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Short Communication

A novel low-temperature dendritic cyclotrimerization of 2,6-diacetyl pyridine leading to mesoporous carbon containing pyridine rings

Yongsoon Shin, Chongmin Wang, Mark Englehard, Glen E. Fryxell *

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

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ABSTRACT

A simple, direct synthesis of a mesoporous carbon containing pyridine rings is described. This synthesis utilizes the $SiCl_4$ induced cyclotrimerization of 2,6-diacetylpyridine to make a dendritic polymer, built of alternating benzene and pyridine rings. The cyclotrimerization allows for a high degree of crosslinking to take place at low temperatures stabilizing the mesostructure and allowing the carbonization to be carried out at only 600 °C, the lowest temperature reported to date for an N-doped mesoporous carbon. The functional mesoporous carbon so formed was found to have a surface area of 1275 m^2/g, 35 Å pores, and contain 6.8% N. XPS reveals two N-containing species, with the predominant species being pyridine N.

1. Introduction

The synthesis of templated mesoporous carbons has received a great deal of attention in recent years [1–13]. A variety of synthetic strategies have been employed including the charring of sugars [1], polymerization of heteroaromatic precursors [2], carbonization of phenolic resins [3], carbonization polycyclic aromatic hydrocarbons [5], carbonization of polyacrylonitrile [6], and self assembly of functional polymers [7,8]. Recently, there has been significant interest in making mesoporous carbon materials that have been doped with N-based functionality [6,9–13,15]. These approaches have commonly used acetonitrile [9–11] or pyrrole [12] as the basic feedstock for the synthesis. Chelating diamine functionality has also been integrated into N-doped mesoporous carbon by using 1,10-phenathroline as the starting material [13]. All of these N-doped materials have been limited to no more than ~8% N. This is presumably due to N loss at the elevated temperatures required for the carbonization stage (900 °C for acetonitrile [9], 850 °C for polyacrylonitrile [6], 800 °C for pyrrole [12] and 700 °C for 1,10-phenanthroline [13]). Pyridine containing polymers are known to undergo ring–ring fusion reactions, along with concomitant loss of N functionality, at temperatures above 600 °C [14]. Therefore, we have been interested in developing chemistry that would be compatible with heteroaromatic functionality and provide the greatest degree of crosslinking at low temperatures so the carbonization process could be completed under the mildest conditions possible, allowing as much as possible of the N functionality to be retained in the final product.

Linear polymers suffer from the potential drawback of thermal depolymerization during the carbonization stage of the synthesis. Cyclotrimerization to form benzene rings is advantageous for this chemistry not only because of the greater degree of crosslinking afforded by the dendritic polymer structure, but also because the benzene ring has great thermodynamic stability and is not readily depolymerized [15]. Cyclotrimerization of diethynylpyridines has been used to make high surface area N-doped mesoporous carbons, and the structure of the final product has been shown to be dependant on the regiochemistry of the acetylene side chains in the starting material [15]. However, these materials still required calcination at 800 °C to complete the carbonization phase of the synthesis, and so loss of N functionality was still a problem, with the final product containing only ~4% N after carbonization [15].

Benzene rings can also be built via the cyclotrimerization of functionalities other than acetylenes. For example, cyclic dehydration of acetyl derivatives can lead to highly substituted benzenes quickly and easily, under relatively mild conditions (see Fig. 1) [16,17]. This chemistry is postulated to proceed via a protonated carbonyl being attacked by an enol (or silyl enolate), subsequent dehydration and then having the process repeated, ultimately leading to the cyclized benzene structure [18]. $SiCl_4$ serves two vital roles in this chemistry. First, solvolysis of the $SiCl_4$ generates the HCl catalyst necessary to catalyze the condensation chemistry, and secondly, the $SiCl_4$ (or possibly the Si alkoxides formed during solvolysis) consumes the water that is formed by the condensation process, helping to drive the equilibrium to completion. The net re-

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* Corresponding author. Tel.: +1 509 375 3856; fax: +1 509 375 2186.
E-mail address: glen.fryxell@pnl.gov (G.E. Fryxell).

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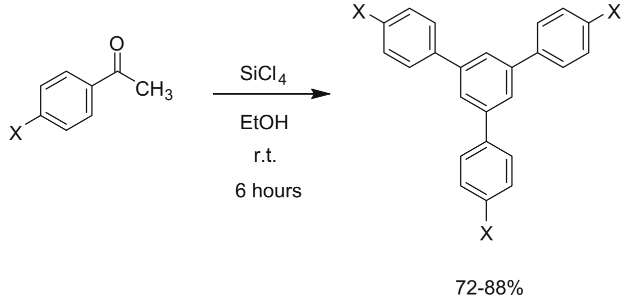

Fig. 1. Schematic showing the cyclotrimerization of substituted acetophenones to give trisubstituted benzenes (see Refs. [16,17]).

sult is a trisubstituted benzene derivative, formed under mild conditions and in good yield. The reaction has been found to be general for a wide variety of acetophenone derivatives [16–18]. This cyclotrimerization reaction has been used to construct some fairly large and complex molecules, including trimeric carbazoles [19], fluorenes [20], carboranes [21], and triphenyl benzene discotic derivatives [22] indicating that this reaction is not particularly sensitive to steric congestion.

