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Applied Surface Science 242 (2005) 192–198
applied surface science
www.elsevier.com/locate/apsusc

Catalytic growth of carbon nanotubes over Ni/Cr hydrotalcite-type anionic clay and their hydrogen storage properties

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Accepted 14 August 2004
Available online 25 September 2004

Abstract

Carbon nanotubes have been prepared by the catalytic decomposition of acetylene over Ni/Cr hydrotalcite-type anionic clay catalyst. Ni/Cr hydrotalcite-type anionic clay precursors have been prepared by co-precipitation technique. The role of stability of Ni nanoparticles obtained in situ from the decomposition of the catalyst on the growth of MWNTs is discussed. The as-synthesized and purified carbon nanotubes are characterized by thermogravimetry, IR spectroscopy, X-ray diffraction, BET analysis, scanning electron microscopy, transmission electron microscopy and Raman spectroscopy measurements. The hydrogen adsorption capacity of as-synthesized and purified multiwalled carbon nanotubes at 298 K has been obtained using a high-pressure hydrogen adsorption set-up and the results are discussed.

Keywords: Catalyst; Nanotube; Ni/Cr hydrotalcite

1. Introduction

The unique physical and chemical properties of carbon nanotubes (CNTs) [1] have stimulated intense research and have enabled them to be applied in many promising fields including high strength composites, sensors, field emission displays, nanometer-sized semiconductor devices and hydrogen storage media [2–4]. It is always desirable to develop a new hydrogen storage media with high capacity, light mass and high stability. CNTs seem to be ideal candidates, due to their chemical stability, large surface area, hollowness and light mass [5]. Gundiah et al. [6] have examined the hydrogen adsorption measurements on well-characterized samples of CNTs with a maximum storage capacity of 3.7 wt.%. In our recent work, the

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doi:10.1016/j.apsusc.2004.08.014

removal of catalytic impurities and amorphous carbon from the CNTs synthesized from the decomposition of acetylene over alloy hydride catalysts has resulted in the increased hydrogen sorption capacity of 3.3 wt.% at 100 bar and 298 K [7]. As the diameters and morphology of CNTs and hence their physical properties are expected to be dependent on the size and shape of catalytic nanoparticles [8], controlled growth of CNTs would require an efficient and reproducible route for catalyst preparation. The growth of CNTs by thermal chemical vapour deposition (CVD) has been reported to be simpler and reproducible [9,10]. Various growth models [11] and thermodynamic analysis [12] have been reported for the nucleation and growth of CNTs. In this approach, it is important to prepare an effective catalyst with appropriate size of active metal particles, usually Fe, Co or Ni. Recently, Yang et al. [13] used benzene as a carbon source to produce quasi-aligned carbon nanotubes in high yield at 650 °C over γ-Al_2O_3-supported Fe–Ni alloy catalysts. As most of the catalysts reported were pre-formed, a precise control on their size becomes difficult. Further, the ease of separation and purification of CNTs varies with the catalyst and catalyst support used. Several support materials have been used during CVD synthesis of CNTs, such as zeolites [14], mesoporous silica [15] and alumina [16]. Zr-based AB_2 and Mm-based AB_5 alloy hydrides obtained by the hydrogen decrepitation technique have been used as catalysts for the CVD synthesis of multi-walled carbon nanotubes (MWNTs) [7]. Physical interactions between the substrate and the catalyst material, together with obstruction of catalyst particle movement on the substrate, reduce the thermally driven diffusion and the sintering of metal particles on the support surface [8]. This results in stabilization of the catalyst particle size distribution during carbon nanotube synthesis. Hence, catalysts with high metallic dispersion showing high particle stability against sintering are essential for the controlled growth of high quality CNTs. Iron catalysts supported on montmorillonite clay surfaces have been used to synthesize clay–carbon nanotube composites by the catalytic decomposition of acetylene [17]. The clay acts as an alternative substrate for immobilizing the catalytic metal centers. In a recent work, smecite clays were used as catalysts to functionalize single-walled carbon nanotubes (SWNTs) [18]. In the present work, we report the synthesis of MWNTs over Ni/Cr hydrotalcite (HT)-type anionic clay catalyst by the catalytic decomposition of acetylene. High stability of the Ni nanoparticles prepared in situ by the decomposition of this catalyst allow better dispersion of the active catalytic sites and hence is expected to result in the growth of MWNTs in high yield. In addition, the hydrogen uptake properties of these samples were also investigated and are discussed.

2. Experimental

The Ni/Cr hydrotalcite-type anionic clay precursors were prepared by co-precipitation under low supersaturation conditions of the hydroxide from the corresponding nitrates [19]. NaOH (0.2 mol) and Na_2CO_3 (0.02 mol) were dissolved in 50 ml of distilled water and were added to nickel (II) nitrate and chromium (III) nitrate solutions (in 300 ml) with constant stirring. The green precipitate was then aged at 100 °C for 24 h, without stirring. The aged precipitate was then filtered several times with distilled water till neutral pH and dried in an air oven at 80 °C over night. The stoichiometry was confirmed by the percentage of Ni and Cr (3:1) taken over a collection of particles from the EDAX measurements.

Carbon nanotubes were synthesized using a fixed-bed catalytic reactor, described elsewhere [20] by the decomposition of acetylene over Ni/Cr HT-type anionic clay catalysts. For each synthesis, 200 mg Ni/Cr HT-type clay catalyst was placed in the quartz boat that was inserted into the center of a quartz tube (30 mm inner diameter and 500 mm long). The quartz tube was then mounted in a furnace and it was heated to 500 °C in argon atmosphere. Subsequently, H_2 was introduced into the quartz tube for 1 h for the reduction of the catalysts. The flow rates of argon and hydrogen were 200 and 50 sccm, respectively. Once the hydrogen flow was shut off, the temperature of the furnace was increased to 700 °C for the deposition of carbon. Acetylene was then allowed (600 sccm) for 30 min. Argon flow was maintained throughout the experiment until the furnace was