

## High surface area mesoporous SiC synthesized via nanocasting and carbothermal reduction process

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Silicon carbide has excellent mechanical strength, thermal stability and chemical inertness, and avoids several of the problems inherent in the performance of commercial supports, such as alumina, silicon oxide and carbon-based materials [1]. SiC supported catalyst exhibit high performance in automotive exhaust treatment, selective isomerization of paraffinic hydrocarbons, and H<sub>2</sub>S removal by direct oxidation into elemental sulfur [1]. SiC is also a wide band gap semiconductor for high temperature, high frequency and high voltage power application and optical sensors in the ultraviolet region [2]. These unique properties of SiC are of great interest to material scientists.

Several routes have been used to synthesize SiC, for instance, carbothermal reduction of silica [3], sol-gel process [4, 5], decomposition of organic silicon compounds [6], chemical vapor deposition [7], and direct combustion synthesis [8]. Pure SiC was obtained by removal of the impurities through calcination to burn away residual carbon and acid treatment to remove SiO<sub>2</sub> and/or catalyst [5, 7].

In the above-mentioned studies, many efforts have been done on the synthesis of high surface area SiC. For instance, SiC, synthesized with activated carbon granulates loaded with small amounts of nickel through fluidized bed chemical vapor deposition, exhibits surface areas ranging between 25 and 80 m<sup>2</sup>/g [9]. SiC synthesized by SiO vapors and activated charcoal reaches a surface area of 50 m<sup>2</sup>/g by a reaction at 1200 °C for 15 hr and a high (Si + SiO<sub>2</sub>)/C weight ratio [10]. Recently, porous SiC has been synthesized with a surface area from 112 to 120 m<sup>2</sup>/g by a modified sol-gel method [5], chemical vapor infiltration and a carbothermal reduction process [3]. In the latter process, MCM-48 silica was filled with pyrolytic carbon using propylene as carbon precursor and treated up to 1250–1450 °C in inert atmosphere leading to the formation of SiC [3].

Generally, due to the high synthesis temperature (higher than 1200 °C), the sintering of SiC particles was inevitable, resulting in a decrease of the specific surface area. In this communication, we report a novel method for the preparation of such materials related to the technique described in ref. [3], combining a nanocasting process and carbothermal reduction resulting in mesoporous SiC with high surface areas of about 160 m<sup>2</sup>/g. Mesoporous silica, SBA-15, was used as nanoreactor, and furfuryl alcohol as carbon source.

SBA-15 was synthesized according to ref. [11]. Briefly, in a typical batch, 4.0 g of the surfactant Pluronic P123 was dissolved in 105 ml of distilled water to form solution (A), then 22 ml of an aqueous 53% HNO<sub>3</sub> solution was added to the solution (A) at 40 °C under vigorous stirring to attain the solution (B). After adding 8.5 g of TEOS to solution (B), the mixture was maintained at 40 °C for 4 hr, followed by aging at the same temperature for 24 hr. The template containing SBA-15 was filtered off and dried at 90 °C overnight. Finally, SBA-15 was obtained by calcination at 550 °C in air for 10 hr.

An amount of 3.8 g of the calcined SBA-15 was infiltrated with 3.5 ml of furfuryl alcohol in the presence of oxalic acid as catalyst by incipient wetness impregnation. The molar ratio between furfuryl alcohol and oxalic acid is 180. After polymerization at 60 and 80 °C, each for one day, the composite was heated to 150 °C and kept at that temperature for 3 hr. Subsequently, the temperature was increased to 850 °C under argon with a heating rate of 2 °C/min and maintained at that temperature for 4 hr. Finally, the temperature was increased up to 1400 °C with a heating rate of 5 °C/min and kept at that temperature for 3 hr. SiC was obtained by burning away the remaining carbon at 600 °C for 12 hr and by removal of silica in an aqueous solution of hydrofluoric acid. EDX-analysis carried out on the

