Monolayer Channelling Mechanism in the Platinum Catalyzed Graphite-Hydrogen Reaction

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Introduction

The catalyzed and uncatalyzed carbon-hydrogen reaction is an improtant reaction. Its application in the direct production of synfuels is obvious but possibly even more important is its application into the basic research of all catalyzed hydrogenation and dehydrogenation reactions. The powerful tool of Etch Decoration Transmission Electron Microscopy (EDTEM) coupled with the well defined structure and properties of graphite makes up an ideal system from which information on the molecular level may be attained. Baker (1) and Keep (2) have used controlled atmosphere electron microscopy to study the catalyzed hydrogenation of graphite observing deep channels cut by particles originating at the edges. Using EDTEM it has been found that catalyst particles can start channeling from monolayer steps and from single vacancies on the graphite surface. Without etch decoration this channeling cannot be seen making continuous viewing of this event in a CAEM not possible.

Experimental

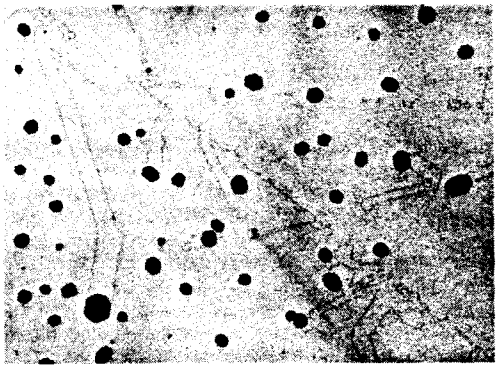
The EDTEM technique is explained in many references (3,4). In the experiments performed the crystals (natural graphite from Ticonderoga N.Y.) are cleaved to a thickness of approximately 700 A and placed on a glass slide. A 100 mesh slotted EM grid is placed on top of the samples and then 500 A of platinum (99.99% pure) is evaporated at a vacuum of better than 2 x 10^{-6} torr. The EM grids leave the samples striped with platinum rather than one continuous layer, leaving area for which signs of hydrogen spillover may be checked. The samples are then placed onto saphire plates, put in combustion boats, and placed inside a quartz reactor with hydrogen flowing through it. The samples are heated in hydrogen up to 500°C and flushed at this temperature for two hours. The hydrogen is then switched to helium and flushed six more hours at 650°C. The temperature is then raised to the reaction temperature and allowed to stabilize. The helium is swiched with hydrogen for the reaction time and then switched back. The reactor is turned off and the split tube furnace is opened to cool the sample rapidly. It takes approximately 5 minutes to go from 900°C to 200°C.

The gases used in the experiments are ultra high purity hydrogen with a minimum purity of 99.999% and high purity helium with a minimum purity of 99.995%. Both supplied by Linde Division of Union Carbide Co. The gases are further purified by passing through a liquid nitrogen trap filled with activated carbon.

Experiments using only helium up to the reaction temperature were found to have no reaction.

Results and Discussion

Experiments were conducted at 700°C, 800°C, 850°C and 900°C. No reaction was found at 700°C or 800°C. At 850°C and 900°C channeling was found. It is known from expereiments performed in this laboratory that pits will be formed by the uncatalyzed hydrogenation at 850°C and up but that the rate is low enough, to make the effect of this reaction negligible. Figures 1 and 2 show the particle shape at 850°C with 45 min. reaction time. Notice the faceting of particle orientation along the <10 1 0> or <11 2 0> directions of the basal <0001> plane. Figure 1 shows that a step in the basal plane is a very reactive site as reported by others (1, 2) and also confirms their observations that channeling does not commence until 845°C for platinum and that large particles channel faster than small particles. Note that channeling does not have to start at a deep step in the graphite and is most likely starting at the vacancies in the basal plane. The channeling is observed not to change its level, thus for the channels originating at vacancies it is likely that they are monolayer in depth. This is confirmed by the observation that when two vacancy originated channels meet there is no step transition thus they were channeling on the same level. Figure 3 shows the particles at 900°C with 30 minute reaction time. The channeling is becoming more orientated along the <10 $\bar{1}$ 0> or <11 $\bar{2}$ 0> directions. Figures 4 and 5 illustrate a phenomena occuring at 900°C where particles formed hexagonal pits. This was found on all 900°C samples. It is not possible that atomic hydrogen produced from spillover is the cause because no pits could be found without a particle inside of them. Atomic hydrogen at 717°C reacts with the basal plane of graphite at a turnover frequency of r = 32.6 $(sec)^{-1}$ (5). Uncatalyzed hydrogenation of the basal plane at 900°C has a turnover frequency of r = .34 $(sec)^{-1}$. The pits found in this experiment at 900°C correspond to a turnover frequency of r = 2.6 $(sec)^{-1}$. If hydrogen "spillover" existed then the size of the pits found would be much larger and many pits without platinum particles inside of them would be found. This does not occur suggesting that atomic hydrogen does not exist on a clean basal plane. Boudart (6) reports that in the platinum catalyzed hydrogenation reaction the carbon-carbon bond breakage is the rate determining step and that platinum acts to lower the activation energy for this step suggesting the reaction is occuring at the platinum-carbon interface. It is known that catalyst particles exert a vapor pressure across the support with the pressure being highest closest to the particle. This phenomena of atomic emmision is believed



