

# Reversible Gasification/Deposition Behavior of Iron Particles on Graphite in Ethane/Steam

by

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## Introduction

Over the past twenty years there have been numerous reports of the influence of metal and metal oxide catalysts on the gasification of graphite in various individual gases, and in a few cases, these studies have been extended to cover the situation where a specimen is reacted in either wet oxygen or wet hydrogen.<sup>1-3</sup> In the present investigation we have explored the consequences of heating a metal/graphite system to high temperatures in a wet hydrocarbon environment; conditions which might be expected to produce unpredictable events.

## Experimental

The specimens used for controlled atmosphere electron microscopy experiments were prepared from single crystal graphite (Ticonderoga, New York State) and contained sections which were between 15 to 100 nm thick. Iron was introduced onto the graphite by evaporation of the metal (99.99% purity) from a tungsten filament at a residual pressure of  $5 \times 10^{-6}$  Torr. The conditions were chosen so as to produce a metal film at least one atom in average thickness.

The reactant gases used in this work, ethane and ethane/5% hydrogen, had stated purities of 99.99% (Scientific Gas Products) and were used without further purification. Steam was added to these gases by allowing them to flow through a bubbler containing deionized water maintained at 20°C; a procedure which created a gas/steam ratio of about 40/1.

## Results

When iron/graphite specimens were heated in 1.0 Torr, ethane/steam nucleation of the evaporated metal film into discrete particles was observed at 570°C. Catalytic attack of the graphite by the channeling mode commenced at 715°C, and this behavior became more prolific as the temperature was progressively raised.

The propagation rate of all channels appeared to increase in a systematic manner up to 975°C and, provided that this temperature was not exceeded, subsequent temperature cycling did not

produce any deviation from the expected behavior. However, at temperatures in excess of 975°C, particles in the range of 10 to 30 nm gradually lost their activity and there was a significant reduction in the forward motion of larger particles. An even more dramatic distinction in particle behavior was observed on raising the temperature to 1025°C. Under these conditions some of the smallest catalyst particles (10-15 nm diam.) started to move in a reverse direction to that of their original motion and still remained within the channels they had created. This reverse motion was accompanied by deposition of material at the trailing faces of the particles so that in many cases it was difficult to discern where the tracks of the channels had been. When the temperature was raised still higher, the limiting size of particles exhibiting this behavior also increased, so that at 1100° particles up to 30 nm in size fell into this category. If the temperature was reduced to 925°C, then these particles proceeded to reverse direction once again and create channels along the original tracks, depicted schematically in Figure 1.

Examination of the rates of the forward and reverse motions as a function of particle size and temperature reveals major differences in the mechanisms of these two processes. The rate of the reverse motion at 1100°C as a function of particle width shows that there is an inverse dependence,  $r \propto 1/d$ .

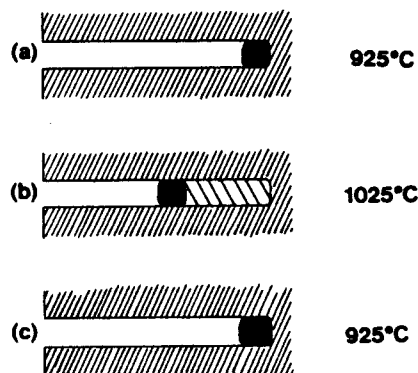


Figure 1. Catalytic reversal behavior of iron.

As the temperature was raised, so the rate of infilling of channels increased. An Arrhenius plot of the data obtained from 14 nm diam. particles undergoing this phenomenon yielded an apparent activation energy of  $32.5 \pm 4$  kcal. mole<sup>-1</sup> (Figure 2). In contrast, during the forward motion, the rate-particle size relationship followed that previously reported for catalytic hydrogenation of graphite, i.e.,  $r \propto d^{2.4}$ , and the apparent activation energy of this process was  $24.3 \pm 3$  kcal. mole<sup>-1</sup> (Figure 2).

