



Synthesis of mesoporous carbons using silica templates impregnated with mineral acids



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ABSTRACT

The pore walls of SBA-15, SBA-16 and KIT-6 mesoporous silica were acidified via the impregnation of phosphoric acid or sulfuric acid prior to their use as a template for mesoporous carbon synthesis with furfuryl alcohol. The effect of acid functionalization on carbon synthesis was investigated using X-ray powder diffraction, N₂ adsorption, transmission electron microscopy, and solid-state ¹³C and ³¹P NMR spectroscopy. The results indicated that a significant portion of the impregnated mineral acid formed an ester with the surface silanol group. Therefore, the impregnated acid could lead to the selective formation of carbon frameworks inside the template pores, preventing external carbon deposition even when furfuryl alcohol was used excessively. The mineral acid impregnation yielded highly faithful carbon replicas of the mesoporous silica.

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1. Introduction

Mesopores are defined as pores in the range of 2–50 nm in diameter. Carbon materials with regular arrays of these mesopores are called ordered mesoporous carbons (OMCs) [1–8]. OMCs with various structures are currently available via a synthetic route using mesoporous silica templates [1–6] or carbonization of ordered arrays of polymeric resin nanobeads [7,8]. In the current work, we focus on the template synthesis. The template synthesis of OMCs was first reported by Ryoo et al. in 1999 [1]. These types of OMCs are referred to as ‘CMK’. The CMK-type of carbon materials have attracted much attention as absorbents, catalyst supports, and electrode materials [3,9–12]. There have been numerous reports on the synthesis, characterization and application of CMK carbons with various structures and pore diameters [2–6,9–14]. Surface modification and functionalization of CMK carbons have also been extensively studied to improve their performance [15–18].

The synthesis procedure for CMK carbons involves three steps [1–5]. In the first step, an organic compound is impregnated into the mesopores of a silica template. The impregnated organic source

is polymerized and subsequently converted to carbon by pyrolysis. The key in this step is to control the carbonization process to occur inside the template mesopores. The confinement of the carbonization process within the mesopores can be realized by converting the organic source to cross-linked solid polymers prior to the final conversion to carbon. The polymerization can be achieved by the incorporation of an acid into the silica template or the carbon source. The silica template can be removed after carbonization with hydrofluoric acid or a sodium hydroxide solution. Ultimately, the carbon product should become a faithful inverse replica of the porous silica template.

Various organic compounds, such as sucrose [1,2,5], furfuryl alcohol (FA) [3], acenaphthene [19], phenol resin [20], and acrylonitrile [15], can be used as the carbon source. FA is one of the most convenient sources of carbon as the liquid-phase compound that can be easily impregnated into silica mesopores. Nevertheless, the carbonization process using FA involves several time consuming steps. For example, incorporation of a solid acid (typically Al) onto the template pore walls is necessary. The procedure involves wet impregnation of an Al compound and evaporation of the solvent followed by calcination. Then, FA is impregnated using an incipient wetness process. The impregnated FA is polymerized by heating at 373 K due to the catalytic function of the acid sites. Upon further heating to 623 K, the carbon source is converted to a black tar with a significant contraction in the volume. An additional amount of FA

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can be added to compensate for the volume loss (*i.e.*, second impregnation) at this point. Then, the procedures for FA polymerization at 373 K and subsequent tar formation are repeated. After all of these treatments, the silica template containing the carbon source is heated to the final carbonization temperature (~1173 K). The resultant carbon from the two-step FA impregnation exhibits a rod-type framework that fills the template pores. If the second FA impregnation is skipped, the carbon often becomes a hollow pipe-type framework [3].

It is important not to exceed the amount of FA beyond the total pore volume in a template. An excessive amount of FA can cause the formation of non-templated (*i.e.*, external) carbon. The acid strength of the template pore walls is also an important factor. Often the polymerization rate of carbon sources including FA, sucrose, glucose, and other organics are very sensitive to acid catalysts [21–28]. For the aluminosilicate template, the acid strength is often so high that FA polymerization proceeds very rapidly before a sufficient time can allow for homogeneous infiltration of FA into the template pores. The rapid polymerization can be a serious problem particularly in a large batch synthesis. The exothermic polymerization process can generate substantial heat that accelerates the polymerization itself [21,22]. The FA polymerization outside the template can result in the formation of external carbon. There were alternative routes involving the use of silica templates without Al incorporation [23–28]. In such cases, a small amount of *p*-toluene sulfonic acid or oxalic acid were added to the FA as a polymerization catalyst prior to the FA being impregnated. This route is prone to suffering from the generation of polymerization heat as well as the formation of external carbon.

