Structure Changes During Carbon Methanation Reactions

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1. INTRODUCTION

The reaction of carbon methanation on graphite surfaces containing platinum particles was studied using electron microscopy, gas chromatography and thermogravimetry. In the electron microscope, the weak beam thickness fringes (1) and topographic refraction images(2) were used. In addition the STEM microdiffraction technique to obtain crystallographic information from individual particles (3) was employed.

2. ACTIVITY RESULTS

Figure 1 shows the results for the activity for methane production as function of the temperature. Below 700°C the methane concentration is undetectable. It starts to increase at this temperature and a maximum is obtained at 800°C. At 850°C the reaction approaches the thermodynamic equilibrium and the concentration is reduced. However at 900°C it increases again. The TEM showed that at this temperature channeling on the graphite surface starts to be produced.(3) Below this temperature the particles produced only pits in the surface.. Figure 2 shows a topographic image of the channels. Irregular large particles are extremely active in this reaction since they produce large channels and therefore remove more carbon from the surface. The weak beam image picture shows that the particles are very rough in shape. They

are flat platelets with a thickness of about 100 Å. A typical example is shown in Figure 3. It was found that well faceted particles did not produce any channeling and therefore they were inactive for the reaction. Particles in the size range below 100 Å produced regular channels moving along <1150> directions of the graphite in most cases, in agreement with the findings of Baker et.al[3] and Tomita and Tamai[4]. However large irregular particles produced irregular channels not oriented along specific directions. The channeling always started along edges or steps on the graphite surface. The activation energy and reaction rate was determined by chromatography in the 700-800°C range and by thermogravimetry in 800-900° interval. The reason for this was that at high temperatures, the methane was decomposed in the post-reaction zone, producing an error in the chromatographic measurements. The values found were 43.5±4 KCal/mol and 0.0415 gr(CH_4) / hr gr(PT) for the activation energy and reaction velocity respectively in the 700-800°C interval and 44.0±4 KCal/mol and 0.026 gr(CH_4) / hr gr(PT) for the 800-900°C interval. These results suggest that the reaction mechanism is the same for the whole range of temperatures. Microdiffraction experiments indicated that particles had an FCC structure corresponding to a cubo-octahedron. However in many cases a complex pattern was obtained not corresponding to an FCC structure. This was probably a carbide or an oxide. It was not possible to identify this phase univocaly and more experiments are being carried out. The reaction appears to be produced on the interface Pt-graphite and is always related to pitting or channeling. The rate determining step seems to be the break of the C-C bond on the graphite surface. The main rate of the catalyst is to reduce the activation energy for the breaking of the C-C bond. The ability of the particles to remove carbon seems to be related to its surface roughness.

REFERENCES

1. M.J. Yacaman and T. Ocana, Phys. Stat. Sol. A) 42, 571 (1977).
2. A. Gomez, P. Hernandez and M.J. Yacaman, Surf. and Interf. Anal. 4, 120 (1982).
3. R.T.K. Baker, R.D. Sherwood and J.A. Dumesic, J.Catal 66, 56 (1980).
4. A. Tomita and Y. Tamai, J. Catal. 27, 293 (1972).

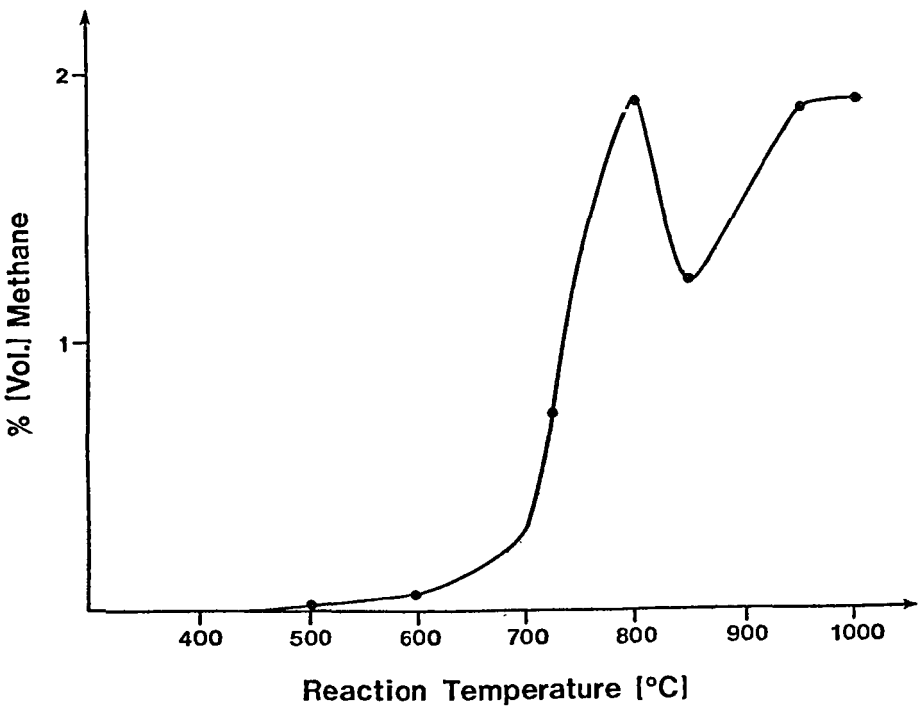

Figure 1. Concentration of methane as a function of the temperature.