The beauty of this approach is that, being an acid-catalyzed condensation process, it takes place at relatively low temperatures (ambient to ~100 °C, very low compared to some of the polymerizations described above). The higher the degree of polymerization that can be accomplished in the initial phase of polymerization, the less cross-linking is needed in the subsequent carbonization stage. By doing things in this manner, it might be possible to perform the carbonization at lower temperatures and preserve as much of the heteroatom functionality as possible.

In order to test this idea, we chose the commercially available 2,6-diacetyl pyridine as our starting material (see Fig. 2), and SBA-15 [23,24] as our template. The following procedure is representative: the 2,6-diacetyl pyridine was pre-loaded into an SBA-15 template [23,24], and then that pre-assembly complex was treated with $SiCl_4$ in toluene. 2,6-Diacetylpyridine (0.714 g, 4.38 mmole) was dissolved in 2 mL of acetone. 1.0 mL of this solution was added to 1.0 g of SBA-15 (pore volume, 1.23 cc/g) and this mixture was heated to 60 °C to evaporate the acetone. A second aliquot was added and the sample once again heated to 60 °C drive off the solvent. To this was added a mixture of 2.0 g of $SiCl_4$ in 0.5 mL toluene. The resulting mixture was heated for 2 h at 120 °C. The resulting brown colored solid was collected and calcined at 600 or 700 °C for 1 h under N_2. The resulting black composite was washed with 20% HF, then with 2.0 M K_2CO_3 solution, and dried.

The crude product obtained after the initial polymerization stage was brown, indicating a high degree of conjugation in the arene portion of the product. Digestion of the SiO_2 template from this material did not result in a free-standing mesoporous carbon, indicating that while polymerization was extensive at this stage, there was inadequate crosslinking to create a free-standing nanoporous architecture. Subjecting this product to carbonization at 600 °C gave rise to a nanoporous carbon after digestion of the silica template. BET surface area analysis revealed a surface area of 1275 m^2/g, and BJH pore size analysis revealed a narrow pore size distribution centered at 3.5 nm. When the crude product was calcined for 1 h at 700 °C, there was no change in either surface area or pore size distribution, suggesting that the carbon framework was stable and the degree of crosslinking was fairly complete at 600 °C.

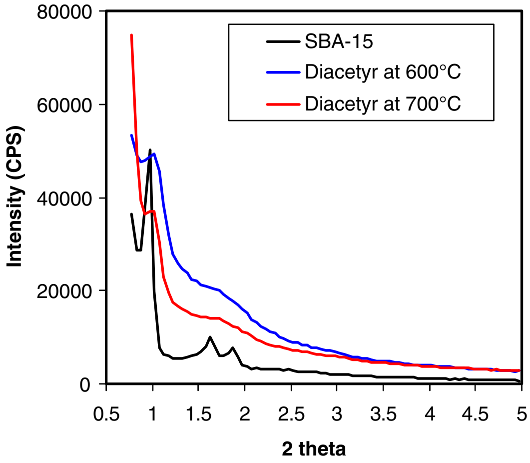

Fig. 3. Low-angle X-ray diffraction (XRD) spectra for the starting SBA-15 template (lower curve), the mesoporous carbon calcined at 600 °C (upper curve), and the mesoporous carbon calcined at 700 °C (middle curve).

Low-angle X-ray diffraction (XRD) spectra were obtained for both of these samples, and are shown in Fig. 3 (along with the low-angle XRD spectrum for the SBA-15 template). The low-angle XRD spectra for these pyridine functional mesoporous carbons (Pyr-FMCs) hint at the hexagonal pore structure of the SBA-15 template, but both spectra clearly show some degradation of hexagonal order relative to the starting silica template.

High resolution transmission electron microscopy (TEM) was employed to gain a better understanding of the pore structure in these Pyr-FMCs. As can be seen in Fig. 4, the parallel pore structure of SBA-15 is preserved in the Pyr-FMC product calcined at 600 °C, although the hexagonal pore symmetry is not immediately apparent from these micrographs. Similar results were obtained with the sample calcined at 700 °C (not shown).

A sample of the Pyr-FMC was subjected to X-ray photoelectron spectroscopy (XPS), and a close up of the N portion of the spectrum

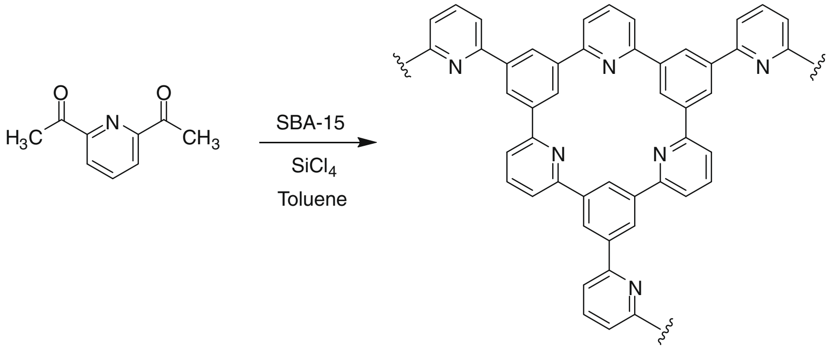

Fig. 2. Schematic showing the cyclotrimerization of 2,6-diacetylpyridine.