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Influence of ethanol in the presence of H_2 on the catalytic growth of vertically aligned carbon nanotubes

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ABSTRACT

The vertically aligned multi-walled carbon nanotubes (VA-MWNTs) were synthesized by a catalytic chemical vapor deposition (CCVD) technique, using ferrocene as an iron catalyst precursor and toluene/ethanol mixture with different ratio as a carbon source/etching agent, in the presence of H_2. The growth rate, efficiency and the structure of the synthesized tubes were investigated. The CNTs growth rate and quality of tubes significantly improve up to 9 vol.% of ethanol whereas a negative influence was observed for higher ethanol concentration (>17 vol.%). Low ethanol content in the reaction mixture (5 vol.%) results in the highest volume density of the tubes within the array along with highest specific surface area. The synergetic effect of EtOH/hydrogen on the growth rate of VA-MWNTs was observed as well.

1. Introduction

Carbon nanotubes (CNTs), a one-dimensional carbon materials with high aspect ratio (the aspect ratio is defined as the length divided by diameter of the nanotube), have received an over increasing scientific interest during the last decades due to their exceptional physical and chemical properties [1–3]. Several advantages such as important mechanical resistance, high electron and thermal conductivity make them interesting for the electronic and reinforcement composite applications. High and fully accessible external surface render them an interesting candidate for catalytic applications. Recent works have pointed out the possible use of carbon nanotubes, either pure or doped with heteroatoms, as catalyst or catalyst support in several reactions [4–7]. The nanoscopic dimension of the CNTs also significantly reduces the problem of diffusion, especially in the case of liquid-phase reaction. Attempts to prepare structured catalytic layers based on vertically aligned CNTs have been reported by several groups working in this field [8,9]. Compared to agglomerated CNTs in powder form, aligned CNTs exhibit several advantageous properties, such as high orientation degree, high purity and easy to be processed regarding the downstream applications [10–13]. Such structured catalyst support allows a development of 3D ordered nanomaterials for several catalytic applications, i.e. support for 3D ordered proton exchange membrane fuel cell (PEMFC) [14,15], catalyst for fine chemical reactions [16,17], selective filter for heavy hydrocarbon separation or virus removal from the water medium [18]. Vertically aligned CNTs can only be synthesized with high rate and purity by CVD methods. It is expected that synthesis environment [19–22], i.e. gas phase composition and flow rate, synthesis temperature and pressure, plays an important role in the morphology and structural change of the active metal catalyst which significantly modify the physical properties and morphology of the final VA-CNTs. Despite the relatively large work devoted to the synthesis of VA-MWNTs by CCVD with immobilized catalyst [23,24], floated CCVD technique [25,26] presents the most promising synthesis method for economically producing large quantities of CNTs in macroscopic form. Additional work is needed in order to improve the CNTs growth rate (yield improvement) and also to reduce as much as possible the amount of amorphous carbon on the surface of the final CNTs (quality improvement). The yield and quality improvement can be achieved when oxidant, i.e. H_2O, O_2, CO_2, CH_3CH_2OH, is added to the feed [27–29]. However, even if this addition method has been comprehensively studied, the influence of alcohol on the overall growth process and quality of the carbon nanotubes has been far

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