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MECHANISM OF THE CATALYTIC GASIFICATION AND REACTIVITY OF GRAPHITE

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ABSTRACT. Graphite is being used as a carbon source for gasification to insure that hydrogen or hydrogen in hydrocarbons is derived from water. Relatively low temperatures (500-800K) are used to favor the equilibrium $C + 2H_2O \rightarrow CH_4 + CO_2$ which is almost thermally neutral. In the presence of alkali hydroxide C_2-C_6 hydrocarbons are formed in addition to H_2 , CH_4 and CO_2 . Formation of hydrocarbons is a stoichiometric reaction proceeding on the crystal edges to form a phenolate and hydrocarbons, e.g. $5C + 4KOH \rightarrow 4COK + CH_4$. Surface spectroscopy has confirmed the presence of phenolate, which can be decomposed over metal oxide to make the reaction truly catalytic: $4COK \xrightarrow{MeOx} 2K_2O + 2C + 2CO$; $2K_2O + 2H_2O \rightarrow 4KOH$. In the presence of both KOH and metal oxide the major products are CO_2 and H_2 with traces of CH_4 and CO. The 2:1 ratio of H_2/CO_2 appears due to either or both watergas shift and Boudouart reaction. The mechanisms will be illustrated by electron microscopy and XPS measurements.

The production of synthesis gas by reaction of various carbonaceous deposits with steam has been frequently investigated and is a commercial process. Gasification in the presence of alkali metal compounds has been reviewed by Wen.¹ The production of low molecular weight gaseous hydrocarbons directly from carbon or from carbonaceous deposits provides an intriguing alternative to syngas production with subsequent methanation or liquefaction. The reaction of carbon with water to produce methane and carbon dioxide $2C + 2H_2O \rightarrow CH_4 + CO_2$ is virtually thermoneutral ($\Delta G_{298K} = 2.89 \text{ Kcal/mol}$) and thermodynamically feasible at low temperatures. By contrast studies of coal gasification with water have been always carried out at high temperature regimes in order to have efficient production of carbon monoxide and hydrogen, a very endothermic reaction. More recent studies by Exxon researchers² reported the production of substantial amounts of methane along with CO and hydrogen during coal gasification using potassium carbonate as a catalyst. These studies employed relatively high temperatures (900-1100 K).

We have studied the gasification of graphite in the presence of

alkali hydroxide and in some cases of earth alkali hydroxide at temperatures in the range 500-800 K and atmospheric pressure. We have used graphite as a carbon source because of its lack of hydrocarbonaceous material and in order to be sure that all hydrogen produced as hydrogen or in hydrocarbons was derived from hydrogen in water. In a few experiments we have demonstrated that char derived from an Illinois No. 6 coal gasifies at better rates but with the same product distribution as graphite.

Two types of equipment have been used in our experiments which were designed to study not only gasification but the mechanism of hydrogen and of hydrocarbon production. These are shown in Figures 1 and 2. Figure 1 shows a high pressure-low pressure (ultra-high vacuum) cell operating at a base pressure greater than 10^{-9} Torr. It is equipped to determine surface composition analysis by Auger electron spectroscopy and by XPS. The system is also equipped with a high pressure cell which isolates the sample and permits the performance of chemical reaction studies at high pressure without removing the sample from the UHV chamber. The product distribution is monitored by gas chromatography with a thermal conductivity detector. The second figure shows a flow reactor in which continuous gasification studies were undertaken at atmospheric pressure.

Early work in the high pressure-low pressure cell indicated that methane could be produced at temperatures as low as 475 K in the presence of potassium hydroxide³ as indicated in Figure 3. Figure 4 shows the methane production with various alkali hydroxides. While the rate of methane production is small as indicated in Table 1 it becomes appreciable if one assumes that not all the geometric surface area of graphite is available for attack and that the attack probably takes place on the edges of the graphite.

We have carried out gasification studies in the environmental cell of a transmission electron microscope similar to the studies that were previously carried out by Baker⁴ who gasified graphite crystals in the presence of nickel and hydrogen and showed that gasification occurred by "basal plane penetration in imperfect regions or by altering the rate of reaction at edges or steps". In our studies thin specimens of highly oriented pyrolytic graphite were obtained by cleavage of graphite crystals. Potassium hydroxide was introduced onto the surface of the graphite by dipping the specimen supported on copper or nickel grids into a .38 M solution of potassium hydroxide and then dried. Transmission electron microscopy was carried out in a Hitachi 650 kV microscope.⁵ Argon at about 1 atm pressure was bubbled through water at room temperature giving an argon/water ratio of about 40/1 and then introduced into the environmental cell to give a pressure of 50 Torr. At 500°C the potassium hydroxide was dispersed as particles of 0.1 to 0.5 microns in diameter on the surface of the graphite. Figures 5 and 6 show micrographs recorded 11 minutes apart taken from a sequence showing the channel growth at 770 K. Channels are evident in two adjacent graphite crystals emanating from the edges of the crystal each channel with a particle at its head. As the reaction continues the particles move and the length of the channels increase. The channels remain roughly parallel sided indicating that

there is little effect of uncatalysed reaction at the channel edges or of wetting of the channels sides by catalytic material. Intercallation of potassium into the graphite does not appear to play a role in the gasification. Samples of potassium intercalated graphite ($C_{24}K$) were subjected to reaction with water at 573 K and exhibited an appreciably lower methane production than graphite impregnated with potassium hydroxide.⁶ Both AES and XPS studies of potassium intercalated graphite also indicated that potassium diffuses to the surface under the influence of the electron beam. The intensity of the potassium peak decreased upon heating.