1μm

Fig. 1. 850°C, 45 min. reaction

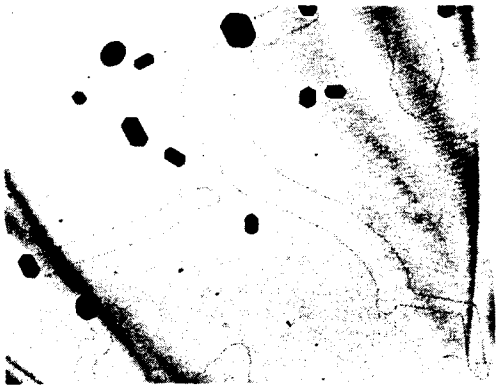


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Fig. 2. 850°c, 45 min. reaction

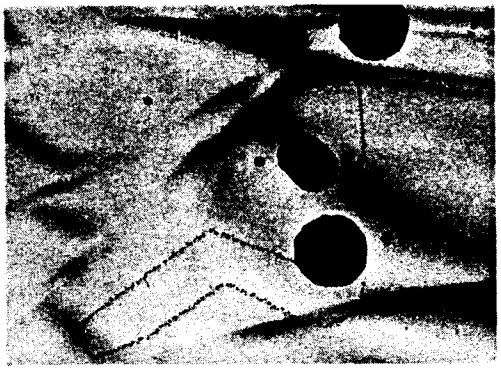

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Fig. 3. 900°C, 30 min. reaction

to be the mechanism by which the pits are formed. Some particles are found to start channeling after they have produced this hexagonal channel. This is evident by the tail of the channel being hexagonal at its end. At 900°C many particles are found to pit two or three layers deep suggesting that the reaction is starting to facilitate removal of carbon atoms from the highly stable lower basal plane. It is

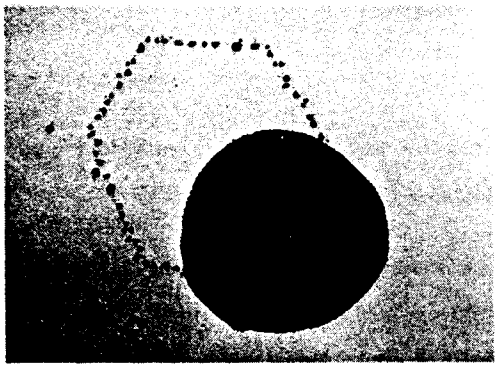

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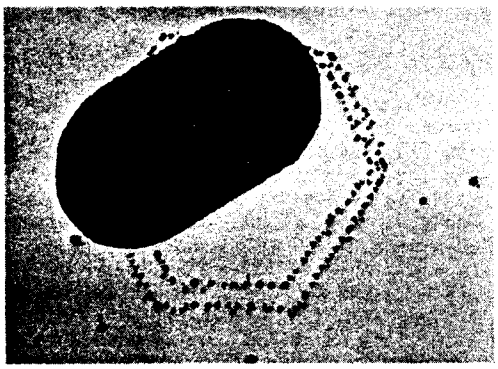
Fig. 4. 900°C, 30 min. reaction



1μm

Fig. 5. 900°C, 30 min. reaction

unlikely that lower basal plane vacancies are the cause for this due to its large degree of occurance compared to the 850°C samples. This high temperature monolayer channeling is very interesting and it is planned to research a greater temperature range along with more of the group VII metals in the future.

References

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