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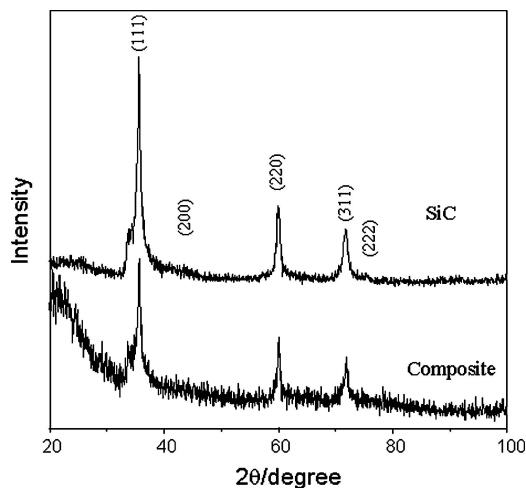


Figure 1. XRD patterns of the composite and the resulting SiC.

obtained sample revealed that the molar ratio of silicon to carbon is roughly 1:1.

The XRD patterns of the resulting samples are shown in Fig. 1. The composite shows a broad peak between 10–30° 2 $\theta$  after the treatment at 1400 °C, indicating an incomplete conversion of the silica and carbon to SiC under the reaction conditions used. A certain amount of amorphous silica and carbon might have remained. However, the XRD reflections with high intensity in the 2 $\theta$  range from 30 to 80° are quite obvious, proving the formation of SiC. In order to remove the possible impurities of carbon and silica, the composite was further treated. It can be seen clearly that after the treatment, the broad peak related to amorphous carbon and silica disappeared. Reflections with strong intensity can be predominantly assigned to the  $\beta$ -phase of SiC. The reflection marked with 's' having a low intensity could be due to stacking faults [12]. The particle size of SiC was calculated according to the Scherrer equation to be about 10 nm. The instrumental peak broadening was determined by measuring Si and LaB<sub>6</sub> (NIST) standards under identical conditions as used for the measurements of the sample.

The general morphology of the resulting SiC was revealed by TEM images, as shown in Fig. 2. It can be clearly seen that the SiC exhibits needle-like or irregular particles. The particle sizes of SiC were estimated to be in the range of 10  $\pm$  2 nm, which is consistent with the XRD results. The HRTEM image of SiC particles demonstrated that the resulting SiC is consisting of well-crystallized SiC nanoparticles. The lattice fringes are spaced at 0.25 nm corresponding to the (111) lattice planes of  $\beta$ -SiC, it confirms the XRD pattern. The Raman spectrum (here not shown) of the resulting SiC shows the presence of a sharp peak at 783 cm<sup>-1</sup>, which also confirms that the nanoparticles consist of well-crystalline  $\beta$ -SiC. Moreover, a Raman shift around 950 cm<sup>-1</sup> might be assigned to Si-O bond, which could have formed during the calcination and acid treatment due to the high reactivity for the SiC nanoparticles. The outer layers of the SiC particles consist of an amorphous phase with 0.3–0.6 nm thickness, which probably corresponds to the Si-O rich part of the crystallites. Therefore, combining the above analyses, the

