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F. Delannay, W.T. Tysoe, H. Heinemann, and G.A. Somorjai

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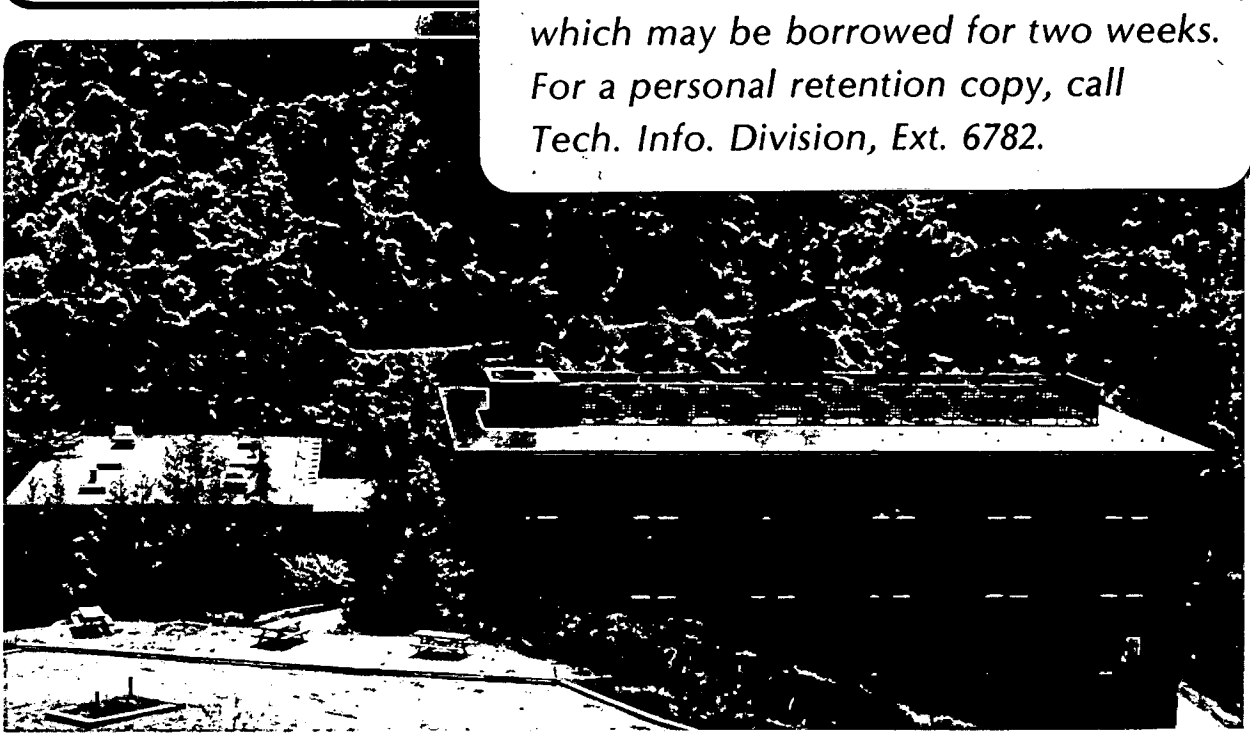

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CATALYSED LOW TEMPERATURE PRODUCTION OF METHANE FROM WATER AND GRAPHITE, F. DELANNAY*, W.T.TYSOE, H. HEINEMANN AND G.A. SOMORJAI.

Materials and Molecular Research Division, Lawrence Berkeley Laboratories, University of California, Berkeley, California, 94720.

Introduction.

Previous work in this laboratory has demonstrated the production of methane at low temperature (500-800K) from the reaction between water vapor and an alkali-loaded highly oriented pyrolytic graphite crystal (1,2). The water vapor pressure during these experiments was limited to 20torr (i.e. the vapor pressure of water at room temperature), which inevitably restricts the range of kinetic investigations and the product yield. In order to operate at higher water pressures (up to 1 atmosphere), a fixed bed flow reactor was designed in which reaction products could be accumulated enabling product distributions to be measured more accurately.

This paper presents a more detailed analysis of the conditions of formation of the reaction products, including H_2 and higher hydrocarbons together with methane, from the reaction between water and graphite in the presence of KOH. The reaction, that eventually deactivates, can be thermally regenerated.

Experimental.

