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Ordered mesoporous silicoboron carbonitride ceramics from boron-modified polysilazanes: Polymer synthesis, processing and properties

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ABSTRACT

Ordered two-dimensional (2D) mesoporous silicoboron carbonitride (SiBCN) ceramics were prepared by a nanocasting approach of a boron-modified polysilazane of the type $[B(C_2H_4SiCH_3NH)_3]_n$ ($C_2H_4 = CHCH_3$, CH_2CH_2) ($[Si_3B_{1.1}C_{10.5}N_{3.0}H_{25.5}]_n$) using mesoporous CMK-3 carbon as hard template. The polymer was synthesized according to a monomer route by hydroboration of $CH_2 = CHSiCH_3Cl_2$ followed by reaction of the as-made tris(dichloromethylsilylethyl)borane ($B(C_2H_4SiCH_3Cl_2)_3$ (TDSB, $C_2H_4 = CHCH_3$, CH_2CH_2) with lithium amide ($LiNH_2$). It was generated as a highly soluble compound which could easily impregnate mesoporous CMK-3 carbon. The derived $[B(C_2H_4SiCH_3NCH_3)_3]_n$-carbon composite was directly pyrolyzed in flowing nitrogen at 1000 °C to generate a SiBCN-carbon composite. The carbon template was subsequently removed through thermal treatment at 1000 °C in a mixture of ammonia and nitrogen to generate ordered mesoporous $Si_{3.0}B_{1.0}C_{4.2}N_{2.4}$ structures. XRD and TEM analyses revealed that the obtained amorphous mesoporous ceramic exhibits open, continuous, and ordered 2D hexagonal frameworks which are strongly dependent on the number of impregnation cycles and the carbon removal step. Using a double impregnation cycle combined with a pyrolysis process up to 1000 °C in flowing nitrogen and a carbon removal step at 1000 °C for 3 h in a volumetric flow ratio between ammonia and nitrogen of 1, the ordered mesoporous SiBCN ceramic displays high surface area ($630\ m^2\ g^{-1}$), high pore volume ($0.91\ cm^3\ g^{-1}$), and narrow pore-size distribution (around 4.6 nm) with a thermal stability which extends up to 1180 °C under nitrogen.

1. Introduction

Since their discovery [1,2], ordered mesoporous materials have attracted considerable attention due to their high specific surface area and narrow pore-size distribution for a wide range of current and emerging technologies such as catalytic supports [3], separation [4–7], chemical sensing [8–10] and more recently hydrogen storage [11]. Among fabrication processes, the nanocasting method which consists in replicating the nanoscale structure of hard template has been widely used to synthesize, organize and nanostructure many ordered mesoporous materials. The latter include carbon CMK-3 and CMK-8 [12–14], sulfides [15], oxides [16,17], metals as well as mesoporous metal oxides [18] by using either mesostructured silica or carbon as hard templates. Even if mesoporous hard templates suffer from several drawbacks such as inefficient filling of the mesopores by the precursor of the materials previously described and removal of the template by harmful etching reagents, they lead to ordered mesoporous materials in relatively high yield in comparison to other processes. More recently, studies were focused on the preparation of ordered mesoporous silicon- and boron-based ceramics such as nanostructured SiC [19,20], SiCN [21,22] and BN [23,24] by nanocasting preceramic polymers. This Polymer-Derived Ceramics (PDCs) route has become one of the most attractive solutions to produce ceramics with a controlled nanostructure and in the desired composition [25,26]. The final atomic structure is in fact designed by the molecular composition of the preceramic polymers which allows producing ceramics with high purity and complex compositions going from classical binary system such as boron nitride [27] and aluminium nitride [28] to complex compositions including four or more

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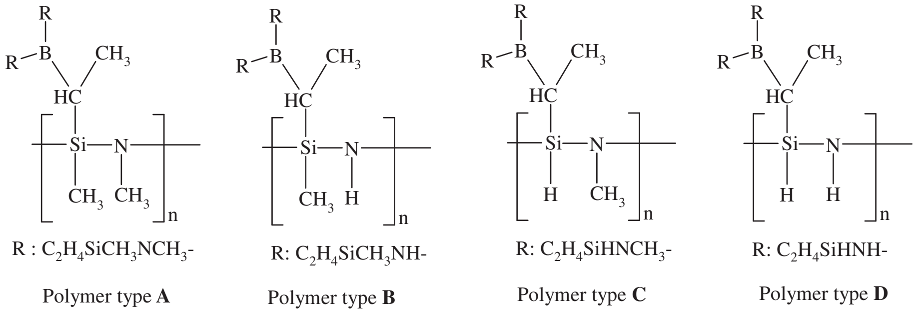

Fig. 1. Boron-modified polysilazanes of the type $[B(C_2H_4SiRNR)_3]_n$ (R = H and/or CH_3; $C_2H_4 = CHCH_3$, CH_2CH_2).

