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Applied Catalysis A: General 301 (2006) 123–132

APPLIED CATALYSIS A: GENERAL

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Catalytic synthesis of carbon nanofibers with different graphene plane alignments using Ni deposited on iron pillared clays

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Received 6 October 2005; received in revised form 9 November 2005; accepted 30 November 2005

Abstract

The present study confirmed that crystalline nanofibers with controlled structure may be prepared at different reaction temperatures over Ni deposited on Fe pillared clays. It was found a large catalytic effect over the growth of carbon nanofibers at temperatures between 450 and 650 °C. TEM pictures revealed different types of CNFs as a function of the reaction temperature: platelet type structures at 450 °C, both platelet and fishbone type structures at 550 °C, and tubular type structures that started to be produced at temperatures above 600 °C. CNFs associated with a reaction temperature of 650 °C were characterized by a very broad diameter distribution; some CNFs had diameters much higher than the freshly reduced metal crystallites. The arrangement of graphite sheets shifted from a situation where a large fraction of the edge sites would be available for gas adsorption to other in which a minor fraction of these sites were available. As a consequence, the CNFs surface area tended to decrease in increasing the reaction temperature. Finally, some improvement of stacking and removal of defects were achieved by raising the reaction temperature.

Keywords: Carbon nanofiber; Chemical vapor deposition; Nickel; Pillared clays; Reaction temperature

1. Introduction

Carbon nanostructures are becoming of considerable commercial importance with a continuous interest growing over the past decades since the discovery of carbon nanotubes (CNTs) and carbon nanofibers (CNFs). Recently, the chemical vapor deposition (CVD) method has emerged as a promising method for nanocarbon synthesis because it is capable of controlling the nanostructure and synthesizing it in large quantities. In this method, carbon nanostructures are prepared by the gas-phase decomposition of hydrocarbons or disproportionation of CO in the presence of catalysts containing principally group VIII metals [1,2]. Consequently, metals supported over different solids promote effectively the synthesis of carbon nanostructures.

On the other hand, it is well documented that the catalyst support can have a great impact on the structure of carbon deposits [3,4]. In this way, physical interaction between the support and the catalyst metal, 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, which result in stabilization of the catalyst particle size distribution during carbon nanotube/nanofiber synthesis [3,5]. Solid supports mostly employed comprise zeolites, mesoporous silica, silica, alumina and graphite [6–9]. Given the increasing interest in preparing nanostructures with supported growth catalysts, the search of new supports is of great interest. In this sense, the use of pillared clays could constitute a good alternative.

Pillared clays (PILCs) constitute one of the families of new microporous materials developed by molecular engineering. They are prepared by a multi-step synthesis process consisting in the exchange of the charge balancing cations of smectitic clays by inorganic polyoxocations formed by polymerization of cations of some metallic elements. Subsequently, the stabilization of a large increase in the basal spacing of the clays and the calcinations, transform the intercalated polycations into metal oxide clusters by dehydration and dehydroxylation processes. These metal oxide clusters, called pillars, are inserted between the clay layers, maintaining them apart for a relatively large

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doi:10.1016/j.apcata.2005.11.026

distance, thus avoiding their collapse and developing a porous network with molecular range dimensions.

Intercalated clays have already been used as catalytic supports after their impregnation with different active phases [10]. In this sense, these materials can act as catalysts in the growth of carbon nanostructures [11]. These authors reported that iron supported on montmorillonite clay can be used to synthesize carbon nanotubes by the CVD of acetylene. Nevertheless, the principal problem related with the use of catalysts containing Fe as the active metal is their fast deactivation, which causes the hydrocarbon conversion to decrease with the reaction time, and leads to a relatively low carbon nanostructures yield [12–14]. The introduction of others metals (i.e. nickel) may increase the activity and stability of the iron-based catalyst and hence the carbon yield. According to Rodriguez et al. [15], iron–nickel alloys with a high content of nickel allowed to synthesize CNTs with different morphologies to those synthesized with just iron.

Final results of a synthesis of nanotubes/nanofibers should normally depend as much on the feed gas as on the reactor operating conditions. In the field of chemical engineering, the reactor operating conditions are considered to be the main factors influencing the chemical reaction, while the detailed features of a given catalyst are secondary ones [16]. Especially, the reaction temperature is crucial for selective and controlled growth of nanomaterials, which is necessary for many applications.