Two different apparatuses were used during the course of these experiments. A schematic diagram of the high pressure/low pressure apparatus is shown in figure 1. Its design and operation have been described in detail in previous publications (1,2). It consists of an UHV chamber equipped with Auger and x-ray photoelectron spectroscopies and a quadrupole mass spectrometer for residual gas analysis and thermal desorption experiments. The sample manipulator can be effectively isolated from UHV by enclosing it within a cell in order to carry out reactions under high pressure. A gas chromatograph is used for the analysis of the gas mixture during reaction.

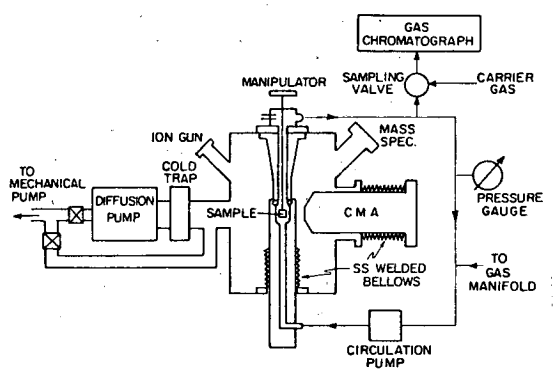


Figure 1: Diagram of the high pressure/low pressure apparatus.

A diagram of the second apparatus, a flow reactor, is shown in figure 2. It consists of a steam generation section, a heated alumina tube containing the sample and a gas collection system.

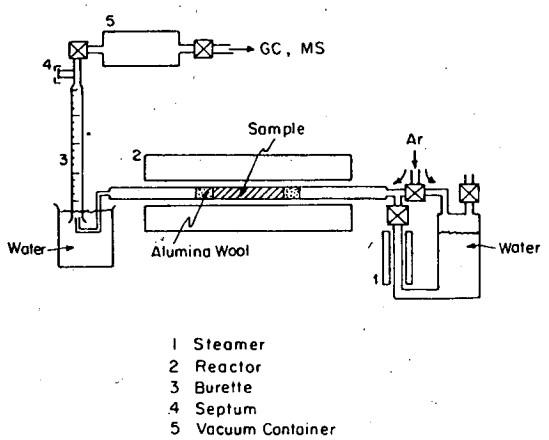


Figure 2: Diagram of the flow reactor.

The pressure of argon over the water reservoir forces water through a heated vaporisation tube so that the inlet steam pressure equals the argon pressure. 5 to 20 wt.% KOH is deposited onto graphite powder (Ultra carbon, ultra "F" purity, $30m^2/gm$) by impregnation from an aqueous solution. After drying, the sample is packed into the tube and held in place by

plugs of alumina wool.

Steam issuing from the flow reactor is condensed in a water-cooled U-tube, and gaseous products collect in a graduated burette. The cooling water volume is kept as small as possible to minimize dissolution of the gas products. The burette is equipped with a septum to allow sampling of the product gases during reaction for GC analysis. The accumulated gases are periodically transferred to an evacuated bottle. After completion of the experiment, the bottle can be attached to the gas-handling line of the high pressure/low pressure apparatus so that the product distribution can be measured either by gas chromatography (Hewlett-Packard, HP 5880A) using both flame ionisation and thermal conductivity detection with argon as carrier gas or by mass spectrometry.

Result and Discussion.

A typical plot of gas production as a function of time obtained from the flow reactor is shown in figure 3. In these experiments, the sample contained 20 wt.% KOH and was exposed to 1 atmosphere of steam at 800K. The gas production is normalized to the number of KOH molecules in the sample. An initial rapid rate is observed, that decreases to a steady rate which is maintained for a few hours. This initial burst and subsequent steady state production correspond to the previously reported behavior for methane formation (1) over HOPG graphite in the high pressure/low pressure apparatus. Analysis of the product gas shows it to be composed almost exclusively of hydrogen and hydrocarbons. The precise product distribution depends on the temperature, extent of reaction and alkali loading. For example, in the case of a sample with 20 wt.% KOH at a reaction temperature of 800K, the volume ratio CH_4/H_2 ranges between 0.001 and 0.02.

