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IR and NMR spectroscopic characterization of graphitization process occurring in the pores of mesoporous silicates in formation of carbon nanotubes

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Abstract

Synthesis of carbon nanotubes (CNTs) from the template molecules of the Si-MCM-41 and Al,Si-MCM-41 mesoporous silicates were investigated. The generation of nanotubes was carried out by graphitization, i.e. applying high temperature treatment of the MCM-41 samples in inert gas atmosphere.

The as-synthesized and graphitized samples were characterized by several spectroscopic and physico-chemical methods such as IR and MAS NMR spectroscopy, XRD, TEM, and BET.

Keywords: Carbon nanotubes; Al-MCM-41; Si-MCM-41; ^{13}C-; ^{29}Si-; ^{27}Al MAS NMR; Pyridine adsorption; IR spectroscopy

1. Introduction

Carbon nanotubes are in the focus of material science since they have peculiar chemical, mechanical and electrical properties [1]. Several methods are used for production of carbon nanotubes [2]. Generally the most frequently applied techniques differ either in the carbon source or in the method to generate high temperature at which the carbon precursor converts to carbon nanotubes. Graphite, mixtures of transition metal compound and carbon, or various hydrocarbons and hydrocarbon derivatives in the vapour phase have been used as carbon sources. The catalytic synthesis of nanotubes, generally called as catalytic chemical vapour deposition (CCVD), requires catalytically active centres, usually metal clusters, and relatively low (700–1000 °C) temperature. Recently, Chinese researchers reported the synthesis of carbon nanotubes in the pore system of AlPO-5 type zeolite [3]. Korean scientists claimed the production of carbon-silicate composite via carbonization of divinylbenzene in the pores of mesoporous silicate of MCM-48 type [4].

In an earlier work [5] we reported on the synthesis of carbon nanotubes from the organic template molecules used for the preparation of mesoporous silicate. The pores of MCM-41 type materials, synthesized with cetyl-trimethyl-ammonium bromide (CTMABr), are filled with well-ordered organic molecules what are ideal carbon sources to produce carbon nanotubes inside. CNTs can be formed by high temperature treatment of the pure silica MCM-41 without active metal content in inert gas atmosphere. For these synthesis relative low CNT production (compared to the CCVD method) was achieved. This finding addresses the question how the acidic centres (Al,Si-MCM-41) influence the yield of carbon nanotubes.

IR Spectroscopy combined with other instrumental analytical methods proved to be useful tool to clarify the questions addressed above.

2. Experimental

2.1. Synthesis of starting materials

The Si-MCM-41 sample was synthesized as described in the literature [6]. 53.6 g of cetyl-trimethyl-ammonium

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bromide (CTMABr, Aldrich) was dissolved in 318.4 g of distilled water with stirring and warming. When the solution became transparent, the heating was stopped and the solution was cooled to ambient temperature. Then 65.44 g of sodium silicate (Aldrich) and 17.92 g of 10% sulfuric acid were added drop-wise to the solution while stirring. After further 30 min stirring the pH of the mixture was adjusted to pH 10 dropping 50% of sulfuric acid to the reacting mixture. The material was transferred into a Teflon-lined autoclave and hydrothermal treatment was carried out at 393 K for 7 days. After a week the autoclave was cooled to room temperature, and the crystalline material was separated by filtration. The solid product was washed with distilled water and dried at 373 K overnight.

When synthesizing Al,Si-MCM-41 two solutions were prepared. For the first solution, a mixture of Ludox HS-40, tetramethyl-ammonium-hidroxide (TMAOH) and distilled water (with a ratio of TMA/Si = 1:1, 10 wt% Si) was prepared and stirred for two days at room temperature to form tetramethylammonium-silicate solution. The second solution was prepared from 8.66 g cetyl-trimethyl-ammonium bromide, 50 g of distilled water and 2.426 g of aluminium-sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$). Then 50 g of tetramethyl-ammonium-silicate solution was dropped to this solution and the stirring went on. After 10 min 12.5 g of SiO_2 (HiSil) and further 10 g of tetramethylammonium-silicate solution was added to the mixture under continuous stirring. This synthesis mixture was transferred into a Teflon-lined autoclave, and crystallization was performed at 373 K for a day. The solid product was washed with distilled water and dried at 353 K overnight.

