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From carbon dots to multipods — The role of nickel particle shape and size

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ABSTRACT

In an attempt to synthesize carbon tripod structures in high yield, we have observed that a wide range of carbon structures are formed as the Ni particle size and shape varied. In using trichloroethylene (TCE), acetylene and their mixtures as a carbon source to make carbon materials over Ni nanoparticle catalysts in a chemical vapor deposition (CVD) process, we have observed that the Ni particle size and shape impacts dramatically on the carbon structure formed. The synthesis of the Ni catalyst was achieved by reduction of Ni(acetate)$_2$ with hydrazine (35%). Ex-situ TEM analysis of the reduced NiO particles revealed that the Ni particles underwent a morphological change in the presence of TCE (and H_2) with change in (i) temperature (350–750 °C) and (ii) H_2 flow rate (20–150 mL/min) and that this affected the shape of the carbon material that formed. In the absence of TCE only particle sintering occurred. At $T = 350$ °C the Ni particles are covered by carbon to form carbon dots. With an increase in T the carbon shapes changed to a bimodal (400 °C) and then to a tripod-like structure (450 °C) and eventually multipod-like structures (500 °C). Carbon fibers were mainly observed for $T > 500$ °C. Similar shape changes were observed at 450 °C as a function of reaction time and H_2 flow rate. It was also found that when acetylene or an acetylene/trichloroethylene mixture was used at $T = 450$ °C, helical and linear fibers were produced. The TEM data reveal that the fragmentation and sintering of the Ni (by the carbon source and other factors) to give differently sized Ni particles, especially as it is affected by H_2, determines the morphology of the carbon materials grown from the Ni. The TCE has the ability to restructure the Ni particles and this leads to the unusual carbon shapes observed. Thus the carbon and the catalyst influence each other during the growth of the carbon materials.

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1. Introduction

The process of producing structured carbon nanomaterials by decomposition of various hydrocarbons has attracted the attention of many researchers. Thus different shaped carbon nanomaterials such as carbon nanofibers (CNFs) [1–4], carbon nanotubes (CNTs) [5–7], as well as carbon spheres (CS) [8–10], have been produced using various sources of hydrocarbons. The CNFs produced generally have diameters between 3 and 100 nm and lengths between 0.1 and 1000 μm. The recent interest in CNFs and their potential applications emerges from their relationship to carbons with graphite like layers such as fullerenes and CNTs; e.g. for use as catalyst supports [11–15]. CNFs produced during the catalytic conversion of carbon containing gases were initially regarded as a nuisance material [11].

Studies have shown that the choice of hydrocarbon, i.e., the carbon source does influence the resulting carbon product produced [16–18]. The different hydrocarbon reactants will influence the type and amount of carbon radicals, compounds, or species formed in the reaction zone and these impact on the CNF growth mechanism. Shaikjee et al. [19] described the effect of the use of substituted alkynes over a nickel catalyst and reported that different alkyne reactants affected the catalyst morphology and hence the morphology of the extruded carbon filaments.

The use of chlorinated hydrocarbons (CHCs) as a carbon source for the synthesis of structured carbon nanomaterials has also been studied [20–23]. CHCs produced in the chemical industry (e.g. PVC) are utilized in many household and industrial products. However, these materials can break down to give toxic compounds and the materials are often found in industrial wastes [24]. The disposal of chlorinated hydrocarbon containing materials is typically achieved in hazardous waste landfills and/or by incinerator procedures [25]. Conversion of these chlorinated waste streams into a high value commodity material; e.g. carbon shaped materials, would provide yet another outlet for the waste materials. It has been reported that chlorinated hydrocarbons are effective carbon precursors that can make a range of shaped carbon materials and they are reported to produce better yields of carbon materials when compared to their equivalent non-chlorinated compounds [26–28].

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Studies using TCE as a carbon source to make shaped carbon materials has been little studied. Nieto-Marquez et al. [20] reported on the catalytic growth of a structured carbon from chloro-hydrocarbons. They produced linear fibers and carbon spheres at $T = 500$ and $T = 650$ °C respectively using TCE over a Ni/SO_2 catalyst. When a non-chlorinated carbon source (acetylene) was used under identical reaction conditions, tubular structures were observed. Shaikjee and Coville [28] have reported that TCE was converted to tripod CNFs over a Ni zerogel catalyst.

This study reports on the use of trichloroethylene (TCE), acetylene and their 1:1 mixtures as a carbon source to make variously shaped carbons over a Ni catalyst. What is remarkable in the study is that a wide range of carbon structures can be made carbon dots (Cdots), bimodal, trimodal, polymodal, straight CNFs, coiled CNFs) using the same Ni catalyst and that the structures can be correlated to the size and shape of the Ni particles. In this study the effect of varying reaction parameters (temperature, N_2 and H_2 flow rate) on the carbons produced using TCE are described.

2. Experimental

All chemicals were purchased from Sigma Aldrich and were used as received unless otherwise stated.

2.1. Ni nanoparticle synthesis

Ni nanoparticles (NPs) were prepared by a micro emulsion technique. In a standard reaction, 1.5 g of cetyltrimethylammonium bromide (CTAB) was dissolved in a mixture of methanol (10 mL), hexanol (10 mL) and xylene (25 mL). $Ni(acetate)_2$ (1.0 g) was added to the reaction mixture and the mixture was stirred for 30 min at room temperature. Ni^{2+} was reduced by the dropwise addition of 3 mL hydrazine (35%) to the solution to form Ni nanoparticles (NPs). The precipitate was filtered and washed with 2-propanol, dried at 120 °C and calcined at 350 °C for 6 h to yield about 0.27 g of catalyst.

