ELSEVIER

Journal of Molecular Catalysis A: Chemical 158 (2000) 267–270

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Symmetric twisted carbon filaments formed from butadiene-1,3 on Ni–Cu/MgO-catalyst: growth regularities and mechanism

V.V. Chesnokov, V.I. Zaikovskii, R.A. Buyanov *

Boreskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5, Novosibirsk, 630090, Russia

Abstract

High-resolution electron microscopy has been used to study the regularities of formation of symmetric helical carbon filaments from Ni–Cu/MgO-catalyzed butadiene-1,3 decomposition at 450°C. Dissymetrical spirally twisted carbon filaments have been shown to grow from a single Ni–Cu alloy particle. As the filaments grow, a microphase of metastable nickel carbide Ni_3C forms on the particles' frontal side, whereas the crystal particle of Ni–Cu alloy possesses a series of twinning planes (111) that is parallel to the dissymmetry plane of the crystal and separates the blocks of twins with a face-centered structure. The mechanism of symmetric helical filamentous carbon growth has been suggested. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carbon; Filament; Nickel; Copper; Alloy

1. Introduction

Until recently, carbon deposition on catalysts was considered as a harmful process and a lot of effort was focused on the process suppression. At present, however, catalytic carbon is in large demand as a valuable material. The properties of this material depend on the carbon morphology and structure.

Formation of straight carbon filaments, as well as ''octopuses'' produced when one metallic particle initiates the growth of several variously directed filaments, has received sufficient study [1–5].

However, the reasons for the formation of twisted carbon filaments are still unclear. Earlier, the twisted carbon filaments or bi-filaments have been observed to form from acetylene on Fe/Sn alloy at temperatures > 1073 K [6]. Single catalytic Fe/Sn alloy particle initiates simultaneous growth of two filaments in opposite directions. These ''corkscrew'' filaments grow at similar rates and symmetrically reproduce all growing fragments.

In the present work, we discuss the causes and regularities of the formation of carbon helical filaments from butadiene-1,3 on the particles of Ni–Cu alloys.

* Corresponding author. Fax: +7-3832-3430-56.
E-mail address: buyanov@catalysis.nsk.su (R.A. Buyanov).

1381-1169/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(00)00088-1

2. Experimental

Reduction and carbonization of the Ni–Cu/MgO catalyst were carried out in a reactor equipped with a quartz balance. The catalyst was reduced in a hydrogen flow and carbon depositing was performed in the medium of butadiene-1,3 diluted with argon and hydrogen at molar ratio C_4H_6:Ar:H_2 = 2:40:75. To study the processes that occur during the growth of carbon filaments on 72%Ni–16%Cu/12%MgO catalyst, we varied the time of carbon deposition on the catalyst at 723 K. Initial catalyst and samples with various carbon contents (weight ratio C/Cat = 0.75; 5, and 28) were studied using high-resolution electron microscopy (HREM) and X-ray diffractometry (XRD).

We have used a high-resolution electron microscope JEM-2010 (Japan) at a lattice resolution of 1.4 A and accelerating voltage of 200 kV. Goniometer has been used to obtain the crystals' images of required orientations. X-ray measurements were performed using URD-63 (Germany) diffractometer equipped with graphite monochromator and operated at CuK_α irradiation.

3. Results and discussion

According to the XRD data, after reduction in hydrogen atmosphere catalyst Ni–Cu/MgO predominantly contains alloy Ni–Cu of cubic structure and phase MgO.

After carbon depositing on Ni–Cu/MgO, the formation of unusual twisted filamentous carbon forms was observed. Fig. 1 shows a typical micrograph of carbon dissymetrical filaments twisted spirally and originating from the same metal particle.

The studied spiral filaments typically ranged from 300 to1000 Å in thickness and up to 1 μm in length. HREM micrographs of metal particles, on which filamentous carbon grows, show that the particles possess almost symmetric oval shape with the plane of principal symmetry in

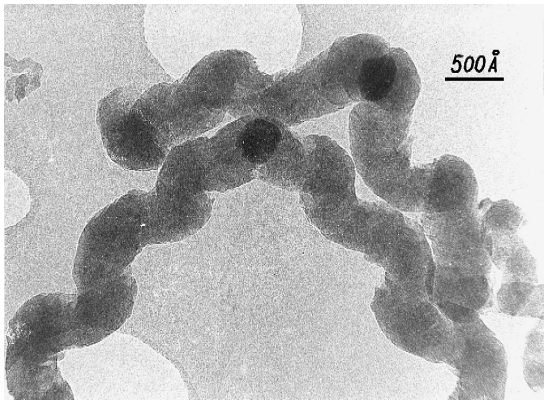

Fig. 1. Catalyst Ni–Cu/MgO, containing 2800% of carbon. Dissymetrical carbon filaments growing from the same particle of Ni–Cu alloy.

their middle part and consist of multiple twins. Frontal surface patch at the center of oval metal particle bears microparticles of 10–15 Å thickness and 30–50 Å length. Such microparticles have been shown by HREM to possess a structure of hexagonal nickel and constitute exactly the active zone where the catalytic process occurs.

