

Effect of catalysts on the yield and morphology of carbon nanotubes using a zeolite template

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Metallic (Fe, Co, Ni, and Cu) ion-exchanged faujasite-type (FAU) zeolite was used to synthesize carbon nanotubes by catalytic chemical vapor deposition (CCVD). Based on the characterization with transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy, the carbon grown on different metal-supported zeolites (FAU) exhibited a variety of nanostructures such as tubes, belts, and fibers. High yields of carbon nanotubes (CNTs) of up to 63.1% and 60.2% were obtained from Fe- and Co-supported zeolite templates, respectively, and the latter had a greater crystallinity.

Key words: Carbon nanotubes, Zeolite, Catalyst, Chemical vapor deposition, Template.

Introduction

Since their first synthesis by Endo and coworkers in 1976 [1] and their detailed structural characterization by Iijima in 1991 [2], carbon nanotubes (CNTs) have become commonly used and studied. Owing to their unique electronic structure, molecular dimensions, and shape, CNTs have been considered as attractive nanodevice components, so the last few decades have witnessed a great deal of intensive research focused on their wide range of potential applications such as in nanoelectronic devices [3], chemical and biochemical sensors [4], energy storage [5], and field emission displays [6].

CNTs are cylindrical nanostructures made of graphene sheets wrapped into a cylinder and capped - or not - by fullerene-like structures [7]. Their formation can be categorized into two types: the first discovered in 1991 by Iijima [2] were multi-walled CNTs (MWNTs) made of a few to a few dozen concentric cylinders placed around a single cylindrical graphite sheet, which represents the second category, called single-walled CNTs (SWNTs) [8].

Worldwide efforts have focused on producing good-quality CNTs in large quantities by simple and reliable techniques. In addition to arc-discharge [9] and laser evaporation [10], chemical vapor deposition (CVD) has proved to be the most efficient method of choice because of its low system cost, simple operating conditions, easy control of experimental parameters, and feasibility with respect to exploring various carbon sources in solid, liquid, and gaseous forms, even though the growth mechanism

has not yet been completely elucidated. In particular, catalytic CVD (CCVD), where CNTs are grown over transition metal catalyst nanoparticles (such as Fe, Co, and Ni) or their related oxides from the decomposition of a carbon feedstock (e.g., CH₄, C₂H₄, EtOH) is the most frequently employed synthesis method [11] and offers great advantages over other synthesis methods.

In principle, finely dispersed, nanometre-sized, metal particle catalysts that preserve their morphology at the CVD processing temperatures are required because controlling the morphology of the catalytic particles during CNT growth strongly affects nanotube characteristics such as uniformity, thickness, and yield. Meanwhile, the nature and chemical composition of the support determine the interaction with the metal catalyst, thus strongly affecting particle characteristics, which in turn determine the carbon growth behavior [12]. However, metal particles tend to agglomerate as their size decreases to the nanometre scale. To prevent this, porous materials have been proposed as supports. A porous support exhibiting a non-continuous surface and high surface area may not only contribute significantly to particle stabilization and produce a fine dispersion of well-defined particles, but also drastically increase the number of catalytic particles, thus increasing the number of nucleation sites, which are advantageous to the synthesis of CNTs [13]. Among all the catalytic supports presently in use, zeolites, which are molecular sieve materials with pore diameters in the range of 3-10 Å, have had a significant impact on CNT synthesis due to their high reactive surface area and structural homogeneity [14], which makes them well-suited host candidates for the different kinds of adsorbing molecules used [15] and, hence, could be used as supports for the catalyst particles used to synthesize and grow CNTs.

In this work, the faujasite-type zeolite NaX (FAU) is

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used as the template aiming at supporting different metals (Fe, Co, Ni, and Cu) to synthesize CNTs by CCVD.

Afterwards, the influence of these metal-supported zeolite catalysts on the yield and morphology of synthesized carbon products was investigated through transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy.

