

FORMATION OF CARBON FROM METHANE - TETRACHLOROMETHANE MIXTURES IN WIDE TEMPERATURE RANGE

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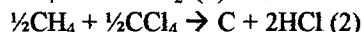
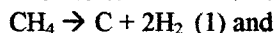
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Introduction

The decrease of the Gibbs free energy of the reactions :



are quite different. For the reaction 1 the Gibbs free energy approximately changes from zero to -100 kJ/mole as the temperature rises from 1000 K to 2000 K. For the reaction 2 the same changes of the Gibbs free energy are locate in the range from -225 kJ/mole to -350 kJ/mole. So we can anticipate that the second reaction is more active, and it was noted by number of authors that in chlorine presence the carbon formation is more intensive. [1 - 3]

Experimental

Precipitation of the carbon films were learned in a vacuum chamber of the flow type with cold wall. The graphite supports were heated by direct passage of electric current. The construction of the unit allowed to control the temperature, pressure, composition of the reactionary mixture and contact time. The deposition rates were measured for different conditions. Simultaneously such properties of the obtained pyrolytic carbon as density, chemical composition, crystallite dimensions, electric resistance were tested.

Results and Discussion

As the reaction (2) is really very fast, it was necessary to determine the border condition which under the carbon formation is observed not only on the support surface but also in volume. (Carbon black formation) The maximum inclination to the carbon formation in volume the system shows for the CCl_4 concentration about 70 mol %. (See Figure 2) The same composition corresponds to the maximum rates of carbon growth. (See Figure 1) It can be explained from assumption about two principal ways of carbon formation - homogenous and heterogeneous. Between these two extremes there are a

wide area of homogenous-heterogeneous ways, where formation of intermediates occurs in the gas phase with consequent growth of carbon on the hot surface.

CCl_4 is a substance which is able to dissociate into free radical CCl_3 and Cl under high temperatures. It occurs easier than dissociation of CH_4 . In addition to CCl_3 is remarkable for its activity and is able to form the intermediates through chain radical processes. For development of such processes concentration of CCl_4 have to be quiet high. But if the concentration is too high it leads to perchloroethane. The formation of last were observed on the cold parts of the reactor.

At temperature 2300°C it was observed etching of the graphite support instead of deposition of carbon. Apparently at such high temperatures HCl , which is another product of the process, is completely dissociated into H and Cl . Due to existing of these radical particles the etching of the graphite surface takes place.

At 2150°C the decrease of HCl formation was observed. In this case we meet transition area where along with the carbon growth the etching starts.

Figure 3 shows variation of the density throughout the composition of the reaction mixture for different temperatures. For high temperatures (>1950°C) the density does not depend on the CCl_4 concentration and is above 2.1g/cc. For intermediate and low temperatures the density of the material varies with the CCl_4 concentration remarkably. The lowest density was observed for concentration CCl_4 about 70 %.

The results of X-ray diffraction analysis are presented at the Figure 4. The main factor which determines crystallite structure is the synthesis temperature. Nevertheless for temperatures 1200°C - 1600°C it was noted some increasing in interlayer space (d_{002}). for the reaction mixture compositions which give the highest carbon growth rate. An unusual crystallite form ($L_c > L_a$) was found for intermediate and high temperatures. It can be explained by assumption about the etching of the crystallite edges.

Conclusions

Rates of growth and properties of pyrolytic carbons were determined for wide range of conditions. Existence of CCl_4 provide high rates of grows at low temperatures and unusual form of crystallites for high temperatures.

References

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- Cullis CF, Manton JE, Thomas JB, Wilman H. The structure and crystal growth of carbon deposits formed by pyrolysis of some hydrocarbons and chlorohydrocarbons. Acta Cryst. 1959; 12:382-384.
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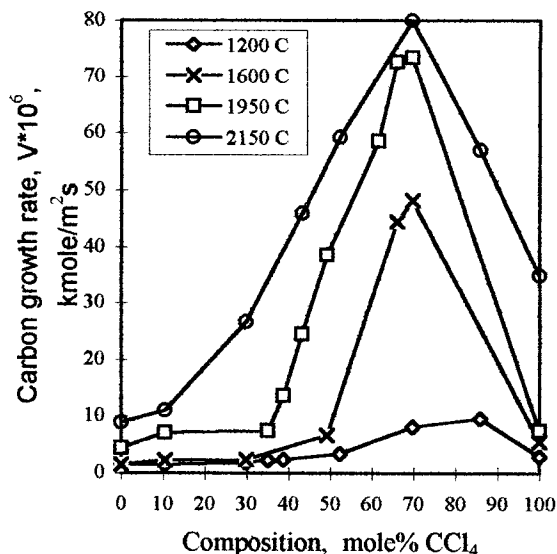


Figure 1. Dependence of the rate of carbon growth on the composition of the reaction mixture. ($P = 0.9$ kPa)

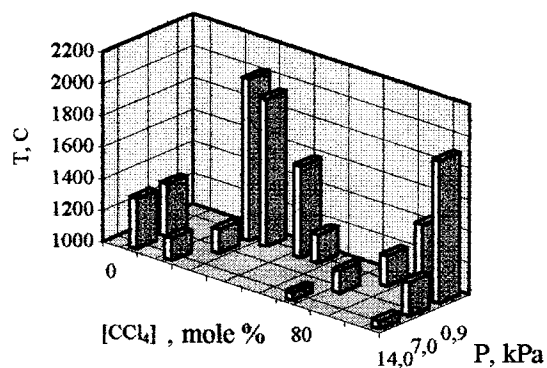


Figure 2. Limit conditions of the carbon black formation.

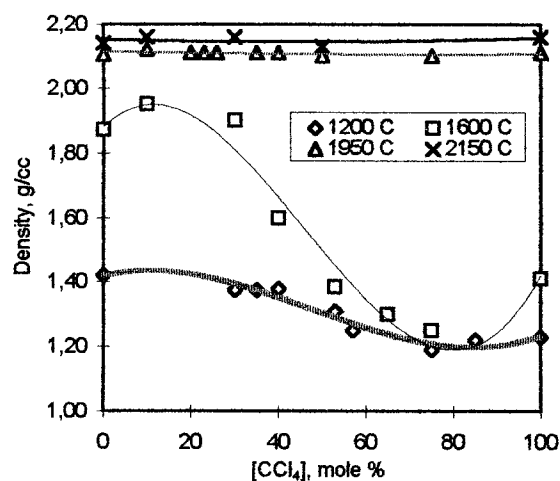


Figure 3. Picnometric density of the pyrolytic carbons synthesised in different conditions.

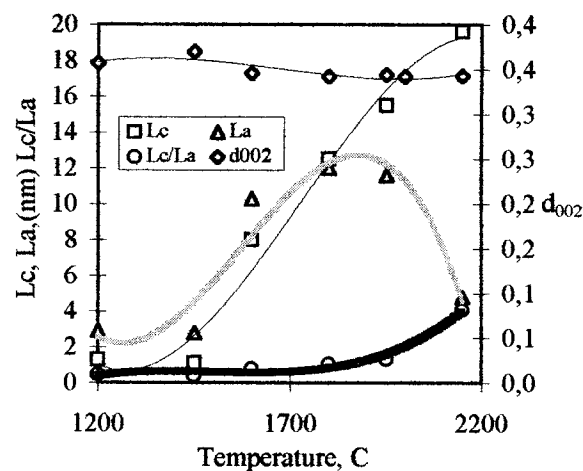


Figure 4. Crystallite sizes (L_c , L_a) and interlayer distance (d_{002}) from X-Ray diffraction data