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Review

Review on synthesis, structure, physical and chemical properties and functional characteristics of porous silicon carbide

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ABSTRACT

The available literary data on the methods of obtaining, structure, sorption properties and functional characteristics of porous silicon carbide were analyzed and summarized. The features and prospects of using of porous silicon carbide in catalysis, adsorption, electrochemistry etc. were shown. Some general comments about the state and possible directions of development of the researches in the area of physical chemistry of porous silicon carbide were presented.

Contents

Introduction

Considering the fact that most of the catalytic reactions take place at high temperatures and in aggressive media, there is a necessity of creation of catalyst supports with high thermal stability and chemical resistance. The energy problems of the present initiate the development of an alternative energy sources and the use of solar energy for realization of catalytic chemical reactions particularly photocatalytic. This leads to the new requirements for materials of different functional purpose – high thermal, mechanical and chemical stability, high thermal conductivity etc. Silicon carbide has almost all of these properties, so it can be considered suitable as a basis of the efficient catalysts [1].

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Creation of stable highly efficient catalysts and supports of catalytically active substances is topical scientific and practically important task. In industry silica and aluminum oxide and carbon materials are primarily used as supports for most of catalytically active substances. The aforesaid catalyst supports have significant drawbacks, in particular, such as low resistance to oxidation at high temperatures (carbon supports), low thermal conductivity and the ability to sintering, which leads to a decrease of the specific surface area of catalytically-active system [2–4] (supports based on oxides of silicon and aluminum). Silicon carbide among the other material is distinguished by its unique physical and chemical properties, such as high thermal conductivity, chemical, thermal and mechanical stability, low coefficient of thermal expansion, resistance to phase transitions, semiconductor nature, high electron mobility, which together determines the possibility and prospects of its various practical applications [5,6].

The aim of the current paper is to analyze the scientific approaches and technological bases of creation of new nanoscale dispersed and porous materials based on silicon carbide for adsorption, catalysis, electrochemical applications etc., determine an influence of the structure type, morphology, porosity on adsorption, catalytic, spectral, mechanical properties, find new areas of application of silicon carbide.

Methods of obtaining of porous silicon carbide

Among the numerous modifications (polytypes) of silicon carbide (~200) [7] cubic 3C–SiC polytype (β-SiC) is considered the most stable (up to ca. 2100 °C) [8]. Primarily synthesis conditions (temperature, pressure, etc.) and the presence of impurities influence the formation of silicon carbide of the certain polytype [9].

Sublimation method (i.e., evaporation and condensation) first proposed by E.G. Acheson is used for growing of semiconductor single crystals of silicon carbide [10]. The method is based on the transport of the substance from the hot source (charge) to a seed with a lower temperature. Silicon carbide crushed powder is mainly used as a charge. Growth during the sublimation occurs at the temperatures 1800–2600 °C. This method was seemed to be suitable to produce abrasives and for growing of single crystals for semiconductor electronics. However, uncontrolled form- and structure formation (presence of a significant number of structural defects) of SiC crystal and their contamination with impurities restrict the use of silicon carbide obtained by the described method in electronics.

Lely method consists in evaporation of polycrystalline SiC at the temperature 1800–2600 °C and subsequent vapor condensation on random nuclei [11]. The large number of nuclei leads to the formation of excess of the small crystals, which does not allow the growing of the large crystals.

Obtaining of the bulk single crystals of silicon carbide became possible due to use of single-crystal seeds—so-called Physical Vapour Transport (PVT, LETI method) [12]. For suppression of spontaneous nucleation and formation of polycrystals condensation of supersaturated vapor on single crystals-seeds was carried out in an inert atmosphere. In order to gradually increase a rate of crystal growth an inert gas is pumped out from a cell.

The methods which allow to prepare porous SiC will be considered below.

For synthesis of silicon carbide different methods, including CVD-method (chemical vapor deposition), electrochemical etching, carbothermal reaction using carbon nanotubes and activated carbons, magnesiothermic reduction etc. are used.

For instance, pyrolysis of carbon particles impregnated with nickel compounds in $SiCl_4$ flow leads to the formation of silicon carbide which has the developed surface area (up to 100 m^2/g) and reproduces the form of the initial carbon [13].

Pyrolysis of organosilicas allows obtaining silicon carbide with high specific surface area (over 100 m^2/g) [14,15]. The obvious advantage of the mentioned method of synthesis of silicon carbide is the presence of Si—C bond in the initial precursors which solves the problem of small contact in the case of use of separate sources of silicon and carbon [16].

A lot of attempts to obtain porous silicon carbide with the developed surface area were done. The proposed various approaches and methods for synthesis of porous silicon carbide are presented in the table (Table 1).

Electrochemical etching of massive silicon carbide

Porous SiC layers obtained by electrochemical etching of corresponding massive material attract special attention. This is

Table 1
Methods of obtaining of porous silicon carbide. Q6

Methods of obtaining	Initial materials for synthesis	Features of obtained silicon carbide	S_{BET} (m^2/g)	References
Electrochemical etching	Massive silicon carbide	Intense luminescence at the room temperature because of the appearance of defect sites during the etching process	Not determined	[17,18]
"Shape memory synthesis"	Activated carbon or coke and gaseous silicon monoxide	Replication of the macroscopic form of carbon during the synthesis; presence of a large number of stacking faults; formation of amorphous layer (thickness of ca. 3 nm) likely of silicon oxycarbide	20–200	[16]
Carbothermal reduction	Carbon and silicon monoxide or silicon dioxide	Possibility of varying of porosity and morphology (particles, fibers, rods, etc.) of silicon carbide	up to ca. 500	[19–21]
Magnesiothermic reduction	Carbon, silica, magnesium	Possibility of varying of porosity of silicon carbide	up to ca. 450	[22,23]
Nanocasting using polycarbosilanes	Silica matrices, polycarbosilanes	Mesoporous spatially ordered structure	up to 800	[24,25]
Other approaches				
-Pyrolysis of organosilicas	-Ethylene-bridged organosilica mesophases	-Wide pore size distribution	up to 620	[26]
-Use of silicon powders	-Carbon and silicon powder	-Replication of the carbon structure during the synthesis; possibility of varying of porosity and morphology of SiC	up to 215	[27,28]

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