Experimental

Preparation of metal-supported zeolite catalysts

Faujasite-type zeolite NaX (FAU) crystals with sizes of 15 μm were synthesized hydrothermally in a mother solution with a composition of 3.5 Na_2O : 1.0 Al_2O_3 : 2.1 SiO_2 : 1000 H_2O . The synthesized zeolite powder (1 g) was refluxed with aqueous solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99.0\%$), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 97.0\%$), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99.0\%$), and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99.0\%$) with stirring for 24 h at approximately 30–40 $^\circ\text{C}$. The solutions were made by mixing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, or $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ powder of a certain mass (0.12 mol%) with 250 ml of deionized water.

After sufficient stirring, the mixtures were further centrifuged, and washed thoroughly with pure ethanol ($\geq 99.9\%$). Ethanol was used instead of water to prevent the metal cations (Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) from dissolving into the water again. The contents of these metal ions in the exchanged zeolite samples were approximately 6.64 wt.%, 6.97 wt.%, 6.96 wt.%, and 7.51 wt.%, respectively. Finally, the powder was dried at ambient temperature and calcined at 450 $^\circ\text{C}$ for 3 h in air prior to the catalytic decomposition of acetylene (C_2H_2). According to the metal ions, the four metal-supported zeolite catalysts were designated as FeNaX, CoNaX, NiNaX, and CuNaX.

Synthesis of CNTs

CNTs were synthesized by catalytic decomposition of C_2H_2 on the calcined, Fe-, Co-, Ni-, and Cu-supported zeolite catalysts in a fixed-bed flow reactor at atmospheric pressure. The reactor setup comprised a quartz boat containing the catalyst samples (approx. 100 mg) which were placed in a horizontal electric tubular furnace. The catalysts were gradually heated from room temperature to 700 $^\circ\text{C}$ in a nitrogen (N_2) flow (500 sccm) and kept at this temperature for about 15 minutes. During the subsequent reaction, a mixture of N_2 (200 sccm) and C_2H_2 (10 sccm) was fed into the reactor for 1 h. The furnace was then cooled to room temperature under a N_2 flow (500 sccm) and the carbon products were collected as a black powder from the quartz boat. These four CNT samples were denoted as CNT-FeNaX, CNT-CoNaX, CNT-NiNaX, and CNT-CuNaX.

Characterization

High resolution TEM (HRTEM) observations were performed on a JEOL JEM-3011 at an accelerating voltage of 200 kV. Samples were prepared by evaporating drops

of the zeolite-CNT-ethanol suspension after sonication onto a carbon-coated lacy film supported on a 3-mm-diameter, 300-mesh copper grid.

Thermogravimetric analysis (TGA) was performed to measure the amount of carbon deposited in the experiment and evaluate the percentage of other forms of carbon.

TGA was conducted under air in a Seiko Extar 7300 (TG/DTA 7300) instrument, with ~ 5 mg samples heated in air from 25 to 750 $^\circ\text{C}$ at a heating rate of 10 $\text{K} \cdot \text{s}^{-1}$. The Raman spectroscopy measurements were performed with a Raman system FRA-106/S using a laser excitation line at 1064 nm (Nd-YAG) in the range of 200–1800 cm^{-1} .

Result and Discussion

TEM results

The morphological characteristics of the metal-supported zeolite powder were investigated by TEM, as shown in Fig. 1(a–d). FeNaX and CoNaX samples both clearly revealed a random dispersion of Fe-containing and Co-containing catalyst particles in the zeolite, and they are presented as the black spots in Fig. 1(a) and (b), respectively. Despite that, the CoNaX sample exhibited less agglomeration and a relatively homogeneous dispersion of these catalyst particles. Moreover, the zeolitic structure of the FeNaX sample had been severely ruptured while that of the CoNaX sample mostly retained its original morphology. As shown in Fig. 1(c) and (d), however, both NiNaX and CuNaX samples exhibited homogeneous dispersions of fine catalyst particles in the zeolite, despite their different morphologies: the former presenting a corn-cob-like shape and the latter showing the shape of a nut with a kernel. Moreover, irregular zeolitic structures were presented after the calcination of all metal-supported zeolites, indicating that the zeolite crystals had been ruptured and contained irregularly shaped cavities with a size distribution in the range of mesopores. This implied that ion-exchanging

