



# Formation mechanism of 0.4-nm single-walled carbon nanotubes in AlPO<sub>4</sub>-5 crystals by low-temperature hydrocracking



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## ABSTRACT

The carbonization mechanism of tripropylamine (TPA) in low-temperature hydrocracking was studied with the aim of increasing the quality and filling density of single-walled carbon nanotubes (SWCNTs) produced in the channels of AlPO<sub>4</sub>-5 crystals. The conversion process of TPA was investigated using a combination of Fourier transform infrared spectroscopy, mass spectrometry, <sup>13</sup>C nuclear magnetic resonance spectroscopy, thermogravimetric analysis and micro-Raman spectroscopy at various hydrocracking temperatures. During the hydrocracking process, hydrogen participated in the cracking reaction of TPA and decreased the required activation energy. The protonated TPA converted into neutral TPA at 210 °C. When the hydrocracking temperature exceeded 260 °C, dipropylamine, *n*-propylamine, propylene, propane, ethane and methane were produced. The hydrocracking rate of TPA increased with increasing hydrocracking temperature. A small amount of aromatic compounds was also detected in the AlPO<sub>4</sub>-5 crystals hydrocracked at 280–350 °C; this amount decreased with increasing hydrocracking temperature. The content of residual TPA and amorphous carbon compounds in the AlPO<sub>4</sub>-5 crystals also decreased with increasing hydrocracking temperature. TPA decomposed completely after hydrocracking for 10 h at 350 °C. SWCNTs with a diameter of 0.4 nm were synthesized at 280–350 °C, and the filling density of SWCNTs increased with increasing hydrocracking temperature.

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## 1. Introduction

Carbon nanotubes (CNTs) [1] have attracted increasing attention because of their novel 1D character, properties and potential applications [2,3]. The lack of purity and uniformity in diameter, chirality and alignment has hindered exploration of the intrinsic chemical and physical properties of CNTs as well as their applications in novel electronic systems [4–7]. In 1998, Tang et al. [8] successfully prepared aligned 0.42-nm single-walled carbon nanotubes (SWCNTs) in the channels of AlPO<sub>4</sub>-5 crystals by thermal cracking. These SWCNTs exhibit favorable properties such as 1D superconductivity fluctuation, characteristic electrochemical properties and high adsorption capacities [9–11].

AlPO<sub>4</sub>-5 (structure code AFI) is a type of microporous aluminophosphate molecular sieve. Its framework consists of 1D open channels with a diameter of 0.73 nm that array in a triangular lattice structure [12]. In the traditional thermal cracking process,

SWCNTs are usually synthesized in the channels of AlPO<sub>4</sub>-5 crystals at ≥550 °C under vacuum for several hours [13–18]. Because the AlPO<sub>4</sub>-5 framework is chemically inert, the adsorption of organic precursors to the channel walls is relatively weak. A considerable amount of hydrocarbon guest molecules easily escapes from the channels, because the hydrocarbon molecules prefer to escape from the channels of the host rather than thermally decompose inside the channels at high cracking temperatures [17]. This results in insufficient carbon atoms for the formation of continuous CNTs. The density of SWCNTs formed in the channels of AlPO<sub>4</sub>-5 crystals is relatively low, and the nanotubes are rich in structural defects.

To improve the filling density and quality of the SWCNTs formed in AlPO<sub>4</sub>-5 channels, the amount of carbon atoms that remain in the channels during pyrolysis needs to be increased. Normally, the adsorption of the organic precursor to the channel walls can be enhanced by introducing a localized dipole charge onto the walls through doping with alternative metals [15,16], which can keep more carbon atoms inside the channels during pyrolysis. Exploiting precursor molecules with a high carbon density has also been shown to increase the density of the resulting SWCNTs [17]. Carbon monoxide or ethylene can be introduced into the channels of

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AlPO<sub>4</sub>-5 as an additional carbon source [18]. There have also been some attempts to prepare CNTs in the channels of AFI crystals at low cracking temperatures [15,17], but it was found that SWCNTs were difficult to synthesize below 550 °C using the traditional thermal cracking process. Recently, we showed that SWCNTs with increased density and quality can be prepared by hydrocracking at 350 °C [19]. With the goal of optimizing the low-temperature hydrocracking process, this work studies the low-temperature hydrocracking process and examines in more detail the carbonization mechanism of the organic precursor.

In this study, we investigated the decomposition products and detailed hydrocracking process of tripropylamine (TPA) molecules in the channels of AlPO<sub>4</sub>-5 crystals. Fourier transform infrared (FTIR) spectroscopy, mass spectrometry micro-Raman spectrometry and thermogravimetric analysis (TGA) were combined to probe the effect of hydrocracking temperature on the structure, quality and filling density of SWCNTs.

## 2. Experimental

### 2.1. Materials

All chemical reagents in this experiment were purchased from Tianjin Chemical Reagent Co., Inc. and were used without further purification. Aluminum isopropoxide (AIP, 99.5% purity) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85% purity) were used as aluminum and phosphorus sources, respectively. Tripropylamine (TPA, 99% purity) was employed as the organic template. Distilled water was used throughout this study.

### 2.2. Synthesis of AlPO<sub>4</sub>-5 molecular sieves

AlPO<sub>4</sub>-5 crystals were synthesized by the conventional hydrothermal method [20]. The molar composition of the precursor solution was 1.0Al<sub>2</sub>O<sub>3</sub>: 1.3P<sub>2</sub>O<sub>5</sub>: 2.4TPA: 150H<sub>2</sub>O. To obtain a translucent alumina sol, aluminum isopropoxide was first hydrolyzed in deionized water by heating with an oil bath at 150 °C for 5 h. Phosphorus acid was added into the alumina sol dropwise, and then the solution was stirred for another 10 h to obtain a homogeneous solution. TPA was added to the solution under stirring, and the resulting mixture was stirred for 3 h. The formed gel was sealed in a Teflon-lined autoclave after aging for 10–12 h, and heated at 180 °C for 24 h. After the reaction was complete, the autoclave was cooled to room temperature in water. The solid products were filtered, washed with distilled water until pH value was about 6, and dried at 120 °C overnight.

