



Effect of the carbon nanomaterials structure on silica carbothermal reduction



V.V. Chesnokov^{a,*}, V.S. Luchihina^{a,b}, I.P. Prosvirin^{a,c}

^a Borekov Institute of Catalysis, Novosibirsk, Russia

^b Novosibirsk State Technical University, Novosibirsk, Russia

^c Novosibirsk State University, Novosibirsk, Russia

ARTICLE INFO

Article history:

Received 10 July 2015

Received in revised form 6 October 2015

Accepted 6 October 2015

Available online 17 October 2015

Keywords:

Carbon nanotubes

Carbon nanofibers

Synthesis

Composite

Silicon carbide

ABSTRACT

“Carbon nanomaterial-SiO₂” composites were synthesized using carbon nanofibers (CNF) and carbon nanotubes (CNT). Oligomethylhydridesiloxane (OMHS) was used as the SiO₂ precursor. The CNT-SiO₂ composite was shown to be thermally stable up to 1100–1200 °C. The calcination temperature increase to 1300 °C resulted in segregation of the CNT-SiO₂ composite into individual components: CNT and SiO₂ particles. In distinction to CNT + SiO₂, the CNF-SiO₂ system showed stronger interaction of the amorphous silica film with the end faces of graphite terminating at the external surface of CNF. Calcination of the CNF-SiO₂ composite in an inert atmosphere at 1300 °C for 1 h did not lead to segregation of the components. Calcination of the CNF-SiO₂ composite in an argon flow at 1400 °C for 1 h changed the phase composition of the sample. Silicon diffused to the interplane layers of graphite. In addition, the formation of silicon carbide was observed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Nanostructural materials have unique mechanical, optical, electronic and other properties, and can be used for development of advanced processes. Such materials are widely applied in various fields of science and technology. Among the promising nanoobjects are the so-called whiskers, which are single-crystal structures having a high length-to-diameter ratio. Of special interest are SiC whiskers, which combine excellent physical and physicochemical properties: high chemical and corrosion resistance, semiconductor properties, and stability in oxidizing and reducing media caused by the covalence of the Si–C bond.

Silicon carbide synthesis in a nanocrystalline state makes it possible to significantly widen its application area [1–11]. The use of finely dispersed SiC powders leads to optimization of the process technological parameters, starting from lower energy consumption for production of ceramic goods at lower temperatures, and development of absolutely new technologies of materials. For example, it has been demonstrated that filamentous SiC crystals can be used for strengthening various matrices and production of materials with novel properties [12–21].

Several methods for synthesis of nanocrystalline silicon carbide are known. First of all, these are chemical deposition from the gas phase, plasmachemical synthesis and carbothermal reduction of finely dispersed SiO₂–C mixture prepared by sol–gel method in the presence of a polymer source of carbon [22–33]. Despite its apparent simplicity,

the thermal reaction between carbon and silicon dioxide is an aggregate of more than 20 different reactions and is a sequence of heterogeneous reactions.

Their rates are determined by both diffusional limitations and the surface of contacting phases. The key factors, which have maximum effect both on the interaction chemistry of contacting phases and on physicochemical properties of the final product, are the morphology of the starting materials and the method used to synthesize a mixture of the contacting SiO₂ and C phases.

Our study was performed with the carbon nanomaterials possessing radically different structures [34–36]: carbon nanofibers (CNF) with the octopus structure and carbon nanotubes (CNT). In these carbon nanomaterials the basal graphite planes are arranged either along the fiber axis (for carbon nanotubes) or across it (for carbon nanofibers), thus forming coaxial cylindrical (CC) and octopus (O) carbon structures (Fig. 1). The external surface of CNT is formed by the basal graphite planes. In the case of CNF, loose end faces terminate at its external surface. The graphite crystal is known to be highly anisotropic in two perpendicular directions, $\langle\langle a \rangle\rangle$ and $\langle\langle c \rangle\rangle$. The basal faces with the closest packing of atoms strongly differ in terms of energy from the loose end faces. The increased activity of the end faces contacting with the air results in their rapid saturation accompanied by the formation of surface functional groups that usually contain oxygen and hydrogen. In addition, it was found that interaction of a deposited metal with the carbon support depends on the faces terminating at the surface of the carbon nanomaterial [37]. The state of palladium deposited on carbon nanofibers with stacked structure

* Corresponding author.

