



Fabrication of nanoporous silicon oxycarbide materials using layered double-hydroxide as a sacrificial template



Xiaojie Yan, Theodore T. Tsotsis, Muhammad Sahimi*

Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1211, USA

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ABSTRACT

We report on fabrication of highly porous silicon oxycarbide (SiOC) material, $\text{Si}_x\text{O}_y\text{C}_z$. The material possesses high surface area, a hierarchical pore size distribution, and an ordered layered structure. We synthesized it using tri-isopropylsilane as a precursor, a layered double-hydroxide as a sacrificial template, and chemical vapor deposition at temperatures 700 °C and 800 °C. Several techniques, such as X-ray diffraction, X-ray photoelectron spectroscopy, and transmission and scanning electron microscopies, were used to characterize the morphology of the material, and is shown to be composed of hollow spheres with a layered interior. Nitrogen sorption validates the hierarchical structure of the material with both meso- and micropores. The material exhibits high BET surface area, ranging from 330 m²/g to 540 m²/g, and a total pore volume from 0.50 cm³/g to 0.91 cm³/g. It was fabricated using low-cost templates and precursors, as well as convenient synthesis procedures, and is a promising material for several applications, such as catalyst support, sorbents, and battery anodes.

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1. Introduction

Inorganic meso- and microporous materials have a large number of applications, ranging from environmental to medical [1] and, therefore, their fabrication has been a rapidly growing research field. Among such materials nanoporous silicon oxycarbide is a relatively new type of porous media, with a structure that is intermediate between silicon carbide and silica, with the chemical formula $\text{SiC}_x\text{O}_{4-x}$, where $x = 1, 2, \text{ or } 3$. These materials are amorphous and their typical black color is mostly due to the presence of elemental free carbon [2]. Silicon oxycarbide possesses promising mechanical properties [3], including chemical durability, such as resistance to HF [4], excellent oxidation resistance [5,6] that are comparable or even better than those of SiC ceramics [7], and high temperature stability up to 1300 °C [8]. Therefore, they have been used extensively in recent years as catalysts and catalyst support, gas adsorbents [9], battery anodes [10–12], light emitters [13,14], and blood contact agents [15].

Silicon oxycarbide has been synthesized using a sol–gel reaction process [2,16–18], laser ablation [19], a templating method [20–25], layer dip-coating on underlying surfaces [26], nano-precipitation [27], emulsification [28], and photo cross-linking [29],

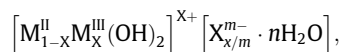
all followed by direct pyrolysis. One of the most successful of such methods is the templating method. For example, microcellular $\text{Si}_x\text{O}_y\text{C}_z$ open-cell ceramic foams were fabricated [8] from a silicone resin using poly (methyl-methacrylate) (PMMA) microbeads as a sacrificial template. Nanotubes made [21] of the same material have been synthesized from mesoporous anodized aluminum oxide (AAO) with polycarbosilane as a precursor [21], while well-aligned tubular structured made of $\text{Si}_x\text{O}_y\text{C}_z$ with high surface area of 1387 m²/g have been prepared using porous anodic alumina as templates using silicone as the precursor [30], or by using poly (hydridomethylsiloxane) (PHMS) as the starting pre-ceramic polymer. In addition, an ordered mesoporous $\text{Si}_x\text{O}_y\text{C}_z$ monolith with surface area as high as 616 m²/g has been prepared [7] with mesoporous carbon CMK-3 as a sacrificial template, using liquid PHMS as the starting pre-ceramic polymer. However, the aforementioned methods either require expensive templates derived from time-consuming procedures, or have not exhibited promising large surface area and pore structure properties. Moreover, none of the porous $\text{Si}_x\text{O}_y\text{C}_z$ materials fabricated so far possesses a hierarchical pore structure with both meso- and micropores.

Two-dimensional (2D) or quasi-2D clay materials may be used as a host for intercalated chemical compounds [31]. Layered double hydroxides (LDHs), also known as anionic clays, hydrotalcites, or pillared clays consist of two types of metallic cations accommodated with the aid of a close-packed configuration of OH[−] groups in a positively-charged brucite-like layer. The interlayer space in LDH

* Corresponding author. Tel.: +1 213 740 2064; fax: +1 213 740 8053.

E-mail addresses: xiaojiey@usc.edu (X. Yan), tsotsis@usc.edu (T.T. Tsotsis), moe@usc.edu (M. Sahimi).

is typically occupied by water and various anions for charge compensation. The general chemical composition of LDH is



where M^{II} is a divalent metal cation (including Mg, Mn, Fe, Co, Ni, Cu, Zn, and Ga), and M^{III} a trivalent metal cation (such as Al, Cr, Mn, Fe, Co, Ni, and La). Here, X^{m-} represents a m^- valence inorganic (CO_3^{2-} , OH^- , NO_3^- , SO_4^{2-} , and ClO_4^-), heteropolyacid (such as $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$), or even organic acid anions [32]. As one of the most popular families of clay minerals, LDHs have been used as templates for polymers/monomers or other precursors penetrating into their structure. Several techniques, including direct intercalation of the polymer itself, *in situ* polymerization of various monomers [33], chemical-vapor deposition (CVD) [34], and intercalation via an anion-exchange reaction with emulsifiers, such as 3-sulfopropylmethacrylic acid (SPMA) or 2-acrylamido-2-methyl-1-propanesulfonate acid [35] have all been used to generate the precursor/LDH composites. The resulting materials may be used to fabricate nanoporous carbon materials. The synthesis of nanoporous carbon from LDH with the CVD technique has exhibited some promise [34].