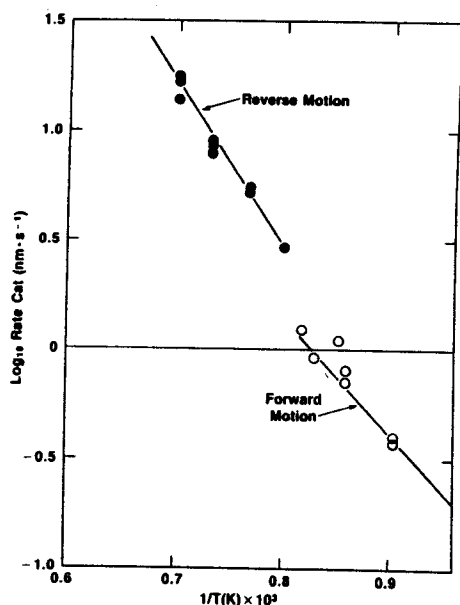


Figure 2. Arrhenius plots of the forward and reverse motion of small iron particles.

In a second series of experiments iron/graphite specimens were reacted in 1.0 Torr ethane/steam containing 5% added hydrogen. In this case, the smaller particles up to 30 nm diam., continued to exhibit the forward and reverse motion, but at a significantly higher temperature than the conditions stated for ethane/steam; channeling action persisted up to 975°C, and evidence of reverse motion of some of these particles was observed at 1075°C.

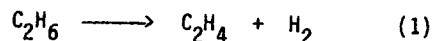
#### Discussion

The results of this investigation provide an excellent example of how catalyst particle size can have a profound effect on the selectivity of a reaction. When iron/graphite specimens were heated in ethane/steam to temperatures of 1025°C or higher, a range of catalyst particle characteristics was observed. Large particles (>50 nm diam.) slowed down in their forward channeling motion, a feature which became more pronounced as the temperature was raised to 1100°C; intermediate sized particles (30 to 50 nm diam.) lost their catalytic activity; and small particles (<30 nm diam.) exhibited a reversal in catalytic action, becoming catalysts for carbon deposition. In order to understand these features we must first consider the chemical state of the catalyst and that of the ambient gas.

Mossbauer spectroscopic studies of iron/graphite samples, treated in 1 atm. flowing ethane/steam (40:1) at 900°C, indicate that under these conditions iron is present as  $\gamma$ -Fe, which

remains thermodynamically stable up to the highest temperature used in the present study. It is, therefore, extremely doubtful that phase changes in the catalyst account for the various observed modifications in particle behavior. It is more likely that these various events are the result of a competition between two catalytic mechanisms; hydrogenation of graphite and carbon deposition.

At temperatures below 975°C, it is probable that under the present conditions the prevailing carbon-gas reaction is steam gasification. Above 975°C, the composition of the gas phase undergoes a significant change due to the increase in the rate of ethane decomposition, reaction (1)



As a consequence, sufficient ethylene and hydrogen are produced so that the gasification reaction is now controlled by catalytic hydrogenation and the concentration of unsaturated hydrocarbons is raised to a level where a potentially carbon depositing environment is created with respect to small iron particles.

The ramifications of this situation can best be understood from a consideration of the manner by which the kinetics of catalytic hydrogenation of graphite and catalytic carbon formation vary with metal particle size. The rate of the catalytic hydrogenation reaction increases with the square of the particle size, which points to a surface controlled process.<sup>4</sup> In contrast, the rate of catalytic carbon formation reaction is inversely proportional to the particle size, suggesting that diffusion of carbon through the particle is the rate limiting step.<sup>5</sup> Consistent with this notion is the fact that the measured activation energy for channel reversal, 32.5 kcal. mole<sup>-1</sup>, is in close agreement with the value for diffusion of carbon through  $\gamma$ -Fe.<sup>6</sup>

Addition of a small amount of  $\text{H}_2$  to the  $\text{C}_2\text{H}_6$ - $\text{H}_2\text{O}$  mixture would be expected to enhance the rate of the catalytic hydrogenation of graphite at the expense of the carbon formation process. Consistent with these arguments was the finding that in a (95%  $\text{C}_2\text{H}_6$ -5%  $\text{H}_2$ ):  $\text{H}_2\text{O}$ ; (40:1) environment higher temperatures were required to induce the onset of the channel reversal phenomenon.

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