In situ CCVD synthesis of carbon nanotubes within zeolite crystal coated porous ceramic foam

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In this study, consolidated zeolite crystal coated porous ceramic foams containing a large quantity of carbon nanotubes (CNTs) within micro-metre sized pores were prepared. An alumina-silica porous ceramic body, having an average pore size of less than 100 µm, was produced by the direct foaming technique. Well-shaped zeolite crystals having an average size of 180 nm were synthesized and homogeneously coated on the porous ceramic body by an in situ process. An Fe-supported zeolite/ceramic matrix, which is used for CNT synthesis, was prepared using ion-exchange by immersing the zeolite-coated porous ceramic body into FeCl₂ aqueous solution. The CNTs were synthesized by a catalytic chemical vapour deposition (CCVD) process for four different reaction times. Both acicular-shaped and randomly bundled networks of multi-walled carbon nanotubes (MWCNTs) were synthesized using these different reaction times. Moreover, the yield of CNTs produced showed a tendency to increase with increasing reaction time.

Key-words : Carbon nanotubes, Chemical vapour deposition, Hydrothermal reaction, Zeolite, Porous ceramics

1. Introduction

During the past few years, CNTs have been attracting the attention of researchers, due to their unique nanostructure dependent physical and chemical properties. Adding to their outstanding mechanical¹ and electrical properties,² CNTs also have a very high thermal conductivity³ and high specific surface area,⁴ which allows their use in a range of applications, including nano-electronic devices,⁵ field emission devices,⁶ composite materials⁷ and hydrogen storage materials.⁸ The amazing properties of CNTs⁹ and thus their promising applications¹⁰–¹² strongly depend on their structural characteristics, such as the number of layers, inner and outer tube diameter and presence of defects in them. CNTs are produced by arc-discharge,¹³ laser ablation,¹⁴ and plasma enhanced¹⁵ and thermal chemical vapour deposition (CCVD).¹⁶⁻¹⁸ sometimes also called Catalytic Chemical Vapour Decomposition (CCVD). CCVD has proven to be the most effective technique, due to its low cost, easy operation, versatility, industrial scalability and effectiveness in producing CNTs with both high quality and large quantity.¹⁹⁻²¹

Ceramic foams are important materials which are widely used in a range of fields, due to their unique characteristics of high permeability, high porosity and high surface area.¹⁹⁻²⁰ Direct foaming, which is one of the most versatile methods of fabricating ceramic foams, offers a simple, low-cost and effective way to produce them. It involves the incorporation of a gaseous phase into a ceramic suspension consisting of ceramic powder, solvent, dispersants, surfactants, polymeric binder, and gelling agents.²¹ It is particularly suitable for the fabrication of open and closed porous structures with porosities ranging from 45 to 97% and cell sizes ranging from 30µm to 1 mm.

Fe-coating catalysts are efficient in promoting CNT growth in CCVD processes. The unique property of Fe to promote the growth of CNTs is related to its catalytic activity for the decomposition of the carbon feedstock (usually a hydrocarbon), the formation of meta-stable carbides, carbon diffusion, and the formation of graphite sheets.²² The size of the catalyst nano particles (NPs) seems to be the main factor determining the diameter of the carbon nanostructures synthesized on them. However, as the size of the metal particles decreases to the nanometre scale, they agglomerate.²³ To prevent this, templates are required as supports to preserve the NP’s morphology during the high temperatures attained in CVD processing. A porous support exhibits a non-continuous surface and high surface area, not only contributing significantly to the particle stabilization and producing a fine dispersion of well-defined NPs, but also drastically increasing the number of catalytic particles (nucleation sites) present in it, which are all properties that are advantageous to the synthesis of CNTs.²⁴ As molecular sieve materials, zeolites have proved to have a significant impact due to their structural homogeneity and high reactive surface area,²⁵ and a pore size ranging from 3–10 Å²⁶ which makes them excellent supports for catalyst particles in the synthesis of CNTs.