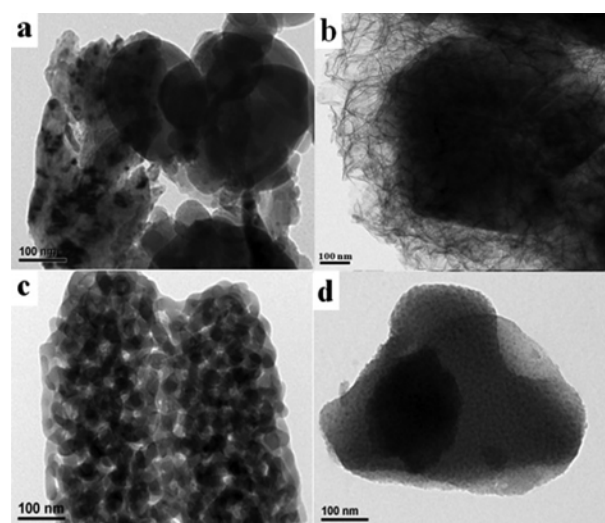


Fig. 1. TEM images of different metal-supported zeolite catalysts : FeNaX, (b) CoNaX, (c) NiNaX, and (d) CuNaX.

led the Ni^{2+} and Cu^{2+} cations to much more homogeneous dispersion in the zeolite compared to the Fe^{2+} and Co^{2+} cations, which had greater agglomeration tendencies.

After the process mentioned in the “Synthesis of CNTs” section, the products were all investigated and their TEM images are shown in Fig. 2(a-d). The CNT-FeNaX (Fig. 2(a)) and CNT-CoNaX (Fig. 2(b)) samples clearly exhibited precise MWNTs.

However, the former had more defects such as amorphous carbon and disordered graphene layers, indicated by arrows on the left side and right side, respectively, of the image shown in the inset of Fig. 2(a). The latter had less amorphous carbon and a much higher crystallinity, even though a few disordered graphene layers were observed outside the outer layer of CNTs, shown by the arrow in the inset of Fig. 2(b).

Moreover, the latter exhibited more uniform-sized products than the former did.

However, the CNT-NiNaX and CNT-CuNaX samples clearly exhibited some obvious forms of synthesized graphitic materials other than CNTs. As seen in the upper inset of Fig. 2(c), some quasi-CNTs were found in the CNT-NiNaX sample in coexistence with the CNTs. These CNTs were termed “quasi” because the products presented a clear inner tube with no outer graphene layers that formed as the walls of the CNTs, but rather belt-shaped outer layers were observed and these were similar to the shape of the carbon nanofibers (CNFs), as shown in the lower inset in Fig. 2(c). This phenomenon indicates that well-dispersed, Ni-containing catalyst particles formed belt-like or other non-isotropic structures in our study, which is slightly different from the result of a former study [16]. Additionally, the products shown in Fig. 2(d) seemed different compared to CNTs or CNFs. Due to their transparent feature and dark vein-like structure indicated by the arrow (Fig. 2(d)), they were considered to be stacks of graphene layers that included curving edges.

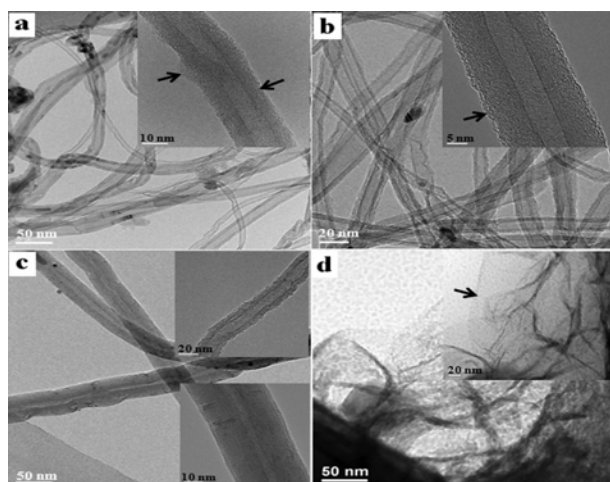


Fig. 2. TEM images of CNTs synthesized by different catalysts: (a) CNT-FeNaX, (b) CNT-CoNaX, (c) CNT-NiNaX, and (d) CNT-CuNaX.