E-mail address: chesn@catalysis.ru (V.V. Chesnokov).

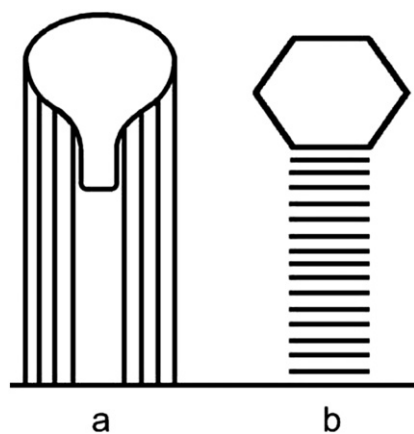


Fig. 1. Cross-section of carbon nanomaterials: a – carbon nanotubes; b – carbon nanofibers with octopus structure.

in a 0.04–0.5 wt.% concentration was studied by X-ray diffraction, transmission electron microscopy and extended X-ray absorption fine structure analysis. Palladium was found to exist as single atoms attached to CNF in the samples with Pd concentration 0.2 wt.% or less. So, it would be interesting to monitor the properties of CNF and CNT in carbothermal reduction of silica.

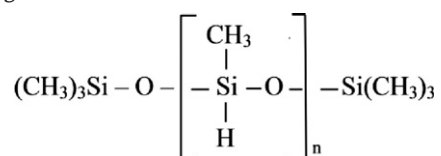
The present work is aimed to investigate how the structure of carbon nanomaterials affects carbothermal reduction of silica. A comparison of experimental data obtained in carbothermal reduction of the SiO_2 –C system with different forms of carbon will allow us to understand general regularities in the synthesis of silicon carbide materials and elucidate the mechanism of chemical interaction in this system.

2. Experimental

Carbon nanotubes (CNT) were synthesized on a Fe–Mo–Co– Al_2O_3 catalyst from a propane–butane mixture at 700 °C in a flow unit [38]. The electron microscopy analysis of the synthesized carbon nanotubes made it possible to estimate their average dimensions. The outer diameter of the nanotubes varied in the range of 7–26 nm with the predominant size of 8–12 nm. The CNT length reached 10^4 nm. The fraction of the carbon nanotubes with the indicated characteristics was close to 95%.

In addition to CNT, CNF with the octopus structure were used in the study. Carbon nanofibers with the octopus structure were prepared from methane on the Ni–Cu/ Al_2O_3 catalyst at 650 °C in a quartz flow reactor with a McBain balance and without temperature gradient. The predominant diameter of CNF with the octopus structure was 40–120 nm.

Oligomethylhydridesiloxane (OMHS) served as the SiO_2 precursor for silica deposition on the surface of carbon nanomaterials. OMHS has the following formula:



where n varies in the range of 4–80. The OMHS purity was 97 vol.%.

An important structural and compositional feature of oligoorganohydridesiloxanes is the presence of Si–H bonds capable of reacting with various functional groups of solid surfaces. Such bonds interact with the surface functional groups to form a thin siloxane film [39]. To create acid sites on the CNT surface and remove the residual catalyst used for the carbon nanotube growth, the samples were treated in a mixture of acids. The starting CNT were treated with aqua regia, heated to the boiling temperature of the solution, and stirred for