### 2.3. SWCNTs preparation

The synthesized AlPO<sub>4</sub>-5 crystals were used as hosts to prepare the SWCNTs. The SWCNTs were produced by hydrocracking TPA in the channels of the AlPO<sub>4</sub>-5 crystals at temperature of 260, 280, 300, 320, 350 and 400 °C. The detailed process was described in Ref. [19].

### 2.4. Sample characterization

Raman spectra of the SWCNT-containing AlPO<sub>4</sub>-5 crystals were obtained at room temperature using a Horiba JY Labram HR800 micro-Raman spectrometer (France), with the 514-nm line of a laser as the excitation source. The content of SWCNTs inside the AlPO<sub>4</sub>-5 crystals was characterized using a Netzsch STA409C/PC thermal analyzer (Germany), by heating from 28 to 900 °C in air (100 mL/min), at a rate of 10 °C/min. Optical images were obtained using a Nikon SMZ1500 stereoscope. The gaseous products of

temperature-programmed reduction (H<sub>2</sub>-TPR) were analyzed by a PC-OMINSTAR mass spectrometer (Germany) interfaced with a programmable furnace (CDS 5200). FTIR spectra were recorded using a FTIR spectrometer (Bruker TENSOR27) to monitor the hydrocracking process of TPA at various temperatures. <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance III 300-MHz spectrometer with ZrO<sub>2</sub> rotors, corresponding to the resonance frequency of 78.7 MHz for the <sup>13</sup>C nuclei. <sup>13</sup>C NMR measurements were performed with a contact time of 1 μs, recycle delay of 4 s, and sample spinning rate of 6 KHz and acquired with 2048 scans per increment. High-resolution TEM images were collected using a JEOL 2010 microscope (Japan) at 200 KV. Samples were first dissolved in 30% (mass fraction) HCl for 30 min, to discharge the SWCNTs from the channels of the AlPO<sub>4</sub>-5 crystals.

## 3. Results and discussion

SWCNTs with a diameter of 0.42 ± 0.02 nm were synthesized in the channels of AlPO<sub>4</sub>-5 and CoAlPO<sub>4</sub>-5 crystals by hydrocracking at 350 °C in Ref. [19], which was confirmed using high-resolution transmission electron microscopy. There are only three possible structures of SWCNTs with this diameter: zigzag (5, 0), armchair (3, 3) and chiral (4, 2) structures. The detailed structural properties of the SWCNTs were analyzed by Raman spectroscopy without destroying the samples. The Raman spectra exhibited three main features, as shown in Fig. 1. The radial breathing mode (RBM) was in the low-frequency region (400–600 cm<sup>-1</sup>), which is characteristic of SWCNTs. The Raman lines at 510 and 550 cm<sup>-1</sup> are attributed to chiral (4, 2) and zigzag (5, 0) nanotubes, respectively [18]. The disordered structure-related D bands were in the central region of 1200–1500 cm<sup>-1</sup>, and the tangential G bands in the high-frequency region of 1500–1620 cm<sup>-1</sup> were characteristic of carbon bond vibrations [21]. Because some of the carbon in the channels was in the form of amorphous carbon which can give rise to G-band signal but no RBM signal, we used the relative intensity ratio of RBM to G band ( $I_{\text{RBM}}/I_{\text{G}}$ ) as an indication of the amount of SWCNTs contained in the channels of the AlPO<sub>4</sub>-5 crystals. No RBM peaks for the sample hydrocracked at 260 °C were observed, indicating SWCNTs can not be prepared at this temperature. The values of  $I_{\text{RBM}}/I_{\text{G}}$  at 280, 300, 320 and 350 °C were 0.083, 0.098, 0.186 and 0.206, respectively, as shown in Table 1. Therefore,  $I_{\text{RBM}}/I_{\text{G}}$  increased with

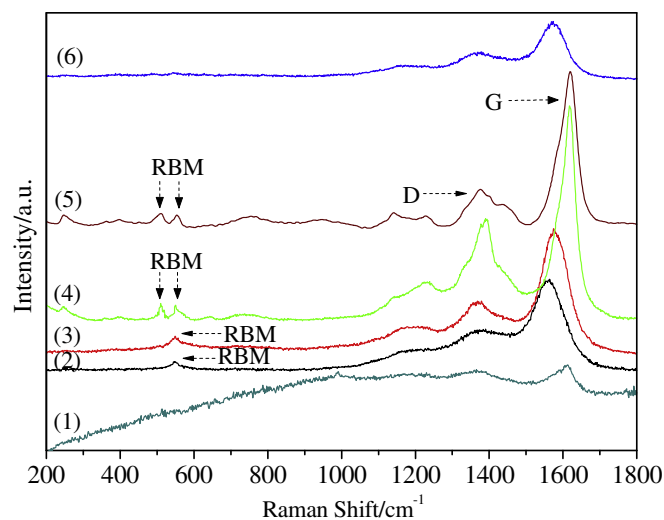


Fig. 1. Raman spectra of the SWCNTs in the AlPO<sub>4</sub>-5 crystals hydrocracked at various temperatures: (1) 260 °C, (2) 280 °C, (3) 300 °C, (4) 320 °C, (5) 350 °C and (6) 400 °C. (A colour version of this figure can be viewed online.)

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