TG results

The thermal stability of all the products was investigated by TGA. Fig. 3 revealed an initial weight loss (up to 325 °C) for all samples, which was attributed to the loss of physically absorbed water on the zeolite, possibly due to the elimination of most of the water inside the catalyst during the CNT synthesis.

However, the CNT-FeNaX, CNT-NiNaX, and CNT-CuNaX samples had much less water than did the CNT-CoNaX sample, which probably indicates that the presence of Co is favorable for absorbing water or it has a stronger interaction with water, thus enabling the CNT-CoNaX sample to absorb more water than the other samples.

After this weight loss, all the CNT samples underwent a two-step weight loss (375–670 °C) due to the combustion of CNTs, except for the CNT-CoNaX sample which only experienced a single-step weight loss (375–670 °C). The rest of the weight can be considered as the catalyst that remained after heat treatment. Generally, the decomposition of C_2H_2 on metal-supported catalysts leads to the formation of a mixture of CNTs and amorphous carbon on the catalyst surface, which can be identified as a two-step weight loss on TG curves. As shown in Fig. 3, the first step (430–550 °C for CNT-NiNaX and CNT-CuNaX, and 350–450 °C for CNT-FeNaX) corresponded to the combustion of the amorphous carbon species and disordered graphitic products. This was confirmed by the TEM results shown in Fig. 2. The weight loss at higher temperatures (550 °C for CNT-NiNaX and CNT-CuNaX, and 450 °C for CNT-FeNaX) corresponded to the combustion of CNTs. Therefore, it is inferred that the CoNaX catalyst is much more effective for synthesizing CNTs with high crystallinity and fewer defects, while the capacity for CNT synthesis of the other catalysts decreased in the following order :

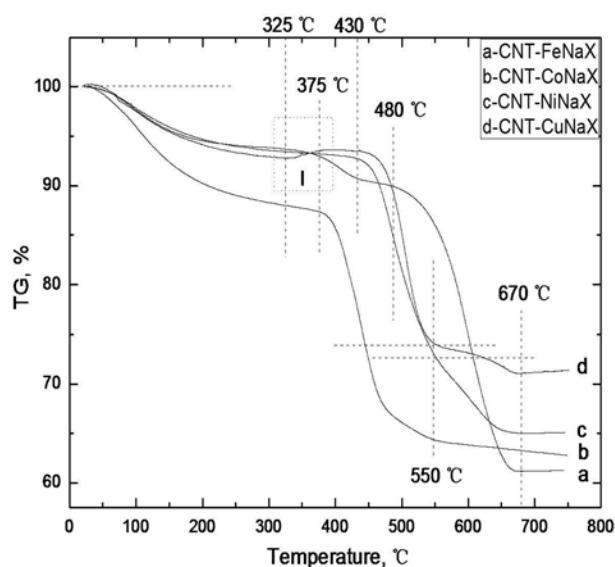


Fig. 3. TGA of CNTs synthesized with different metal-supported zeolites : (a) CNT-FeNaX, (b) CNT-CoNaX, (c) CNT-NiNaX, and (d) CNT-CuNaX.

FeNaX > NiNaX > CuNaX. Additionally, Fig. 3 revealed an emphasized region I exhibiting a slight weight increase (325–375 °C) for the CNT-CuNaX sample. This might correspond to the formation of oxides.