Crystal particles of Ni–Cu alloy have a set of twinning planes (111), which is parallel to the principal symmetry plane and separates thin (about 20 Å and smaller) flated twin-blocks of face-centered structure. The HREM patterns show that visible interplanar distances in each twin-blocks equal d_{111} = 2.03 Å and d_{002} = 1.7 Å. Twinning planes group under the microphase particle on the frontal side; other locations are rare. In catalyst with C/Cat ratios of 20–50, the width of metal twin-blocks usually exceeds 20 Å.

At the reaction beginning the twins repetition, frequency is much higher. The micrograph of Ni–Cu/MgO catalyst, on which carbon was deposited for 10 min, revealed the period of twinning boundary occurrence to be around 4 Å (Fig. 2). Only three closely packed layers of atoms of face-centered metal lattice with interplanar distances d_{111} = 2.03 Å fall on this space. As a result, the crystallographic sequence of close-packed planes in this extreme case will be

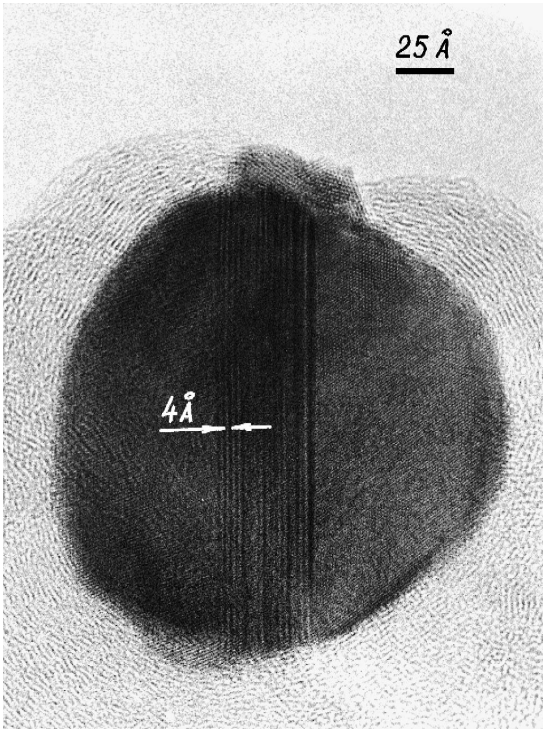

Fig. 2. Catalyst Ni–Cu/MgO, containing 75% of carbon. Middle part of Ni–Cu alloy particle contains twinning boundaries repeated at an interval of ~4 Å. Sequence of closely packed layers corresponds to alternating hexagonal and cubic alloy structures.

ABCBABCBABCBA, which corresponds to the hexagonal polytype structure.

We suggest the following mechanism for the formation of symmetric carbon filaments from the decomposition of butadiene-1,3 over Ni–Cu/MgO catalyst at 723 K. In the induction period, decomposing butadiene-1,3 produces carbon and hydrogen atoms. Carbon atoms diffuse into the bulk of Ni–Cu alloy and gradually oversaturate it. As the critical oversaturation is achieved and the crystal graphite-nucleating centers appear on the surface of alloy particle, carbon atoms quickly diffuse to these centers from the bulk of alloy. Planes (111) of Ni–Cu alloy are the most preferable for the graphite phase nucleation since graphite plane (002) and alloy plane (111), which determine the direction of filament growth, are similar in symmetry and inter-atomic distances. At the same time, the metastable microphase Ni_3C forms on the frontal side of the alloy particle (Fig. 3).

Since the frontal zone of the metal particle is highly oversaturated with carbon, intensive diffusive flow of carbon atoms towards crystallization centers in graphite phase occurs. Fast diffusion of carbon atoms intensifies generation of defects in Ni–Cu alloy. The alloy, keeping solid state, becomes viscous-flow. This allows the Ni–Cu alloy particle to acquire the most energetically efficient spherical shape. However, diffusive flows of carbon atoms cause dislocation of metal atoms and thus distort the spherical shape of the particle, making it elongated (Fig. 3). This is when the regime of self-organizing the metal particle symmetric shape appears. As a result, metal particles take symmetric oval shape with a principal symmetry plane in their middle part. Besides, each symmetric piece is oriented so that the direction of its plane [111] coincides with the direction of the filamentous carbon growth.