It was also observed when using calcium hydroxide for the gasification of graphite that a new photoelectron emission peak corresponding to a C_{1s} electron binding energy of 290 eV is formed representing a more reactive form of carbon probably in connection with oxygen. As we will show later this probably constitutes a phenolate species also observed by Mims and Pabst.²

In experiments with the flow reactor shown in Figure 2 it was found that two regimens of gas production prevailed as illustrated in Figure 7. In the first one hydrogen, methane and higher hydrocarbons were produced with almost no carbon monoxide or carbon dioxide production.⁷ In the second regime hydrogen and CO were produced at a lower rate. The first regime prevails until exactly one-half mole of hydrogen as either hydrogen or in hydrocarbon has been produced per mole of KOH present. This then would indicate that we are dealing with a stoichiometric reaction in which carbon reacts with potassium hydroxide to form a phenolate and one-half mole of hydrogen which in turn may react with carbon to form hydrocarbons. Such a reaction can be described as: $5C + 4KOH \rightarrow 4COK + CH_4$. The fact that higher hydrocarbons up to C_6 are also formed is of considerable interest.⁸ Figure 8 shows a gas chromatogram of these hydrocarbons indicating that many of them are olefinic. The distribution of the higher hydrocarbons relative to methane and hydrogen is shown in Figure 9.

The presence of the stoichiometric phenolate compound is confirmed by XPS as previously shown.

When a sample of potassium hydroxide impregnated graphite which has been reacted to completion of the stoichiometric reaction is heated to about 1300 K the phenolate is decomposed with production of carbon monoxide. Following this, gasification at low temperature can again begin in line with the regime 1 in Figure 8.

We have found that the overall reaction can be made truly catalytic by adding a co-catalyst to the potassium hydroxide. Suitable materials are metal oxides and particularly nickel and iron oxide as shown in Figure 10. It appears that in the presence of the metal oxide the phenolate is decomposed as quickly as it is formed and gasification occurs at 800 K at a steady rate which has been followed up to 25% conversion of the graphite. This is illustrated in Figure 11. The reaction proceeding can be simulated by the following equations:

In the gasification with potassium hydroxide plus metal oxide the products are essentially hydrogen and carbon dioxide in a ratio of 2:1. Only traces of hydrocarbons are found. It was at first suspected that in these reactions methane might be a primary product which is then steam reformed to CO and hydrogen. Addition of methane to the water feed illustrated, however, that only minor amounts if any of steam-reforming take place. Decomposition of methane over the metal oxide may occur to a small extent and this may be the reason why only traces of hydrocarbons are found. The high hydrogen to CO₂ ratio and the absence of carbon monoxide are attributed to a watergas shift reaction proceeding simultaneously with the gasification. We have considered the possibility of a Boudouart reaction with subsequent gasification of the carbon from the disproportionation but consider it less likely than the watergas shift reaction. It is important to note that the production of hydrogen to carbon dioxide in the 2:1 molar ratio allows high hydrogen production directly from the gasification of carbonaceous material without a separate shift reactor and that the reaction proceeds at temperatures appreciably lower than those previously observed. One must also note that the reaction is carried out at essentially atmospheric pressure and that the kinetics should be appreciably improved by operating at higher water partial pressure. Studies in this direction are under way. We have repeated the experiments in the flow reactor with char from Illinois No. 6 coal and have obtained identical product distribution at higher rates than with graphite.

It can be concluded that phenolate type compounds are formed from the reaction of carbon, water and alkali hydroxide as intermediates in the production of hydrogen and/or of hydrocarbons from carbonaceous material and water in the presence of alkali hydroxides.

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(a)

(b)

XBL 814-5584

Figure 1. High pressure-low pressure ultra-high vacuum cell.

- 1 Steamer
- 2 Reactor
- 3 Burette
- 4 Septum
- 5 Vacuum Container

XBL 832-5326

Figure 2. Flow reactor.

XBL 814-5650

Figure 3. CH_4 production as a function of temperature in the presence of KOH.

XBL 817-10520

Figure 4. CH_4 production with various alkali hydroxides.

Figure 5. Micrograph of KOH catalyzed reaction.

Figure 6. Micrograph of KOH catalyzed reaction ten minutes later.

XBL 833-8665 A

Figure 7. Gas production in the flow reactor.

Retention time

XBL 833-8664 A

Figure 8. Gas chromatogram of hydrocarbons produced.

XBL833-8659B

Figure 9. Distribution of higher hydrocarbons.

Metal oxide/KOH=1

KOH/C=0.04

T = 900 K

XBL 851-5706

Figure 10. Gas production and activation energy for various metal oxides.

XBL 851-5705

Figure 11. Temperature controlled gas production for three catalysts.

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