The quantity of carbon deposited during decomposition of small hydrocarbon molecules on metal-containing catalysts by CVD is usually calculated as follows:

$$\text{Carbon yield (\%)} = (m_{\text{tot}} - m_{\text{cat}})/m_{\text{cat}} \times 100\% \quad (1)$$

where m_{cat} is the initial amount of catalyst (before the reaction) and m_{tot} the total sample weight after the reaction. The estimates for the products synthesized by different metal-supported zeolites are given in Table 1.

Raman spectroscopy

Fig. 4 shows the Raman spectra of the synthesized CNTs observed under a Nd-YAG laser with a wavelength of 1064 nm (excitation energy 2.41 eV) at 110 mW power.

All spectra for the synthesized CNTs showed two characteristic peaks which were identified as D- and G-bands. The G-bands for the CNT-FeNaX, CNT-CoNaX, CNT-NiNaX, and CNT-CuNaX samples were at the same frequency of 1600 cm^{-1} , representing the tangential stretching (E_{2g}) mode of the highly ordered graphitic layers [17]. The G-bands for all products clearly had a sharp single peak without any other side peaks, indicating a good crystallinity. However, the D-bands were shifted towards a

higher frequency, which is associated with the disordered, sp^3 -hybridized carbon present as impurities and dispersive defects in the graphitic sheets [17]. In particular, the G-bands for the CNT-NiNaX and CNT-CuNaX samples were much broader than those of the CNT-FeNaX and CNT-CoNaX samples, which indicated a greater complexity of the defects and impurities in the former two samples as confirmed by the results shown in Fig. 2. Thus, the shifts might have been caused by the influence of these complex impurities on the vibrational movements of the C-C bonds on the graphene plane. In addition, the relative intensity ratios of the D- to G-bands are shown in Table 1, which are always used as measures of the degree of disorder in graphite sheets and thus can be used for evaluating the crystallinity of the synthesized products.

Conclusions

The morphology of carbon nanostructures grown by CCVD on porous zeolite (FAU) is strongly affected by the ion-exchanged metals utilized and the morphology of the metal-supported zeolite catalysts utilized. Using this zeolite as the template, the carbon grown on different metal-supported zeolites using acetylene as the carbon source resulted in a variety of carbon nanostructures, such as belts, fibers, and tubes.

Fe and Co favored the growth of CNTs with a high yield and high quality, respectively, while Ni yielded fibrous and belt-like structures, and Cu only yielded stacks of graphene layers. These results indicate that the carbon morphology can be readily controlled by appropriate modification of the catalysts.

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Table 1. Carbon yield and quality of the carbon products catalyzed with different metal-supported zeolites

Catalyst sample	Carbon yield %	Raman ratio (I_D/I_G)
CNT-FeNaX	63.1	1.20
CNT-CoNaX	60.2	0.83
CNT-NiNaX	43.8	0.76
CNT-CuNaX	31.0	0.75

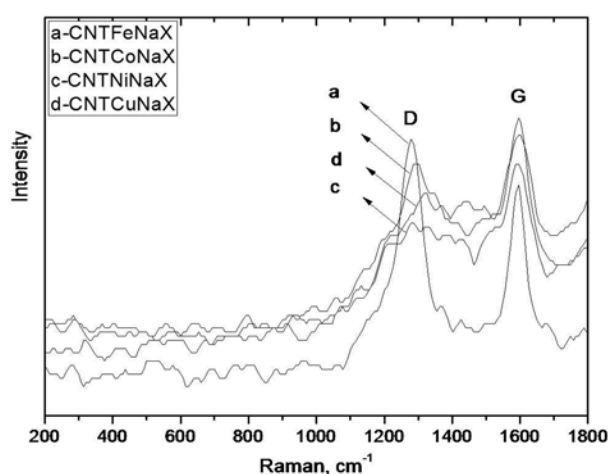


Fig. 4. Raman spectra of CNTs catalyzed with different metal-supported zeolites : (a) CNT-FeNaX, (b) CNT-CoNaX, (c) CNT-NiNaX, and (d) CNT-CuNaX.

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