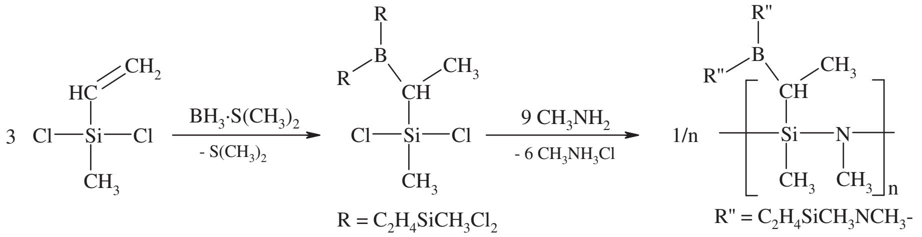

Fig. 2. Synthesis of boron-modified polysilazanes of the type $[B(C_2H_4SiCH_3NCH_3)_3]_n$ ($C_2H_4 = CHCH_3$, CH_2CH_2) by aminolysis with methylamine (**MA**) of tris-dichlorosilylethylborane (**TDSB**) of the type $B(C_2H_4SiCH_3Cl_2)_3$ ($C_2H_4 = CHCH_3$, CH_2CH_2).

elements [29]. The main motivation to implement the PDCs method lies in the special advantages offer by preceramic polymers in processing materials in particular shapes from 0D to 3D morphologies, difficult or even impossible to obtain by conventional routes [30,31].

In the end of the nineties, this procedure has been applied to develop Si–B–C–N systems from boron-modified polysilazanes (Fig. 1) [29,31–36].

The particular structure of these boron-modified polysilazanes which represent polysilazanes cross-linked by C–B–C bridges leads to solid solutions having unique physical and chemical properties (excellent thermal stability, better stability towards oxidation than silicon carbide), which make them appropriate ordered mesoporous ceramics for applications in harsh environment. Within this context, we recently reported the synthesis of ordered mesoporous SiBCN ceramics via preceramic polymer nanocasting using a boron-modified polysilazane of the type $[B(C_2H_4SiCH_3NCH_3)_3]_n$ ($C_2H_4 = CHCH_3$, CH_2CH_2, polymer type **A** in Fig. 1) [37].

We demonstrated that this highly soluble preceramic polymer, synthesized by reaction between tris((dichloro(methyl)silyl)ethyl)borane (**TDSB**) of the type $B(C_2H_4SiCH_3Cl_2)_3$ ($C_2H_4 = CHCH_3$, CH_2CH_2) and methylamine (**MA**) as reported in Fig. 2, could easily impregnate ordered mesoporous CMK-3.

The composites was then cured in flowing ammonia at 200 °C followed by re-impregnation and final curing, pyrolysis and carbon removal steps according to the strategy depicted in Fig. 3.

This 2D hexagonal mesoporous ceramic displayed a high BET surface area ($600\ m^2\ g^{-1}$) and a narrow pore-size distribution as well as an excellent stability in air. However, according to the fact that this polymer displayed a low thermal reactivity due to poorly reactive CH_3 units linked to silicon and nitrogen atoms, depolymerisation and evolution of low-molecular-weight species occurred during the polymer-to-ceramic conversion in flowing nitrogen. Therefore, we have developed a cross-linking process under ammonia at 200 °C prior re-impregnation of the carbon template, ceramic conversion and template removal to limit depolymerisation; thereby to increase the ceramic yield of the polymer. However, despite the application of a cross-linking step, complex rearrangements still occurred during the pyrolysis leading to the formation of an undesired macroporosity which affected the ceramic homogeneity and thus its properties. To overcome this problem, the use of an alternative polymeric system with higher ceramic yield which does not require a particular cross-linking step has been considered in the present paper.

Herein, we describe the use of a soluble boron-modified polysilazane of the type $[B(C_2H_4SiCH_3NH)_3]_n$ ($C_2H_4 = CHCH_3$, CH_2CH_2, polymer type **B** in Fig. 1) with a relatively high ceramic yield to infiltrate mesoporous carbon CMK-3 then to produce 2D ordered mesoporous SiBCN materials by pyrolysis in a nitrogen atmosphere. In the present paper, our objective is to provide a detailed investigation of the fabrication process of $[B(C_2H_4SiCH_3NH)_3]_n$-derived ordered mesoporous SiBCN through (1) the study of the

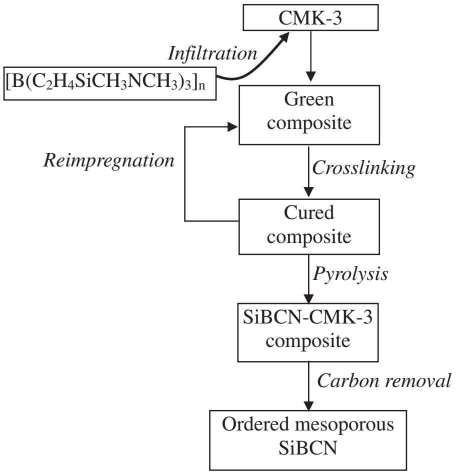

Fig. 3. Flow diagram of the fabrication process of polymer-derived SiBCN mesostructures.