In this paper we report on successful fabrication of highly porous silicon oxycarbide materials with high surface area, a hierarchical structure and ordered layered structure, using tri-isopropylsilane (TPS) as a precursor and low-cost LDH material as a sacrificial template, via the convenient route of CVD at relatively low temperatures of 700–800 °C. Moreover, the texture properties of the materials obtained at various deposition temperatures and total amount of precursors are compared. To the best of our knowledge, no previous study on synthesizing nanoporous silicon oxycarbide materials using a LDH as template has been carried out.

The rest of this paper is organized as follows. In the next section we describe the experimental procedure. The results are presented and discussed in Section 3. The last section summarizes the paper.

2. Experimental

In this section we describe the procedure for the preparation of the porous material.

2.1. Material fabrication

The TPS (from Sigma–Aldrich Co.), tetrahydrofuran (THF) (from VWR International), and hydrochloric acid (37 wt.%, from VWR International) were used without further purification. The MgAl-LDH powder was provided by Sasol Corporation (Sasol Mg 70 with a Mg/Al ratio of 3.0). First, the part of the MgAl-LDH powder with particle sizes less than 25 μm was separated using a 500 mesh sieve. Next, the LDH powder was heated at a rate 1 °C/min in a tube furnace to either 700 °C or 800 °C, and was held at the target temperature for 3 h. When the temperature of the furnace reached 120 °C, a mixture of argon with TPS with a fixed certain concentration was flown through the tube furnace. The heater was then turned off in order for the system to cool down in an argon gas atmosphere to ambient temperature. The resulting dark brown powder was dipped into an 18 wt.% HCl solution to remove the template. The mixture was then vigorously stirred for 48 h before the powder was filtered and washed with de-ionized water to remove any potential soluble impurities. After drying overnight at 90 °C, a fine black powder was obtained. Due to the high probability of free carbon existing in the $\text{Si}_x\text{C}_y\text{O}_z$ material, part of the powder was calcined in a muffle oven in an air atmosphere at 450 °C for 3 h to eliminate the elemental carbon. Further characterizations were then conducted on both the uncalcined and calcined samples, the results of which are described shortly.

2.2. Characterization

The characterization began with X-ray diffraction analysis, which was carried out using a Rigaku X-ray diffractometer, with the $\text{CuK}\alpha$ line used as the X-ray source with a monochromator positioned in front of the detector. Scanning was performed over angles 2θ ranging from 10° to 90°, or from 0.2° to 50° with a scanning rate of 4°/min and stepwise increase of 0.05. X-ray photoelectron spectroscopy measurements were performed using a Thermo ESCALAB 250 spectrometer. A monochromatic $\text{AlK}\alpha$ radiation source ($h\nu \sim 1486.6$ eV) was used at a spot size of 400 μm . A pass energy of 100 eV for the survey scan and 20 eV for the high resolution scan were used with the analyzer. Low-resolution survey scans were acquired at binding energies between 1 eV and 1400 eV with a resolution of 1 eV. High-resolution scans of the C-1s and Si-2p regions were acquired with a resolution of 0.05 eV. Data analysis was performed using the XPSPEAK, Version 4.1, software. The samples, before and after sectioning, were examined by scanning electron microscopy with a 6010LA variable pressure W-SEM, using secondary electron imaging (SEI). Before imaging, the powder was sprinkled on a copper tape. The sample was sectioned by a JEOL cross-section polisher, utilizing an argon-ion beam at 6 kV, at a milling rate of 100 $\mu\text{m}/\text{h}$ for 25 min. Analysis of the morphology was also carried out utilizing transmission electron microscopy, using JEOL JEM 2100 LaB6 under room temperature, 220 kV acceleration voltage and bright field illumination.

Nitrogen adsorption–desorption isotherms in the porous samples were measured with a Micromeritics ASAP 2010 adsorption analyzer at -196 °C (77 K). Prior to the measurements, the porous silicon oxycarbide materials were degassed overnight at 110 °C. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the surface areas. The pore volume and pore size distributions were derived from the isotherms using the Barrett–Joyner–Halenda (BJH), as well as the Horvath–Kawazoe (HK) methods.

3. Results and discussion

Four samples were prepared at 800 °C, and another four at 700 °C. In each case, two samples were fabricated using 0.6 ml of TPS, and two with 1.0 ml of TPS as the precursor. In addition and for the sake of comparison, we also measured the properties of the pure MgAl-LDH template, both at room temperature and at 800 °C. As expected, since LDH materials collapse at temperatures much lower than 800 °C [36], the template had no useful properties at such a high temperature. If the template is not removed at the intended temperature of 700 °C or 800 °C, the porous material will still not possess useful properties. But, the important point to emphasize is that although the LDH materials are not useful at high temperatures, they can still be used as a template for fabrication of the type of porous materials that we describe in this paper and, because they are inexpensive, they represent an attractive alternative to other types of materials used in the past for fabricating porous materials.

Fig. 1 presents the XRD data for four samples prepared by CVD, two each at the two high temperatures. All the samples display the spectra for amorphous materials. No typical template peaks corresponding to MgO , Al_2O_3 , or MgAl_2O_4 can be identified, hence indicating that the template has been removed completely. The XPS elemental analysis, to be described below, verified this conclusion. The broad diffraction peak at about $2\theta = 21\text{--}24^\circ$ is attributed to silica oxycarbide glass. For one sample, referred to as sample A in Fig. 1 that was fabricated with 0.6 ml of TPS at 800 °C without calcination, the (200) peak, which is attributed to $\beta\text{-SiC}$, is in the spectrum, whereas for sample B that was prepared under similar conditions but was also calcinated, the corresponding peak is much

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