In this study, we grew CNTs on zeolite coated porous ceramics, on which Fe ions were supported, using the in situ CCVD process. Porous ceramics acts as a rigid base to the CNTs synthesized within them. Hence, this may be used as a filter material or for hydrogen storage purpose in near future. The reaction for CNT synthesis was carried out for 40, 60, 120 and 180 min. Zeolite (NaA type) crystals were synthesized and coated simultaneously within porous ceramies by the hydrothermal method and were subjected to cation exchange using an aqueous FeCl₂ solution. Finally, the CCVD process was carried out on the zeolite coated porous ceramics supporting Fe ions to synthesize Fe-coating catalysts.

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the CNTs. Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) images of the synthesized CNTs were obtained to analyze their morphology, surface quality and structure analysis. The crystallinity and defects of the CNTs were studied by Raman spectroscopy and thermo gravimetric analysis (TGA).

2. Experimental

2.1 Raw materials

α-Al2O3 powder with an average particle diameter of 4 μm and density of 3.95 g/cm³ was purchased from KC, South Korea. SiO2 powder with an average particle diameter of 3.5 μm and density of 2.65 g/cm³ was purchased from Junsei Chemicals Co. Ltd., Japan. Aluminium isopropoxide [Al(i-pro)₃], 98+%, Tetraethyl orthosilicate (TEOS, 98%), Tetramethyl ammonium hydroxide (TMAOH, 25% hydroxide solution), and Sodium hydroxide pellets (NaOH 99.998%) were purchased from Sigma-Aldrich. Ethanol (EtOH, 94.5%) was purchased from Samchun Chemicals. Iron (II)-chloride tetra hydrate (FeCl₂,4H₂O ≥ 99.0%) was purchased from Samchun Chemicals. Nitrogen (N₂) gas (99.99% pure) was purchased from Doekyang Co.ltd. Acetylene (C₂H₂) gas was purchased from Kyungsin Chemical Industry. In addition, double de-ionized water was used whenever necessary throughout the complete experiment.

2.2 Porous ceramics

The porous ceramic matrices were synthesized by the direct foaming technique using Al₂O₃ and SiO₂ particles as raw materials and propyl gallate as a surface modifying agent. A schematic diagram for the direct foaming process is shown in Fig. 1. In this process, Al₂O₃ powder was added to deionized (DI) water to make an aqueous suspension. Homogenization and de-agglomeration of the suspension were carried out on a ball mill for at least 48 h. After ball milling, 2 wt% propyl gallate as a surface modifier was added drop-wise to the suspension under mechanical stirring. The solid content of the final aqueous suspension was set to 30 vol% by adding the required amount of water. Finally, an aqueous suspension of unmodified SiO₂ powder, which was also ball milled separately in the same condition, was added to the surface modified Al₂O₃ suspension with a mole ratio of Al₂O₃/SiO₂ of 1:0.25. Foaming of the final suspension was carried out at room temperature using a household hand mixer (150 watt, Super Mix, France) for 15 min. The wet foams were poured into cylindrical moulds and left to dry at room temperature for 24–48 h. After drying, the specimens were sintered in a furnace at 1300°C for 1 h. The heating and cooling rates were set to 1 and 3°C/min, respectively. The resulting ceramic blocks were pre-treated in EtOH using ultra-sonification. The matrices were then dried at room temperature.

2.3 Zeolite Coating and ion exchange

Following the preparation of porous ceramics, zeolites NaA has been synthesized and coated on the porous ceramics by an in-situ method. Then the zeolite-porous ceramic matrix was subjected to ion exchange reaction and finally placed in the furnace for synthesis of CNTs by CVD method. The schematic diagram for the total experimental process is given in Fig. 2. The zeolite mother solution was prepared in a Teflon vessel with a molar composition of Al(i-pro)₃:TEOS:TMAOH:NaOH:H₂O being 1:2.2:2.4:0.3:200. It was stirred for 12 h. The porous ceramic matrix was immersed into the mother solution and allowed to age for 48 h. It was then poured into a Teflon-lined stainless steel autoclave which was then hydrothermally treated at 90°C for 72 h. The zeolite-coated porous ceramic bodies were subjected to ion-exchange by immersing them into an aqueous FeCl₂ solution having a metal content of 0.8 mmol. In this process, the Na ions of the zeolites are exchanged with Fe ions in the solution. After that, the ceramic body was collected and spray-washed using EtOH and dried at room temperature overnight. The dried ceramic body was then calcinated at 450°C for 3 h and the Fe ions supported zeolite crystals coated porous ceramic body was named as FeA/C (FeA is the product formed by the ion exchange reaction between zeolites NaA and aqueous FeCl₂ solution).