These samples are labeled as AS-Si-MCM-41 and AS-Al,Si-MCM-41 samples. AS refers to samples containing organic template molecules in their pores.

To remove the template, a part of the as-synthesized samples was placed in a ceramic boat and put in an oven under nitrogen flow. The temperature of the oven was adjusted to 823 K with a heating rate of 2 K/min. At this temperature the nitrogen flow was switched for oxygen and the template was burned off from the pores for 5 h. These samples are denoted B-Si-MCM-41 and B-Al,Si-MCM-41, where B means that the template has been burned off. The color of the template free sample was white. These samples contain no carbon even in traces.

2.2. Preparation of carbon nanotubes

Synthesis of carbon nanotubes was performed with simple graphitization of the organic template molecules filling the pores of mesoporous materials at high temperature under inert atmosphere. A portion of the as-synthesized samples was placed in a quartz boat and the boat was put into a quartz reactor. The reactor was flushed out with nitrogen at a rate of 100 cm^3/min for 30 min before drawing it in an oven, temperature of which was previously adjusted to 1073 K. After different reaction times, the reactor was removed from the oven and the system was cooled to room temperature under nitrogen flow. The products of these treatments are labelled GAS-Si-MCM-41, GAS-Al,Si-MCM-41. These samples are silicate carbon composites.

In order to obtain the carbon nanotubes the silicate component was removed by dissolution with 38% HF solution. The treatment of GAS samples was repeated several times to extract the silicate completely. These samples were regarded to CNTs.

2.3. Characterization of samples

For TEM analysis the grids were prepared as follows. Approximately 1 mg of product was sonicated in 10 cm^3 ethanol for a few minutes. Then a few drops of the resulting suspension were put on a holey-carbon TEM grid. TEM images were taken by a Phillips CM 10 electron microscope operated at 100 kV.

XRD patterns of each sample (AS-, B- and GAS-samples) were recorded. X-ray diffraction patterns were run on a DRON 3 Russian made diffractometer operated under computer control. Diffractograms were registered in the 2Θ range of 0.5–10° using Cu Kα radiation. The position of the first reflection is characteristic of the pore diameter of the ordered mesoporous structure. The XRD patterns of GAS samples allowed us to observe the change of silicate structure during the graphitization process.

A Bruker Avance DRX-500 spectrometer was used for ^{29}Si, ^{27}Al and ^{13}C NMR measurements. From ^{29}Si and ^{27}Al MAS NMR spectra the coordination of these nuclei in the silicate structure and from ^{13}C MAS NMR spectra the state of organic template can be revealed. The ^{29}Si and ^{13}C chemical shifts were referenced to liquid Me_4Si. ^{29}Si spectra were taken at 99.36 MHz, ^{27}Al at 130.33 MHz. Cross polarisation (CP) was also applied for ^{13}C MAS NMR measurements.

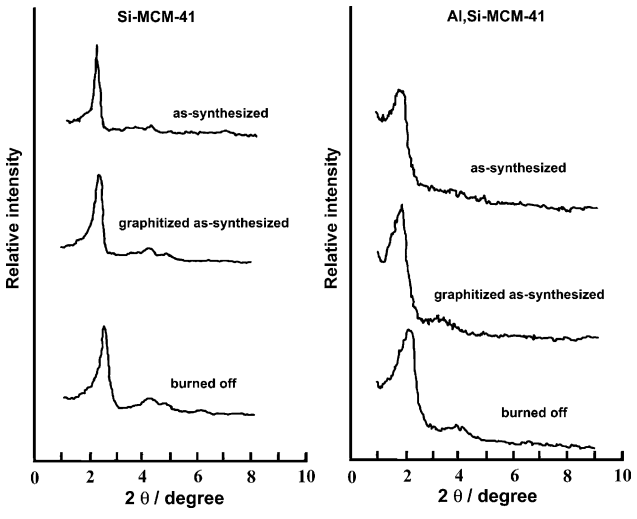

Fig. 1. XRD profiles of MCM-41 samples after various treatments.