The current work was undertaken to improve the synthesis procedure for OMC materials using FA in mesoporous silica templates. In particular, this study was aimed at preventing the generation of external carbon by selecting a moderately weak acid that would slowly catalyze the FA polymerization. As a first candidate, phosphoric acid was impregnated into ordered mesoporous silica prior to FA infiltration. The resulting carbonization process was investigated using X-ray powder diffraction, N₂ adsorption, and transmission electron microscopy. The chemical state of the phosphoric acid in the silica template was analyzed by solid-state ³¹P NMR spectroscopy. Based on the chemical information from the ³¹P NMR data, we were able to extend the phosphoric acid-based method to the use of sulfuric acid. In this paper, we introduce a mineral acid impregnation method, and its application to the synthesis of OMCs with various mesoporous silica templates, such as SBA-15, KIT-6 and SBA-16.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of silica templates

SBA-15 silica was synthesized according to the procedure described in the literature [29] using tetraethoxysilane (TEOS, TCI) as a silica source and Pluronic P123 [EO₂₀PO₇₀EO₂₀ (EO = ethylene oxide, PO = propylene oxide, M_n ~5800, Aldrich)] as the mesopore-directing surfactant. The gel composition was 1 TEOS: 0.017 Pluronic P123: 5.3 HCl: 194H₂O. All of the starting materials were mixed at 308 K for 12 h using a magnetic stirrer. Then, the resulting gel mixture was heated for 12 h at 403 K under static conditions in a Teflon-lined autoclave. The precipitated SBA-15 product was filtered, washed with deionized water and dried at 373 K for 12 h. The product was calcined in air at 823 K for 4 h. SBA-16 and KIT-6

were synthesized according to previously reported procedures [6,30].

2.1.2. OMC synthesis using aluminated SBA-15

In a typical procedure for post-synthetic alumination of SBA-15 with Si/Al of 20, 0.5 g of the calcined SBA-15 silica was added to 20 mL of ethanol (99.9%, Merck) containing 0.055 g of AlCl₃ (anhydrous, Aldrich). The mixture was magnetically stirred at room temperature for 6 h. Then, ethanol was removed using a rotary evaporator. The SBA-15 containing Al (*i.e.*, Al-SBA-15) was further dried in an oven at 373 K for 3 h followed by calcination in an air stream at 823 K for 4 h. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis indicated that the Si/Al ratio of Al-SBA-15 was 22.

An ordered mesoporous carbon (OMC) sample was prepared using Al-SBA-15 as a template and FA (98%, Aldrich) as a carbon precursor. In a typical synthesis, 0.1 g of Al-SBA-15 was impregnated with 0.14 mL (amounting to 130% of the total pore volume of Al-SBA-15) of FA in a polypropylene bottle. This polypropylene bottle was tightly closed, and it was heated at 308 K for 1 h. Then, this bottle was heated at 373 K for 6 h. The composite inside the bottle was transferred into a fused quartz reactor, which was equipped with a capillary cap to prevent air from entering from the outside while releasing gaseous by-products. The fused quartz reactor was heated to 1173 K (heating rate of 3.5 K min⁻¹), and the final temperature was maintained for 3 h. The reactor was cooled to room temperature, and the sample was dispersed in 20 mL of a 10 wt% hydrofluoric acid solution under magnetic stirring to remove the silica template. The resulting OMC was filtered, washed several times with distilled water, and dried at 373 K.

2.1.3. OMC synthesis using mineral-acid-impregnated silica templates

In a typical procedure for phosphoric acid impregnation in mesoporous silica, 0.1 g of calcined SBA-15 was mixed with 5 mL of a 4 mM aqueous solution of phosphoric acid (85 wt%, Aldrich) in a beaker under magnetic stirring for 1 h. Then, the beaker was heated in a convection oven at 443 K for 12 h to evaporate water and anchor the phosphoric acid onto the mesopore walls via covalent bond. The physically adsorbed phosphoric acid was removed by a repeated washing and filtration process using distilled water until the pH of the filtrate reaches 7. The product was dried at 373 K for 12 h. The Si/P ratio of the synthesized sample was 26. The impregnation of sulfuric acid was also performed following the same procedure as that employed in the phosphoric acid impregnation, except for the use of sulfuric acid (49 wt%, Daejung) instead of the phosphoric acid. The SBA-15 impregnated with phosphoric acid or sulfuric acid is referred to as 'PA-SBA-15' and 'SA-SBA-15', respectively. The phosphorous and sulfur content in the silica template impregnated with mineral acids was determined by ICP-AES analysis.

For OMC synthesis, we used various volumes of FA (equivalent to 130 or 170% of the total pore volume of the silica template). In a typical synthesis procedure, 0.1 g of PA-SBA-15 was added to a mixture of 2 mL of an ethanol solution and 0.13 mL (amounted to 130% of total pore volume of PA-SBA-15) of FA at room temperature. Then, the solution was magnetically stirred for 3 h and heated in an oil bath at 333 K under magnetic stirring to evaporate the ethanol solvent. The composite was placed in a drying oven at 373 K for 8 h. The FA polymerization, subsequent carbonization and template removal were performed according to the procedure used for OMC synthesis using Al-SBA-15. The resulting OMC samples synthesized

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