Particle of microphase hexagonal Ni_3C on the frontal side serves as a nucleus for the growth (generation) of hexagonal structure within the viscous-flow catalytic Ni–Cu particle. Under reaction conditions, catalytic particles consist of alternating layers of cubic and hexagonal Ni–Cu alloy. Hexagonal Ni_3C [7] and metallic nickel [8] possess almost the same lattice constituted by Ni atoms (hexagonal super-close packing). In Ni_3C, carbon atoms occupy 1/3 of octahedral vacancies (voids) in the packing of metal atoms. The transfer of carbon

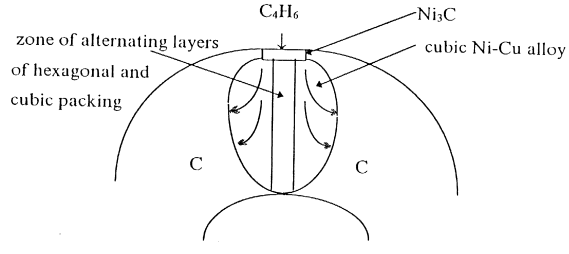

Fig. 3. Schematic diagram of the growth mechanism of helix filamentous carbon produced from butadiene-1,3 on Ni–Cu crystals.

atom through the metal hexagonal layer can be considered as the consecutive stages of carbide formation and decomposition continuously following one after another. However, moving away from the microphase of hexagonal Ni_3C, the saturation of hexagonal layers with carbon will decrease. Thus, during the reaction the layers of hexagonal metal most likely represent non-stoichiometric carbide of variable composition. This structure corresponds to the Ni–Cu–C phase existing only during the reaction run.

During reaction, the twinning planes transfer from the central zone of Ni–Cu alloy towards the crystal periphery. The driving force for the transfer of inter-block boundaries and transformation of respective structure is the diffusion of carbon atoms; besides, hexagonal Ni–Cu alloy is less stable than the Ni–Cu alloy with cubic structure.

Due to intensive flow of carbon atoms directed from the central part towards the periphery of the crystal (shown by arrows on Fig. 3), the layers adjacent to twinning planes acquire defects that cause the layers reconstruction. In other words, twinning plane starts to move in the same direction as the carbon atoms transfer towards the carbon crystallization center in the graphite phase. Thus, hexagonal plane inclusions, containing carbon and representing non-stoichiometric carbide of variable composition, scatter from the center of oval metal–carbon particles. Most likely, the layers' moving away from the central zone is filled up by their repeated generation by the microparticle on the surface of large oval particle, and the process is repeated many times.

Graphite filaments grow symmetrically and almost over the whole surface of Ni–Cu alloy particle. As seen on Fig. 3, different carbon atoms pass unequal diffusion ways from the places where they enter alloy particle through the nickel carbide microphase to different surface patches where graphite phase grows. This results in differing growth rates and filament twisting.

Acknowledgements

We gratefully acknowledge the support provided for this work by the Russian Foundation for Basic Research (Grant Nos. 96-15-97560, No. 99-03-32420a).

References

[1] V.I. Zaikovskii, V.V. Chesnokov, R.A. Buyanov, Appl. Catal. 38 (1988) 41.
[2] R.A. Buyanov, Chem. Sustainable Dev. 3 (3) (1995) 177, (in Russian).
[3] V.V. Chesnokov, V.I. Zaikovskii, R.A. Buyanov, V.V. Molchanov, L.M. Plyasova, Kinet. Katal. 35 (1) (1994) 146, (in Russian).
[4] R.A. Buyanov, V.V. Chesnokov, Chem. Sustainable Dev. 5 (3) (1997) 619.
[5] R.A. Buyanov, V.V. Chesnokov, J. Appl. Chem. 70 (6) (1997) 978.
[6] R.T.K. Baker, P.S. Harris, S. Ferry, Nature 253 (5486) (1975) 37.
[7] S. Nagakura, J. Phys. Soc. Jpn. 12 (5) (1957) 482.
[8] G. Carturan, G. Cocco, S. Enzo, R. Gauzerla, M. Jenarda, Mater. Lett. 7 (1988) 47.