30 min. Then, the solution was decanted. The carbon nanotubes were washed with distilled water and dried in a muffle furnace at 120 °C for 30 min. OMHS was deposited from an alcohol solution. CNT (5 g) was coated with 40 mL of 10 wt.% OMHS solution in ethanol. The solution was evaporated by heating on a magnetic stirrer. The resulting OMHS–CNT composite was dried at 150 °C for 1 h. The CNT weight increased by ca. 35–40% after the OMHS deposition. The OMHS–CNT samples were then heated to 720 °C in a quartz flow reactor with a McBain balance with the mass change sensitivity of 1×10^{-4} g in an argon flow and calcined at the same temperature for 1 h. The use of a McBain balance made it possible to control weight changes directly during heating and calcination [40]. The main weight loss occurred during heating in the temperature range of 350–600 °C. After calcination at 720 °C, the silica content in the CNT– SiO_2 composite was ca. 15 wt.%. A similar method was employed for silica deposition on the CNF surface.

Calcination of the CNT– SiO_2 and CNF– SiO_2 composites was performed at 720–1450 °C in a corundum tubular flow reactor. For the heat treatment 5 g of each sample was poured into a graphite crucible that was placed into a corundum tube with the diameter of 20 mm. A silicon carbide heater was used in the furnace. During the heat treatment the reactor was slowly purged with argon.

X-ray diffraction (XRD) study of the samples was performed using a Siemens D-500 diffractometer with $\text{CuK}\alpha$ monochromatic radiation.

High-resolution transmission electron microscopy (HRTEM) images were obtained with a JEM-2010 (JEOL, Japan) microscope with a 0.14 nm lattice resolution. Local energy dispersive X-ray microanalysis (EDX) was carried out using an EDAX (EDAX Co.) spectrometer equipped with a Si (Li) detector with energy resolution of 130 eV.

The synthesized C– SiO_2 composites and their transformations during the high-temperature calcinations were examined by X-ray photoelectron spectroscopy (XPS). The spectra were recorded on a SPECS (Germany) photoelectron spectrometer with Mg $\text{K}\alpha$ radiation ($h\nu = 1253.6$ eV, 200 W). The binding energy (E_b) scale was preliminarily calibrated against peak positions of the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.67 eV) core levels. The samples were loaded on a double sided conductive copper tape (3 M, USA). The charging effect caused by photoemission of electrons was accounted for by the internal standard, which was represented by the C 1s line (284.5 eV) of carbon used as the support.

The relative content of elements on the catalyst surface and the ratio of atomic concentrations were found from the integrated intensities of photoelectron lines corrected for the corresponding atomic sensitivity factors: Si 2p – 0.865, C 1s – 1.0, O 1s – 2.85 [41].

Both the survey spectra and the individual spectral regions (Si2p, C1s and O1s) were recorded using pass energy of 20 eV.

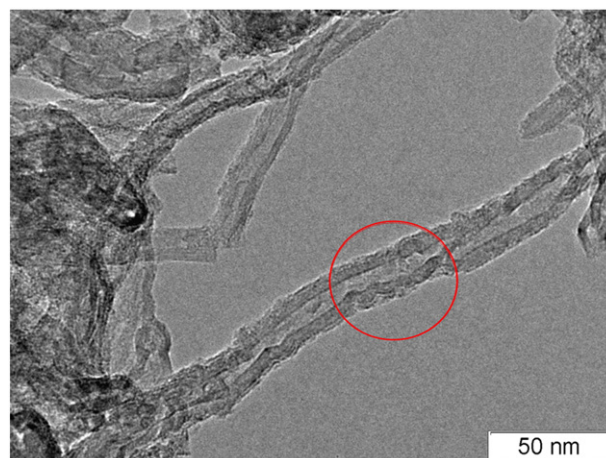


Fig. 2. TEM image of the CNT– SiO_2 composite.

Download English Version:

<https://daneshyari.com/en/article/701801>

Download Persian Version:

<https://daneshyari.com/article/701801>

[Daneshyari.com](https://daneshyari.com)