2.4 Synthesis of CNTs

A quartz boat containing the FeA/C sample was placed in a horizontal electric tubular furnace. The substrate was gradually heated under N₂ flow (500 sccm) from room temperature to 700°C at a rate of 5°C/min. When the temperature reached 700°C, the flow rate of N₂ was reduced to 200 sccm and at the same time, C₂H₂ was fed into the reactor with a flow rate of 10 sccm to carry out the reaction. For the 40 min reaction time experiment, the C₂H₂ flow was ceased after 40 min and the N₂ flow rate was restored to 500 sccm in order to blow out the residual C₂H₂. The same procedure was followed for synthesizing the CNTs for 60, 120 and 180 min, where the only exception was the feeding time of C₂H₂ into the furnace which was dependent on the reaction time.

3. Characterization

FESEM images were collected on a SEM LEO 1530 VP microscope. TEM observations were carried out on a High Resolution TEM, JEOL JEM-2100F at an accelerating voltage of 200 kV. Samples were prepared by evaporating drops of a zeolite-CNT-ethanol suspension after sonication onto a carbon coated lacey film supported on a 3 mm diameter, 200-mesh copper micro grid. TGA was performed to measure the amount of carbon deposited in the experiment and also to evaluate the percentage of other forms of carbon. It was conducted under air in Seiko Exstar 7300 (TG/DTA 7300) instrument, with samples of approximately 5 mg heated in air from 25 to 750°C, at a heating rate of 10 K/min⁻¹. The Raman spectroscopy measurements were
performed with a Raman system FRA-106/S using a laser excitation line at 1064 nm (N-YAG) in the range of 200–1800 cm⁻¹.

4. Results and discussions

The microstructure of the micro-porous alumina-silica obtained after drying and sintering the wet foam prepared with propyl gallate was characterized by FESEM. As shown in Fig. 3(a), open pores were observed, leading to the formation of interconnected porous ceramics. This ensures that C₂H₂ is able to travel through the porous ceramic body, so that CNTs can be formed even in the inner-most core of the sample. The average pore size of the sample was found to be 231.4 μm. Zeolite NaA crystals synthesized by the hydrothermal method were characterized by FESEM. As shown in Fig. 3(b), the NaA zeolite showed a regular cubic shape with an average dimension of 180 nm. A slight variation in the morphology of the zeolite crystals was observed due to the presence of minor impurities, hampering their growth and development. From the FESEM image in Fig. 3(c), it was shown that the porous ceramic structure was covered with fully grown zeolite crystals, which is more obvious in the inset of the figure. This indicates that the hydrothermal method used in this experiment succeeded in producing a monolayered coating of zeolite crystals on the porous ceramic body. After the CNT synthesis process, CNTs were observed inside the porous ceramic body, as shown in Fig. 3(d). From the inset, it can be seen that CNTs were formed in abundance, creating a very close network. The area of magnification for the inset image was randomly chosen in Fig. 3(d) which shows that the same abundance of CNTs is present throughout the sample.

