{13}CO_2$ formed in two distinct peaks, while $C^{16}O^{18}O$ formed in several peaks which were less reproducible. The $^{13}CO_2$ spectrum in Fig. 4 is quite different from that of $C^{16}O^{18}O$ in Fig. 9. The $C^{16}O^{18}O : C^{18}O_2$ ratio was also large (80 : 1). These results all indicate that the rates for oxygen and carbon exchange were not the same; the carbon–oxygen bonds in the carbonate broke and reformed during the exchange. Apparently, exchange of the ^{13}C between the carbonate and the gas-phase CO_2 was a slower step than isotopic scrambling of the oxygen.

The reproducible double peak for carbon exchange (Figs. 4 and 5) implies that two separate surface species were present which exchange ^{13}C with the gas-phase CO_2, and that the activation energies for exchange were different for these two species. The species must have originated from the $K_2{}^{13}CO_3$. Perhaps the monodentate and bidentate forms of adsorbed carbonates observed in infrared studies (*14–16*) were present. Some of the many peaks for ^{18}O exhange were also invariably observed at the same two temperatures that ^{13}C exchange occurred (Fig. 9); thus it is probable that CO_2 molecules were the basis for the ^{13}C exchange, rather than carbon atoms. In other words, the ^{13}C exchange involved $^{13}CO_2$ from the carbonate surface complexes changing places with $^{12}CO_2$ molecules from the gas phase. Amerikov *et al.* (*17*) observed isotopic scrambling between gas-phase $C^{18}O_2$ and $C^{16}O_2$ over several oxides. In their case, the $C^{18}O_2$ and $C^{16}O_2$ apparently first adsorbed on the surface, and assumed perhaps ionic or dentate forms. Oxygen isotope exchange evidently occurred among the adsorbed species because when the ionic and dentate forms reverted to CO_2, a significant fraction of the molecules was $C^{16}O^{18}O$. Apparently a similar phenomenon took place in our study, except that the surface species originated with carbonate.

Decomposition of the Surface Complexes in CO_2/He Flow

Figure 6 shows an increase of the $^{12}CO_2$ signal above the steady gas-phase flow level beginning at 950 K, which indicates the start of surface complex decomposition in the presence of 10% CO_2. On the other hand, there is no corresponding increase of $^{13}CO_2$ here. Rather, the $^{13}CO_2$ signal does not begin to increase until carbon gasification commences (Fig. 4). Similar behavior is seen in the ^{18}O products (Fig. 8). These spectra indicate that there are carbon and oxygen atoms, originally in the carbonate, which have become strongly bonded to the substrate. These carbon and oxygen atoms do not exchange, and do not appear until gasification begins. During gasification, they appear in both the CO_2 and CO.

Presence of Potassium Atoms

Devitrification of the reactor was observed in all runs where K_2CO_3 was mixed with carbon black. Devitrification was more severe for pure-He flow than for CO_2/He flow. Two explanations are consistent with this result if we assume similar complexes form in both types of experiments. Decomposition occurs at lower temperatures in pure He than in CO_2/He, so the K atoms are present in higher concentrations and for a longer time. Also, gas-phase CO_2 can react with available K atoms to form an intermediate and thus decrease K atom concentration. Wood *et al.* (*13*) saw a small decrease in potassium atom gas-phase concentration in the presence of CO_2.

Catalytic Gasification

Decomposition of surface complexes began at 950 K (see above), and catalytic gasification began at 1050 K, while the decomposition presumably was still in progress. The catalytically promoted rate was much higher than that of the uncatalyzed reaction at all temperatures. The K : C : O ratios at gasification temperatures were not determined easily since most of the labeled carbon and oxygen atoms in the carbonate had exchanged by 1000 K.

Since the surface complexes decomposed prior to the onset of catalyzed gasification, this indicates that potassium carbonate is not part of the catalytic process. Further support of this is found in the experiment where the system was cooled after heating to 1250 K, then reheated, all in CO_2/He flow. No CO_2 peak from carbonate decomposition was seen during the second heating, indicating that the carbonate did not reform during the cooling process. Yet the gasification during the reheating began at a temperature lower than during the original heating. It can be inferred that the reaction began at a lower temperature during the reheating because the active catalyst was already present; it had formed during the initial heating above 1000 K. It seems that the surface complexes had to decompose before catalytic gasification could occur, and this decomposition was inhibited by gas-phase CO_2. During the first heating, therefore, gasification did not began until

1050 K. Apparently neither the complexes nor the carbonate reformed upon cooling in 10% CO_2, and thus the catalytic agent was in place and the gasification could began at a much lower temperature during the second heating.