2.2. Carbon synthesis

The different carbons were synthesized using a catalytic CVD method. The Ni catalyst (4 mg) was spread over a quartz boat (12 mm × 28 mm) at room temperature and placed in the centre of the quartz tube reactor (18 mm × 310 mm) that was then placed in a furnace. The furnace was then heated at 10 °C per minute while hydrogen was passed over the catalyst. Once the reaction temperature was reached (350–750 °C), the H_2 flow rate was maintained at the desired temperature for 30 min prior to the introduction of TCE into the system. Different H_2 flow rates were also used (20, 50, 80, 100 and 200 mL/min). Once the catalyst was reduced, nitrogen was then bubbled through TCE (held at 50 °C) at different flow rates (20, 50, 80, 100 and 120 and 150 mL/min). H_2 was also used as a carrier gas. All reactions were carried out for 30 min. In separate reactions, acetylene and acetylene/TCE mixtures were also used as carbon sources. After the reaction, the carbon material formed was collected after cooling the reactor to room temperature under a constant flow of H_2 (100 mL/min).

2.3. Characterization techniques

CNFs and Ni were characterized by transmission electron microscopy (TEM) using a Spirit T12 instrument. About 0.5 mg of a sample to be analyzed was placed in a glass vial containing 2 mL of methanol. The mixture was then sonicated for 10 min to give a homogeneous suspension of CNFs in the solvent. A drop of the suspension was then spread on a Structure Probe, Inc. (SPI) carbon copper grid (200 mesh) and allowed to dry at room temperature. The grid was then mounted onto an exchange rod and placed into the TEM chamber and analyzed. CNFs sizes were measured from TEM images (typically about 100 particles measured) to give the width/diameter of the CNFs. It was assumed that the Ni particle correlated with this diameter and that this allowed for the determination of the Ni particle size. This assumption was also used to determine the sizes at low carbon coverage, where the Ni particles tended to be irregular in shape. Thermal stability of the CNFs was monitored using a Perkin Elmer Thermogravimetric analyser (TGA) 4000. In a standard run, CNFs (10 mg) were placed into a high temperature alumina cup that was supported on an analytical balance located in the furnace chamber. X-ray diffraction (XRD) images were collected on a Bruker D2 phaser in Bragg Brentano geometry with a Lynxeye detector using Cu-Kα radiation at 30 kV and 10 mA. The scan range was $10° < 2\theta < 90°$ in 0.040 steps, using a standard speed with an equivalent counting time of 1 s per step. The diffraction peaks were then compared with those of standard compounds reported in the Diffracplus evaluation package using the EVA (V11.0, rev.0, 2005) software package. Temperature programmed reduction (TPR) data were collected with a Micromeritics Auto Chem II unit. The catalyst (approximately 50 mg) was placed in a quartz tubular reactor and 5% H_2/Ar was passed through the reactor (50 mL·min^{-1}) as the temperature was raised at a rate of 10 °C·min^{-1} from 50 to 850 °C. The quality of the CNFs was studied using a Jobin-Yvon T64000 Raman spectrometer. The external morphology of CNFs was studied using Field Electron and Ion (FEI) focused ion beam/scanning electron microscopy (FIB/SEM) on a Nova Nanolab 600.

3. Results and discussion

3.1. Characterization of the NiO catalyst

The morphology of the synthesized Ni catalyst was characterized using TEM. The Ni catalyst was calcined in air at 350 °C (5 °C/min heating rate) for 6 h to give NiO. Fig. 1 shows the TEM image of the synthesized NiO catalyst. The NiO catalyst particles can be seen as small agglomerates that formed clusters that took a spherical shape (Fig. 1a; see supplementary Fig. S1 for larger TEM image). The XRD pattern of the synthesized NiO confirmed that NiO had been synthesized with no other diffraction impurities (Fig. 1a inset, supplementary Fig. S2a). The peaks appearing at about $2\theta = 37.2°$, 43.2°, and 62.8° are indexed as (111), (200), and (220) respectively and represent the face-centered cubic (fcc) crystalline structure of NiO [29]. The NiO catalyst was further characterized using TPR to study its reduction behavior (supplementary Fig. S2b). The TPR profile shows a single reduction peak at 421 °C. The catalyst was then treated in H_2 at different temperatures (400–500 °C) to study its behavior under H_2. The flow rate of H_2 was set at 100 mL/min and the catalyst was reduced for 30 min to give Ni particle catalysts. The TEM images of the catalyst reduced at different temperatures (400, 450 and 500, 600 and 750 °C) are shown in Fig. 1.

It is observed from the TEM image that the catalyst at 400 °C is in made up of small particles that form near spherical agglomerates. This is more clearly seen in supplementary Fig. S1. When the reduction temperature was increased to 450 °C, the Ni crystallites sinter to give larger particles with smoother surfaces. At 500 and 600 °C, it is observed that the Ni particles sinter to give even bigger particles (Fig. 1d and Fig. 1e respectively). It is however not possible to quantify the size of the Ni particles as they increase in temperature. Interestingly, a further increase in temperature (750 °C) results in catalyst particle fragmentation to form smaller particles.

3.2. Synthesis of nano carbons: temperature study

Reaction temperature is expected to have an influence on the type of carbons that are generated when TCE decomposes in the CVD process [30,31]. Differently shaped/sized carbons were synthesized at the different temperatures (350, 400, 450, 500, 600, and 750 °C; same N_2 and H_2 flow rates). In the absence of H_2, no reaction took place. TEM images (Fig. 2) show that the morphology of the synthesized CNFs and Ni particles changed dramatically with temperature. At 350 °C, the Ni catalyst

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