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Catalysis Today 24 (1995) 265–267

CATALYSIS TODAY

Morphology of carbon from methane on nickel-containing catalysts

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Abstract

High-resolution electron microscopy (HREM) and X-ray techniques were used to study the reasons for the various morphology and structure formations of filamentous carbon from methane on Ni-containing catalysts.

1. Introduction

It is agreed that carbonaceous deposition on catalysts is a harmful process and serious attempts have been made to suppress this process. Today catalytic carbon is in great demand as a valuable material. Material properties depend on the morphology and structure of carbon.

Metals of the iron subgroup are known as the most active catalysts for carbon formation [1]. The carbon formation follows a carbide cycle mechanism and consists of two steps [1,2].

The first step is the formation of carbon atoms through an intermediate carbide-like compound. The second step includes the topochemical formation of the graphite phase from carbon atoms.

Metal particles of 50–500 Å diameter initiate the growth of the carbon filament. The key step in the mechanism of the carbon filament is believed to be the carbon atoms diffusion through the particle. The faces of Ni crystal exhibit different properties and functions at the carbon formation: (100) and (110) faces initiate catalytically the carbon atoms generation from methane, while the (111) face accounts for carbon building of graphite structures [3,4]. Here we would like to elucidate the factors governing the morphology and structure of the graphite phase.

2. Experimental

Ni/MgO and Ni–Cu/MgO catalysts were used to study the carbon formation. The catalysts were prepared by a new mechanochemical activation method of oxide and hydroxide metal powders. Catalysts were usually reduced by hydrogen (99 vol.-% pure) during a 20–30 min heating to 823 K. Methane was 99.92 vol.-% pure. The kinetics of carbon formation from hydrocarbons was studied in a flow quartz reactor equipped with a Mac-Ben balance at 800–873 K. HREM studies of carbonized catalysts were carried out on a JEM-100 CX device. X-ray diffraction analysis were performed on a D-500 (Siemens) diffractometer using CuK_α monochromatic radiation.

SSDI 0920-5861(95)00040-2

3. Results and discussion

Carbon filaments have various structures. With nickel, the shape of catalytical particles is well-faced (Fig. 1).

Face (100) Ni is orientated to the direction of filament growth. (111) faces form a pyramid with a vertex opposite to the direction of the filament growth. Carbon filaments consist of coaxial cone-shaped (002) graphite layers, which were aligned parallel to the direction of the metal–carbon interface.

The concentration gradient provides carbon diffusion across the nickel crystal. The carbon concentrations on the front side faces of the catalyst particles were close to that of carbon in Ni_3C. The carbon concentration on (111) faces on the opposite side of the particle were equal to that of the saturated solution of carbon in nickel.

Kinetic studies of carbon formation from methane on Ni/MgO and Ni–Cu/MgO catalysts have shown a decrease of carbon rate formation upon copper addition. Since the rate of carbon filament formation decreases, the process of carbon atom aggregation becomes more ordered. The tendency of carbon atoms to aggregate in the graphite on the (111) face of Ni–Cu alloy becomes more pronounced. When copper content increases, the lattice parameter of Ni–Cu alloy grows and the crystallographic similarity of the (111) alloy and the (002) graphite faces becomes more precise.

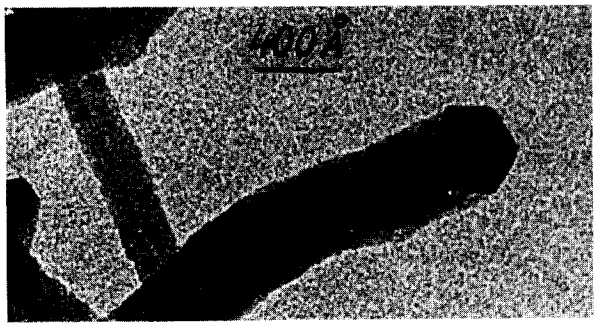

Fig. 1. A micrograph of the carbon filaments obtained from methane on Ni/MgO catalyst at 823 K.

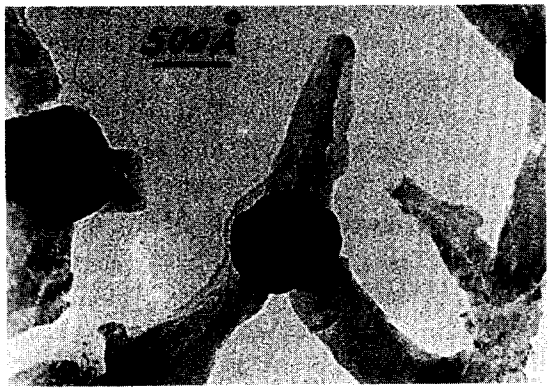

Fig. 2. A simultaneous growth of carbon filaments on several (111) faces of Ni–Cu alloy.

From the electron microscopic data, a 1 min carbonization of Ni–Cu/MgO catalysts in methane provides the formation of carbon filaments containing a metallic particle at the end. The shape of the metallic particle is usually flattened and well pronounced. The diameter of the metallic particle exceeds that of the filament. Selective area diffraction (SAD) proves that the (111) face is the most developed in the metal structure. This face is perpendicular to the direction of the filament growth and contacts with (002) planes of graphite. Unoccupied side (100) faces, which have no contact with carbon, appear to be centers for methane decomposition.

Carbon forms simultaneously on two opposite (111) faces of the flattened alloy particle, thus providing the appearance of ring filaments with a metallic inclusion. In some cases carbon releases simultaneously on three (111) faces of Ni–Cu alloy and initiates the carbon filaments formation in three directions (Fig. 2).

Electron micrograph data show that the structure of these filaments contains (002) graphite layers directed perpendicular to the filament growth. When filamentary carbon forms from methane on nickel–copper monocrystal, nickel is removed to the filament, and copper enriches the alloy; monocrystal fragments providing a polycrystal structure.

4. Conclusion

The study performed permits control of the morphology and structure of carbon filaments from methane on Ni-containing catalysts.

5. Acknowledgement

We gratefully acknowledge the support of the Russian Foundation for Fundamental Research (Grant No. 94-03-08379[a](440) for this work.

6. References

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