In this work, we report the use of a Fe–pillared clay, as an alternative for immobilizing the catalytic metal (Ni), in the synthesis of carbon nanostructures using ethylene as the carbon source. Additionally, the obtained products were characterized using various experimental tools in order to investigate their structural and textural properties. The investigation was also focused on the effects of the reaction temperature over the yield and characteristics of the carbon nanostructures here synthesized.

2. Experimental

2.1. Catalyst preparation

The starting clay was a purified-grade bentonite supplied by Fisher Scientific, with a cation exchange capacity of 94 meq/100 g clay and the following chemical composition (wt.%): SiO_2, 52.22; Al_2O_3, 16.81; Fe_2O_3, 3.84; Na_2O, 1.26; MgO, 0.88; CaO, 0.74; K_2O, 0.80 [17,18]. Particle sizes of $<2\ \mu m$ were used in the pillaring process.

A typical Fe–PILC synthesis procedure was as follows: $FeCl_3 \cdot 6H_2O$ was added to NaOH solutions to obtain a OH/Fe molar ratio of 2. In order to avoid precipitation of iron species, the pH was kept constant at 1.7. The resulting solution was aged for 4 h with stirring at room temperature. The pillaring solution was then slowly added to a suspension of bentonite in deionized water. The mixture was stirred and allowed to react. Finally, the solid was washed by vacuum filtration with deionized water until it was chloride free (conductivity lower than $6\ \mu S\ cm^{-1}$). The aim of this stage was to remove excess chloride ions, which could prevent the diffusion of polyoxocations within the interlayer space [19]. The solid was air-dried and the resulting product was calcined for 2 h at 450 °C [20].

Subsequently, Ni was introduced in the Fe–PILC structure by impregnation. Several grams of Fe–PILC were placed in a glass vessel and kept under vacuum at room temperature for 2 h in order to remove water and other compounds adsorbed on the structure. A known volume of an aqueous $Ni(NO_3)_2$ solution (the minimum amount required to wet the solid) was then poured over the sample. After 2 h, the solvent was removed by evaporation under vacuum at 90 °C. Ni content in the catalyst was 9 wt.% by weight. Finally, this sample was calcined at 550 °C during 2 h (10 °C min^{-1}).

2.2. Catalytic synthesis of carbon nanofibers

Carbon nanofibers growth was carried out at atmospheric pressure in a fixed bed reactor (quartz-tube of 2.5 cm diameter and 75 cm length), located in a vertical oven, in the temperature range of 400–800 °C. In each synthesis run, 100 mg of the prepared catalyst was placed in the center of the reactor and then was activated by heating (10 °C min^{-1}) in 100 ml min^{-1} dry 20% (v/v) H_2/He to the desired reaction temperature. The reduced activated catalyst was thoroughly flushed in dry He (100 ml min^{-1}) during 1 h before introducing the C_2H_4/H_2 feed (gas hourly space velocity (GHSV) of 30,000 h^{-1} with a C_2H_4/H_2 molar ratio of 2/1). The reaction time was adjusted to allow a uniform growth of carbon. The reactor was subsequently cooled to ambient temperature in He flow. After the decomposition of ethylene, the weight of carbon deposit (W_c) was calculated using the equation:

$$W_c\,(\%) = \frac{(m_{tot} - m_{cat})}{m_{cat} \times 100}\,(g_{carbon}/g_{cat})$$

where m_{cat} was the initial amount of the catalyst (before reaction) and m_{tot} was the total weight of the catalyst plus the carbon deposited at the end of the reaction. This yield was also quoted per gram of metal (g_{carbon}/g_{Ni}).

The product stream was analyzed by on-line capillary chromatography using a SHIMAZDU GC17A chromatograph, equipped with a split injector and a flame ionization detector, and a RESTEK Q-plot (30 m length and 0.32 mm i.d.) capillary column. The yield of solid carbon was calculated using the expression:

$$\text{Yield to carbon} = \frac{((C_2H_4)_{input} - (CH_4/2 + C_2H_4 + C_2H_6)_{output})}{(C_2H_4)_{input}}$$

2.3. Purification of carbon nanofibers

Clay support was separated from the carbon product by leaching the primary product with hydrofluoric acid (48%) for 15 h under vigorous stirring, followed by filtration and washing. Upon treatment of the catalyst–carbon mixture, the metal component of the catalyst is generally transferred into the