In Fig. 4, the FESEM and TEM images of the CNTs synthesized on the FeA/C matrix sample for four different reaction times are shown. The CNTs synthesized for 40, 60, 120 and 180 min were termed as CNT40, CNT60, CNT120 and CNT180, respectively. As shown in Fig. 4(a), acicular CNTs were found to be synthesized in the CNT40 sample. However, on analysing the CNT60 sample, acicular CNTs were no longer found. As shown in Fig. 4(b), coiled MWCNTs were found, creating a close network. Similar observations were made for CNT120 and CNT180.
CNT180, as shown in Fig. 4(c–d), respectively. The CNTs were synthesized in abundance and were seen to be in bundles, forming a close network throughout the porous ceramic structures. Also, as it can be seen in the FESEM images in Fig. 4, that the reaction time resulted in the formation of a more densified network of CNTs. For a more detailed study of the samples, TEM analyses were done. When the TEM scanning was carried out, no single-walled carbon nanotubes (SWCNTs) were found to have been synthesized within any of the four samples; rather, MWCNTs were found all over the samples. Furthermore, as shown in the insets in Fig. 4, when random CNTs from each sample were investigated, an average increase in the diameter of both the inner and outer walls was observed.

**Figure 5** shows the TG curves of the CNTs synthesized on the FeA/C matrix sample for (a) 40 min, (b) 60 min, (c) 120 min, and (d) 180 min reaction times. All of the CNT samples underwent an initial weight loss (up to 571.57°C), which was attributed to the elimination of physically absorbed water on the zeolite.27) In the subsequent heating process, the four samples of CNTs showed similar weight loss tendencies: a single-step weight loss (starting from 571.57°C). The residue is likely to be the catalyst material after the heat treatment. Generally, the decomposition of C2H2 on metal-supported catalysts leads to the formation of a mixture of amorphous carbon and CNTs on the catalyst surface, which can be identified as a two-step weight loss process in the TG curves.23) However, in this experiment, it can be seen that the weight loss is a single-step process. Therefore, for the CNTs synthesized from the Fe-supported zeolite, the single-step weight loss corresponded to the combustion of the CNTs. This result is in accordance with the aforementioned observation, indicating that the CNT samples [see the inset of Figs. 3(a)–3(d)] exhibit good crystallinity. Therefore, it is inferred that Fe is effective for synthesizing high-quality CNTs.

**Figure 6** shows the Raman spectrum for the CNTs synthesized for 40, 60, 120 and 180 min. All of the spectra images demonstrate two characteristic peaks for the synthesized CNTs which are termed as D- and G-bands. The G-bands in Fig. 6(a–d) are centred in 1604, 1578, 1603 and 1611 cm−1, respectively. The tangential stretching (E2g) mode of highly ordered graphitic layers can be inferred from this. The G-bands for all the products typically synthesized MWCNTs were in the ranges of 4.92–12.96 and 14.97–16.49 cm−1, respectively. Both acicular and randomly bundled CNTs creating a network were observed. At a reaction time of 40 min, acicular shaped CNTs were observed, but for reaction times of 60, 120 and 180 min, bundles of CNTs creating a close network were observed, rather than acicular shaped CNTs. As the reaction time increased, a growth tendency was exhibited in terms of the number of wall layers.

**5. Conclusion**

Fe catalysis has the peculiar ability to promote and initiate the growth of CNTs, due to the catalytic activity involving the decomposition of the hydrocarbon feedstock and formation of various carbonaceous products including CNTs. The TGA analysis confirmed good crystallinity of the CNTs, which means that Fe succeeded in providing a good catalytic platform or nucleation site for CNTs synthesis. Upon FESEM and TEM analyses, MWCNTs were observed. This was again confirmed by the Raman Spectroscopic data, which confirmed the sole presence of MWCNTs. On average, the inner and outer tube diameters of the typically synthesized MWCNTs were in the ranges of 4.92–12.96 and 14.97–16.49 nm, respectively. Both acicular and randomly bundled CNTs creating a network were observed. At a reaction time of 40 min, acicular shaped CNTs were observed, but for reaction times of 60, 120 and 180 min, bundles of CNTs creating a close network were observed, rather than acicular shaped CNTs. As the reaction time increased, a growth tendency was exhibited in terms of the number of wall layers.

**Acknowledgement** This research was financially supported by Hanseo University, Korea.

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