Carbon and SiC Macroscopic Beads from Ion-Exchange Resin Templates

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During the past decade, the synthesis of materials with controlled porosity and shape has attracted rapidly growing attention. In the case of carbons, the interest is driven by the numerous potential applications of these materials as adsorbents, catalyst supports, electrodes for electric double-layer capacitors, column packing materials in liquid chromatography, etc. For silicon carbide materials, the high mechanical strength, thermal conductivity and stability, and chemical inertness make them attractive candidates for catalytic and separation processes.[1] In this context, numerous processes based on templating methods have been developed, where the template determines the shape or the porosity of its replica.

A number of periodic porous carbons have been prepared by replicating crystalline microporous materials (e.g., zeolites[2]), ordered mesoporous silica (e.g., MCM-48 and SBA-15[3]), or macroporous colloidal crystal templates.[4] Nonordered porous carbons with mesopore volumes above 4 cm^3 g^{-1} and with extremely high adsorption capacities for dyes have been synthesized using silica nanoparticles as templates.[5] Regarding morphology, carbon nano-capsules with sizes in the range 15−340 nm have been fabricated using polymer core,[6] porous shell silica templating,[7] and self-assembly approaches.[8] Microbead silica gel has also been used as a template for the preparation of porous carbon beads.[9] The use of such a templating procedure could be also a very promising and attractive alternative for the production of an array of low-cost, net-shape ceramic materials. For instance, the preparation of SiC fibers, macroporous structures, or high-surface area particles have been recently described.[10] However, the preparation of SiC micro-beads starting from a C/SiO₂ artifact have been not reported.

Macroscopic beads (e.g., with a size exceeding 0.1 mm) are often advantageous in the areas of application of carbons and SiC due to easy handling and limited attrition and are particularly beneficial for SiC, which is known as an abrasive material. In addition, macroscopic spheres reduce diffusion limitations when used in, e.g., fixed-bed reactors or chromatographic columns. Here we report a method of preparing carbon and SiC macroscopic beads using ion-exchange resins as macrotemplates that determine both the mac-roshape and the pore structure of the product materials. Moreover, ion-exchange resins are particularly interesting for the preparation of carbon materials, as waste resins can be used and the resin polymer chains carbonized into carbon. Ion-exchange resins are commercially available in a variety of bead sizes and are fabricated as either gel or macroreticular resins. Gel (G) resins are character-ized by an "apparent porosity" of no greater than 4 nm, which represents the average distance of separation of polymer chains, and have a very low surface area of less than 10 m^2 g^{-1} in the dry state.[11] Macroporous (MP) resins have a permanent network of pores (100 nm on an average) and high surface areas in the dry state,
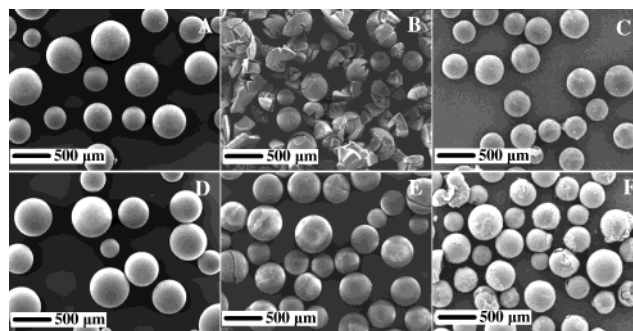

Figure 1. SEM micrographs of the initial macroporous (A) and gel (D) resins and the corresponding carbon (B, E) and SiC materials (C, F).

typically ranging from ∼50 to ∼1000 m^2 g^{-1}. Their uses for the synthesis of self-bonded zeolitic and high-surface area amorphous silica beads by resin templating were recently reported.[12]

The synthesis of shaped C and SiC beads consisted of the following steps: (I) Preparation of a resin−silicate composite by silicate-ion exchange using the MP and G type resin. (II) Carbon-ization of the resin/silicate materials to obtain carbon/silicate (C/SiO₂) composite beads. At this step, two different procedures were followed: (a) silica dissolution in hydrofluoric acid (HF; **Caution! HF is a corrosive and hazardous substance**) of the C/SiO₂ composite to obtain carbon beads and (b) carbothermal reduction of the C/SiO₂ materials, which leads to the formation of SiC. The unreacted C and SiO₂ were successively removed by a mild oxidation and HF treatment, respectively. The detailed synthesis procedure is better described in Supporting Information.