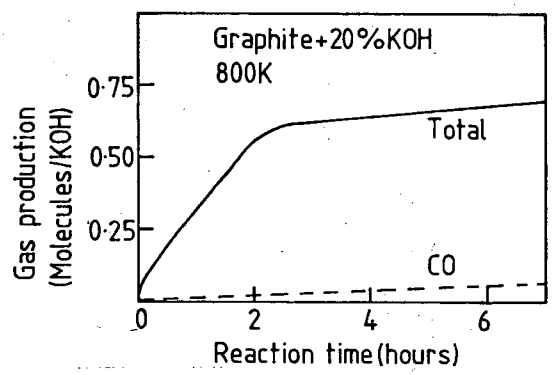
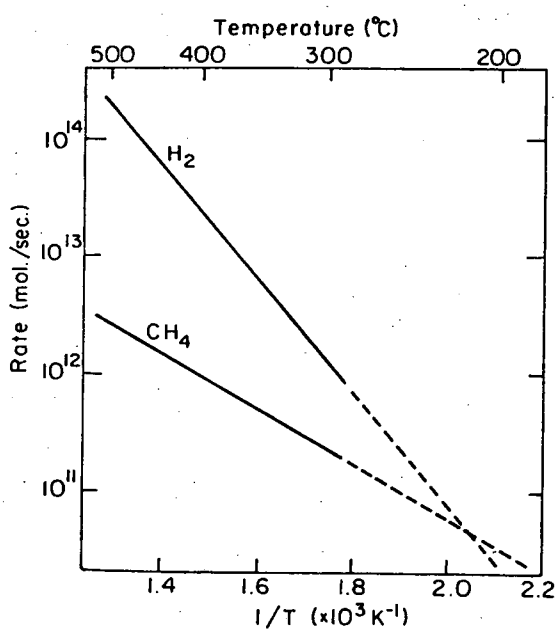


Figure 3: Plot of gas production as a function of time.



The activation energy for hydrogen and methane formation during the steady state has been measured between 600 and 800K in the high pressure cell. The results of these experiments are shown in figure 4, which indicate that the proportion of CH_4 in the products may be increased by lowering the reaction temperature.

Figure 4: Arrhenius plots for hydrogen and methane formation during the first steady state of the reaction.

The dependence of the rate of methane formation on water vapor pressure has been measured both in the high pressure cell and the flow reactor. Figure 5 shows that the dependence on water pressure remains first order in the range 5 to 600 torr.

Analysis of the hydrocarbons that are produced indicates the presence of hydrocarbons up to C_6. Figure 6 shows a typical chromatograph trace obtained using the flame ionisation detector. In a similar way to its behavior during the catalyzed hydrogenation of carbon monoxide (Fischer-Tropsch reactions), it appears that increasing alkali loading shifts the hydrocarbon product distribution to higher molecular weights. It also decreases the proportion of hydrocarbons in the products.

Figure 3 shows that the activity of the sample decreases substantially after the production of 1 H_2 for every 2 KOH in the sample. This may be due to the saturation of the surface with an oxidized species since no oxygen containing products were collected up to this stage of the reaction. In the case of reactions carried out in the high pressure cell, the low water pressure would have required exceedingly long times before such a saturation could have been observed. The H_2/CH_4 ratio could imply that the reaction merely involves the dehydrogenation of KOH. However, the first order steam pressure dependence (figure 5) indicates that water is also required for the reaction.

During the first steady state (t<2.5 hours in figure 3), no CO was detected in the products. However, in the second steady state period (t<2.5 hours) the ratio $CO/H_2 \simeq 1$. The CO production rate is indicated in figure 3 by a dashed line. Some CO_2 was also detected, but amounted to only a few percent of the CO.

Heating the sample under argon from the reaction temperature (800K) to 1300K evolves almost exclusively CO.

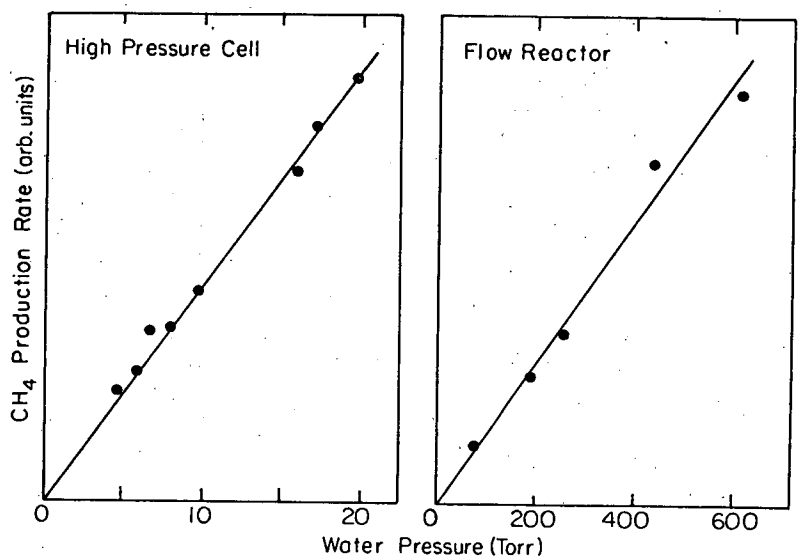


Figure 5: Plot of methane formation rate as a function of water pressure.