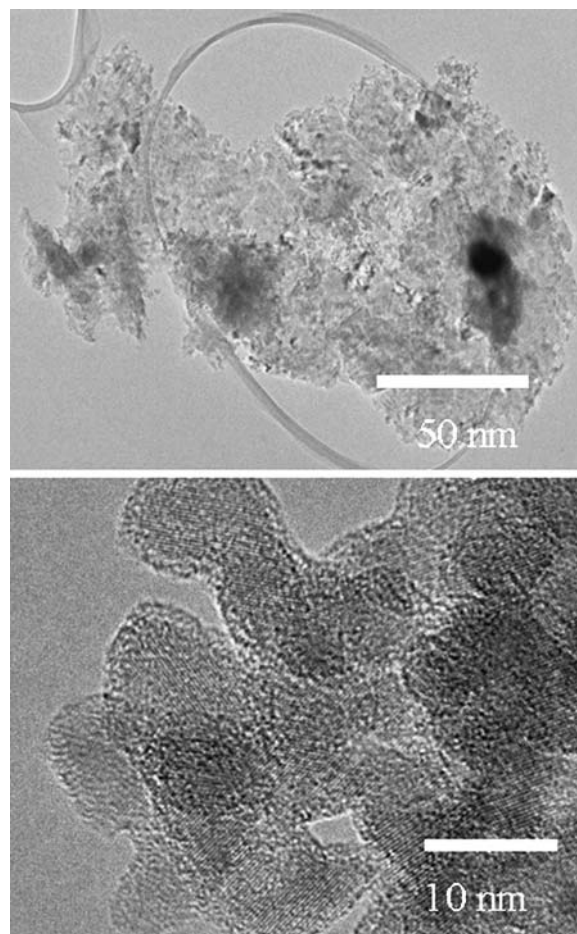


Figure 2. TEM images of SiC.

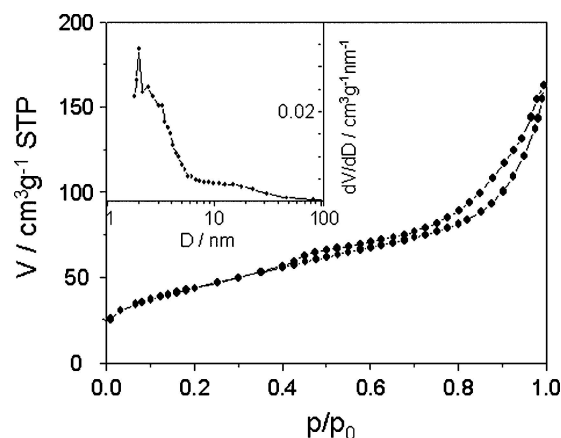


Figure 3. Nitrogen sorption isotherm of the resulting SiC (insert is the pore size distribution).

SiC nanoparticles are consisting of a well-crystallized phase and an amorphous phase corresponding to a core and shell structure, respectively.

The porous properties of the resulting SiC was characterized by nitrogen adsorption. The nitrogen adsorption isotherm of SiC is shown in Fig. 3. It shows a hysteresis loop exhibiting the mesoporous characteristics of the SiC. The specific surface area of the material without the contribution of the micropores is 159 m<sup>2</sup>/g. The volume adsorbed on the micropores is only 5.9% of the total pore volume, indicating the surface area can mainly be attributed to the mesopores.

It is noteworthy to point out that the surface area of SiC synthesized by the current strategy, nanocasting and carbothermal reduction, is higher than those synthesized by sol-gel process and chemical vapor deposition [5,7]. Therefore, the current synthesis strategy is an alternative method to synthesize high surface area SiC.

As seen in Fig. 3 (insert), the pore size distribution has a maximum between 2 and 4 nm. These pores might result from the removal of the unreacted carbon and silica, which can be clearly observed in TEM image. Moreover, the resultant SiC also contains larger mesopores, for instance, interparticle or intraparticle pores, which might correspond to the hysteresis loop around the relative pressure 0.8 in the nitrogen adsorption isotherms.

In summary, high surface area SiC can be synthesized through nanocasting and carbothermal reduction process. The advantage of this method is that carbon can be infiltrated not only in the channels of SBA-15 but also in the silica walls where micropores exist, resulting in a periodical and nanometer scaled dispersion of carbon and silica. This has been proved by a previous study on the synthesis of CMK-3 [13]. The carbothermal reduction takes place at the boundary of silica and carbon. By control of the degree of the reaction, it should be possible to tailor the particle size of the resultant SiC. Moreover, the residual carbon and silica, remaining after the reaction, might act as a pore former to isolate the formed SiC particles. After removal of these residues, porous SiC with high surface area is formed.

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