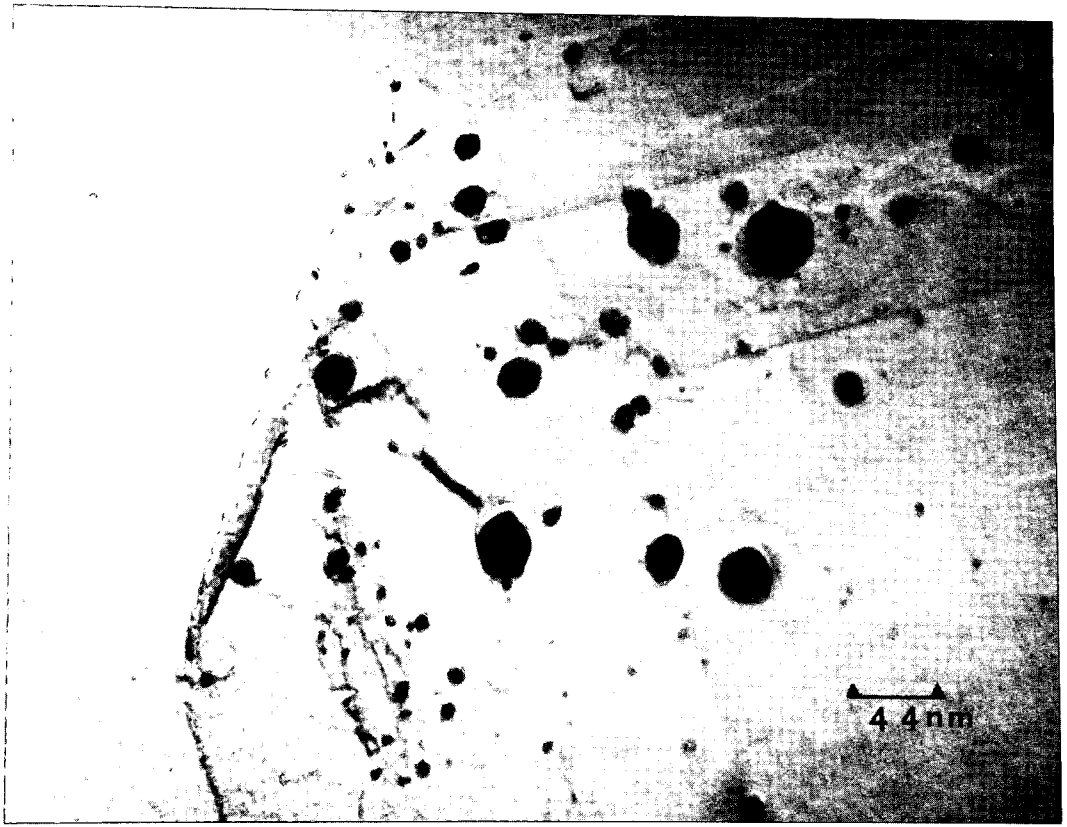

Figure 2. Topographic image of channeling in graphite surfaces.

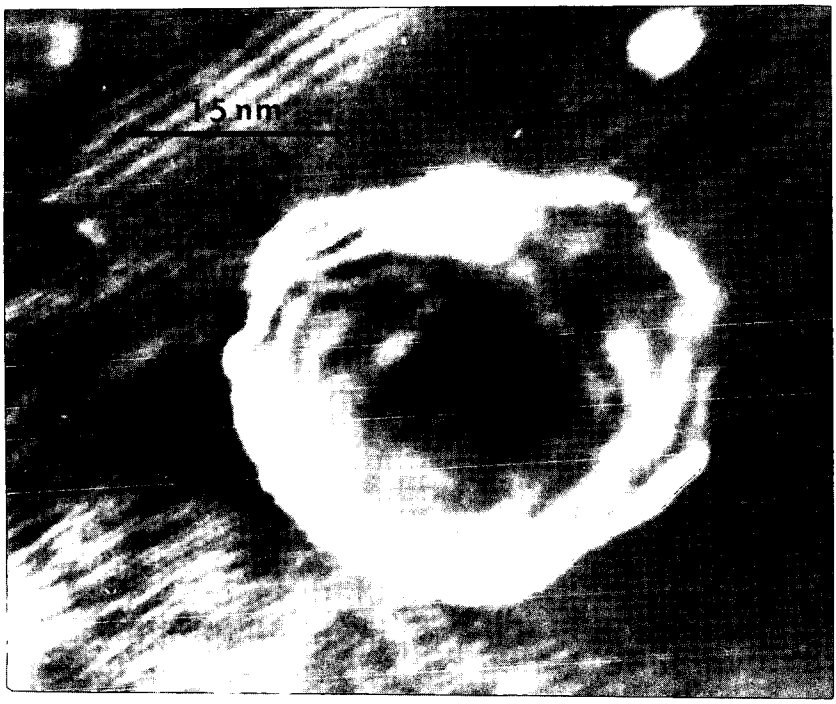

Figure 3. Weak beam image of a large particle showing rough surfaces.