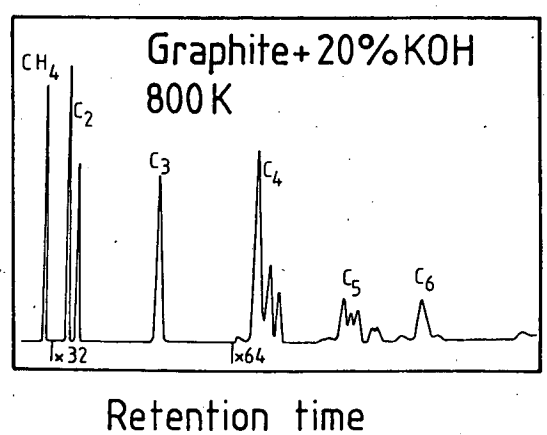


Figure 6: A typical gas chromatogram of the hydrocarbons products. (FID detection)

Figure 7 shows the rate of desorption of gas when the furnace temperature is increased linearly with time at a heating rate of 15K/min. The maximum CO desorption rate coincides with the beginning of the constant temperature regime. As continuing heating may have yielded a higher peak temperature, no data on the CO desorption energy may be obtained from the peak position. However, the leading edge region may be analysed to yield the CO desorption activation energy (assuming that the coverage of the surface species giving rise to CO desorption remains constant in this region). One obtains 31±3 kcal/mole. Characterization by XPS and x-ray diffraction which should be performed shortly, should help to identify the oxygen

containing species responsible for deactivation of the low temperature gasification process.

The total volume of CO collected during this high temperature treatment amounts to 1.5 to 2 times the volume of H_2 and hydrocarbons produced during reaction with steam. This indicates that the potassium ends up in a more reduced state after this treatment than it was before reaction.

When the sample is then reexposed to steam at 800K, hydrogen and hydrocarbons are again produced. The activity is however much lower than it was during the initial reaction. This shows that the regeneration procedure does not completely restore the sample to its original state. It is also possible that high temperature treatment causes some potassium intercalation (3) which does not completely disintercalate on exposure to steam.

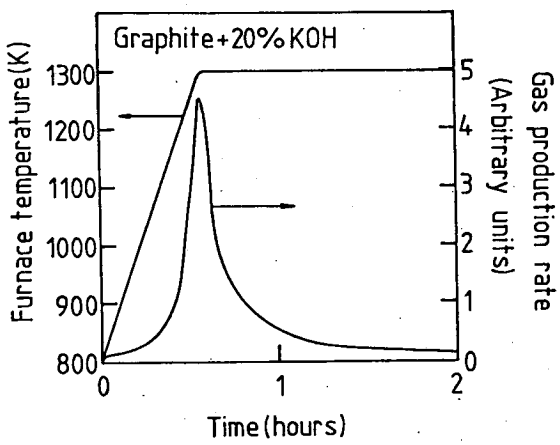


Figure 7: Plot of CO desorption during heat treatment.

Conclusion.

The reaction of water vapor + KOH at 800K is first order in water pressure and produce predominantly hydrogen along with methane and other hydrocarbons up to C_6. This reaction eventually deactivates. Heating the sample to 1300K evolves CO and hence it is probable that the species responsible for deactivation contains an oxidized carbon. At higher temperature, alkalis are known to be catalysts for the reaction between water and carbon. Since thermal decomposition of the oxidized species results in restoring part of the activity of the sample, this species is probably also an intermediate for the reaction at high temperature. In such conditions, this intermediate presumably decomposes so as to maintain the catalyst activity whereas below 800K this intermediate merely accumulates on the graphite surface.

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References.

1. A.L. Cabrera, H. Heinemann and G.A. Somorjai, J. Catalysis 75, 7 (1982).
2. R. Casanova, A. Cabrera, H. Heinemann and G.A. Somorjai. Fuel, in press.
3. F. Kapteijn, J. Jurrians and J.A. Moulijn, Fuel 62, 249 (1983).

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