Our TPR results are consistent with recent experiments which indicate that the active catalyst is a surface oxide (*13*, *18*, *19*). A cycle between an oxide and potassium atoms apparently occurs during gasification. Mims and Pabst (*18*) point strongly to the presence of K–O–C bonds and hint that there may be additional K–C bonds on the active surface. Cerfontain and Moulijn (*19*) concluded the active catalyst was a surface oxide with a K : O ratio of one. Wood *et al.* (*13*) indicated that a suboxide of potassium was the active catalyst.

Thus our data and those of others (*13*, *18*, *19*) do not support the three-step oxidation–reduction cycle in which a carbonate reforms (e.g. (*7*, *20*)); carbonate does not reform upon cooling in CO_2. In addition, this mechanism (*7*, *20*) does not account for the formation of CO_2 prior to gasification, nor does it have the K : O ratio seen by Cerfontain and Moulijn (*19*). Similarly, our results are not consistent with the suggestion that carbon reduces the carbonate directly to potassium atoms and carbon monoxide (*7*, *20*). Instead, we see the formation of surface complexes that decompose to form carbon dioxide and the catalytically active surface.

Mechanism

The characteristics of the potassium carbonate–carbon–carbon dioxide system developed in the preceding discussion can be summarized:

At low temperatures, surface complexes form between the carbonate and either a surface oxide species or the carbon itself. Oxygen bonds continually break and reform within these complexes. These complexes promote the exchange of carbon and oxygen between gas-phase CO_2 and the complexes. Carbon atoms do not exchange between the carbonate and the carbon black. Some carbon and oxygen atoms in the carbonate become strongly bound to the substrate species and do not exchange.

At higher temperatures the complexes decompose and form CO_2 as the initial product; the decomposition can be inhibited by gas-phase CO_2. Complexes containing carbon from the carbonate decompose more easily. These complexes are precursors of catalytic gasification, since decomposition of the complexes is necessary to create the gasification catalyst.

Potassium atoms are present in the vapor phase during the catalytic gasification, and perhaps at lower temperatures. More potassium atoms are available when there is almost no CO_2 in the gas phase. Potassium carbonate does not appear to be a part of the catalytic process.

Other recent contributions add to the picture. The catalyst involves K–O–C bonds (*18*, *19*) and probably K–C bonds (*18*); the K : O ratio is one (*19*). These groups would be the surface products from decomposition of the surface complexes.

A probable sequence has the K–O–C groups decompose to form CO and a K–C bond. The K–C complex created then reacts with carbon dioxide from the gas phase to produce CO and reproduce the K–O–C complex, completing the cycle. The K–C bond prevents total loss of the potassium atoms, which have a high vapor pressure at gasification temperatures. Some potassium atoms do escape and attack the reactor walls, causing the devitrification seen in our experiments and by others.

The cyclic oxidation–reduction cycle also occurs when the carbon–carbonate mixture is heated in pure helium. Carbon dioxide that results from decomposition of the complex subsequently reacts with K–C complexes before it can leave the reactor bed. The CO is observed to increase as the CO_2 signal decreases (Figs. 1 and 2). This occurs at lower temperatures in pure-He flow than CO_2 flow because gas-phase CO_2 inhibits decomposition of the complex.

CONCLUSIONS

Combining temperature-programmed reaction with isotopic labeling is shown to be a valuable approach for studying catalytic gasification of carbon. Between 500 and 1000 K, potassium carbonate and surface carbon atoms or surface carbon oxides interact very strongly to form complexes which exchange carbon and oxygen with the gas phase. Both carbon and carbonate are necessary for the exchanges. Carbon from the substrate does not exchange. Oxygen atoms exchange rapidly among the complexes but carbon atoms do not.

As the temperature rises, the complexes decompose, yielding CO_2 from both the carbonate and the carbon black. The decomposition temperature appears to be a function of CO_2 partial pressure. The complexes are precursors to catalytic gasification, for they must decompose to form the surface catalyst. Catalytic gasification yields CO. Potassium atoms also are formed. The active catalyst is not converted back into a carbonate on cooling in CO_2, yet the catalytically promoted reaction recurs upon reheating the cooled system. Thus, the oxidation–reduction cycle during catalytic gasification of carbon apparently does not involve a carbonate. A cyclic process involving a potassium oxide is indicated.

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