Scanning electron micrographs (SEM) of the initial resins and the corresponding inorganic replicas (C and SiC) are shown in Figure 1. Both resins have similar bead size distributions (Figures 1A and 1D) but different network structures as detailed previously. Their direct carbonization resulted in hollow particles and shells with a substantial reduction of the sphere sizes for the macroreticular resin (see Supporting Information). The C/SiO₂ composite beads were identical in shape and size to the original resin beads, and no broken or cracked particles were observed by SEM (not shown). This behavior indicates that the silicate species, ion-exchanged into the resins, allow the macroshape of the resin beads to be maintained during the carbonization step. The amount of carbon in the carbonized carbon/silicate composite was 24 and 46 wt % for the MP and G resins, respectively. After HF etching, the carbon spherical particles were similar in size to the original resins as well. However, the majority of the particles disintegrated for the sample prepared using the macroreticular resin (Figure 1B) and a few cracked particles can be seen in the sample prepared with the G resin (Figure 1E). The differences observed are related to the peculiar structure of the starting resins. The higher final carbon
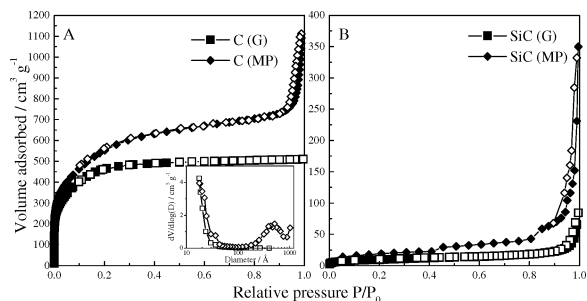
Figure 2. Nitrogen adsorption−desorption isotherms for carbon beads (A) and SiC beads (B) from the gel (G) and macroporous (MP) resins. Solid symbols, adsorption; open symbols, desorption. Inset: the corresponding BJH desorption dV/d$\log(D)$ plots.

Table 1. N$_2$ Adsorption Data for the Materials Prepared

materials	S_{BET} (m^2/g)	V_p (cm^3/g)
C (G)	1670	0.79
C (MP)	2026	1.69
SiC (G)	35	0.13
SiC (MP)	63	0.54

content and the microporous structure of the carbon prepared with the G resin may be the reason for its faithful macroshape replication.

The C/SiO$_2$ composites heat-treated above 1250 °C led to cubic SiC (β-SiC) with traces of its hexagonal polytypes as shown by X-ray diffraction (see Supporting Information). The SiC(MP) and SiC(G) materials were similar in shape and size to the original resins (Figures 1C and 1F) and could stand various laboratory manipulations. Moreover, "cauliflower" and whisker SiC morphologies were observed and related to the type of resin used and to the mechanisms of SiC formation. In the former case, the morphology is typical of a β-SiC growth via a solid−gas reaction,[13] whereas the latter is typical of a SiC growth via gaseous species.[13]

The two types of carbons, obtained via the C/SiO$_2$ composites, yielded carbons of different pore structures (Figure 2 A). The nitrogen adsorption isotherms of the carbon obtained from the G resin was of type Ib[14] characteristic of a secondary microporous material. The carbon prepared from the MP resin contained both micropores (steep increase in the volume adsorbed at low relative pressures) and large mesopores (hysteresis loop at high relative pressures). As seen in the inset of Figure 2, the substantial part of the pore volume of this sample is found in pores with a size of 30−40 nm. Differences in the specific surface areas and pore volumes of carbons obtained by replication of MP and G resins were also observed (see Table 1). Our previous studies showed that variations in, e.g., the degree of cross-linking of resins, led to changes in the pore structure of the corresponding silicate beads.[12] Thus, the difference in the pore structure of gel and macroporous resins results in different silicate embedding as well as a different amount of carbon upon resin carbonization, which all affect the porosity of the derived carbon replicas.

The pore structure of the SiC materials was dependent on the type of the resin used as well. Thus, type II isotherm typical of macroporous material is obtained for the sample prepared with the

G resin, whereas mesopores are present in the SiC synthesized using the MP resin (Figure 2B). The measured surface areas of the SiC beads were relatively high compared to SiC material prepared from the conventional process with a substantially higher total pore volume of the SiC (MP) material (Table 1).

In summary, shaped porous carbon and SiC spheres were prepared using ion-exchange resins as templates. Silicate anions were first ion-exchanged to fix the resin polymer chains and prevent loss of shape during subsequent carbonization. The type of the resin used (G or MP) was of paramount importance for the macroshape and pore structure of the final materials. Very high-surface area carbons and relatively high-surface area SiC were prepared. This synthesis route appears to be a very promising way to manufacture the shape of SiC and C beads, which can be used in various applications fields.

Supporting Information Available: Details of the experimental procedure, SEM micrographs of carbonized resins, SEM micrographs of SiC bead surfaces, XRD patterns of SiC beads, and DFT pore size distributions of carbon beads (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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