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Comment

A novel processing of carbon nanotubes grown on molecular sieve coated porous ceramics

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ABSTRACT

The present study focuses on the growth of carbon nanotubes (CNTs) on Fe-containing zeolites coated porous ceramics by implementing three different and independent techniques, successively. Direct foaming-derived porous ceramics were subjected to hydrothermal reaction for on-site growth of NaA zeolites within it. The porous ceramics-zeolite composite was subjected to ion-exchange reaction to obtain the catalyst for CNT synthesis. Multi-walled CNTs (MWCNTs) were grown by catalytic chemical vapour deposition (CCVD) process using acetylene as carbon source. Microstructural, thermogravimetric and spectroscopic analyses showed distinctive differences in terms of hollow structural feature, yield and crystallinity of the MWCNTs with different reaction temperatures.

1. Introduction

Due to their unique nanostructure-dependent physical and chemical properties, CNTs have become a subject of intensive research since the last two decades. Owing to the substantive efforts of researchers, many potential applications of CNTs have been found and realized in numerous fields, such as, nano-electronic devices, hydrogen storage media, composite materials, chemical sensors and filters, and field emission devices [1–5]. Since these applications are strongly related to the quality of CNTs, their synthetic methods have always been significant. As far as we know, a variety of CNT synthesis methods have been developed, which includes laser evaporation [6], arc-discharge [7], and chemical vapor deposition (CVD) [8]. The catalytic CVD (CCVD) has proven to be more efficient and promising for the synthesis of CNTs due to its simple operating conditions, low costs and high-yield production ability [9]. In this process, CNTs are synthesized on catalyst containing particles of a transition metal (e.g., Fe, Co, Ni, etc.) or related oxides, by the chemical decomposition of a carbon source (CH_4, C_2H_2, C_2H_4, C_2H_5OH).

However, the metal particles tend to agglomerate as their size decreases to the nanometer range. Zeolites, having molecular sieving capabilities due to its well-defined pore structures (pore size < 1.3 nm) and high surface areas [10], act as hosts to support the catalytic transition metal ions. Thus it contributes significantly to catalyst particle stabilization by producing a fine dispersion of catalyst particles, preserving their morphology at CVD processing temperatures and increasing nucleation sites, which leads to high-yield production of CNTs [11].

Porous alumina ceramics with open and interconnected pores has high stiffness and thermal stability along with low density. The combination of CNTs and alumina to develop functional composites offers a very attractive system for research and development [12]. The open porosity offers the feasibility of in situ homogeneous growth of CNTs within the ceramic matrix which leads to multi-functional engineering ceramics.

In this work, CNTs were synthesized from Fe-containing zeolite-coated alumina porous ceramics by CCVD. Zeolite (NaA type) crystals were synthesized and coated onto the porous ceramics matrices by an in situ hydrothermal method. With the cation exchange in an aqueous $FeCl_2$ solution, Fe-containing zeolite-coated alumina ceramic matrix was obtained as the catalyst of interest. Thereafter, CNTs were successfully grown from these catalysts by CCVD technique at different temperatures for 60 min. The effect of the reaction temperature on the growth and structural morphology of the CNTs was investigated. The ability of CNTs embedded on various structural media including porous ceramics, have been explored for the development of a wide range of

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new filters for water and air filtration [13]. Moreover, CNTs embedded within ceramic matrix composites (CMCs) possesses a unique microstructure with nano-scale objects dispersed throughout the ceramic matrix grain boundaries, which allows tailoring of physical properties with a revolutionary combination of remarkable engineered transport properties as well as superior mechanical properties. Hence, the significance of this work is to develop a CNT-ceramic composite material which can find its application on the above mentioned areas [14,15]. The novelty of this study is the combination of three different processing techniques: the direct foaming for porous ceramics synthesis, the in situ hydrothermal reaction for zeolite synthesis and coating on porous ceramics and finally, the CCVD technique for CNTs synthesis on the porous ceramics.

2. Experimental

2.1. Raw materials

(i) α-Al_2O_3 powder, d_{50} ~4 μm (KC, South Korea), (ii) SiO_2 powder, d_{50} ~3.5 μm (Junsei Chemicals Co. Ltd, Japan) are used to prepare the ceramic suspension. 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 and are used to produce NaA zeolite. Iron (II)-chloride tetra hydrate ($FeCl_2.4H_2O \geq 99.0\%$, Samchun Chemicals) is used as the catalyst and acetylene (C_2H_2, Kyuongin chemical industry) is used as the carbon source. Further chemicals used for this study are Nitrogen (N_2, 99.99%, Doekyang Co. Ltd), double deionized water and Ethanol (EtOH, 94.5%, Samchun Chemicals).

2.2. Porous ceramics

The direct foaming technique was employed for the synthesis of porous ceramics, using Al_2O_3 and SiO_2 particles as raw materials and propyl gallate as a surface modifying agent [16]. In this process, an aqueous Al_2O_3 suspension was first prepared and subjected to homogenization and de-agglomeration using a ball mill for at least 48 h. After that, propyl gallate as a surface modifier was added to the suspension in order to avoid destabilization of the suspension. Subsequently, another aqueous suspension of SiO_2 was added to the Al_2O_3 suspension with a molar ratio of Al_2O_3/SiO_2 being 1:0.25. Foaming of the resultant mixture was carried out using a hand mixer (150 W, Super Mix, France) for 15 min. The wet foams were dried and sintered at 1300 °C for 1 h to obtain the porous ceramic matrices. The porous ceramics were then pre-treated in EtOH using ultra-sonification and dried at room temperature.

2.3. Zeolite coating and ion exchange

To synthesize the NaA zeolite crystals, a mother solution was prepared with a molar composition of Al(i-pro)$_3$:TEOS:TMAOH:NaOH:H_2O of 1:2.2:2.4:0.3:200 and stirred for 12 h. Subsequently, the porous ceramic matrix was immersed into the zeolite mother solution and allowed to age for 12 h. Afterwards, the porous alumina ceramic matrix was transferred into a Teflon-lined stainless steel autoclave with a certain amount of zeolite mother solution to immerse it and was hydrothermally treated at 90 °C for 72 h. The obtained zeolite-coated porous ceramic matrices were then subjected to ion-exchange by immersing them into an aqueous $FeCl_2$ solution (metal content ~ 0.8 mmol). In this process, the Na ions of the zeolites were exchanged with Fe ions from the solution. The ion-exchanged ceramic matrices were spray-washed using EtOH followed by overnight drying at room temperature and calcined in an electric furnace at 450 °C for 3 h. The Fe-containing zeolite-coated alumina porous ceramic matrices were designated as FeA/C. The schematic diagram for the experimental process is given in Figure 1.

2.4. Synthesis of CNTs

The catalytic decomposition of acetylene on the FeA/C sample was carried out in a quartz boat centred in a horizontal tube

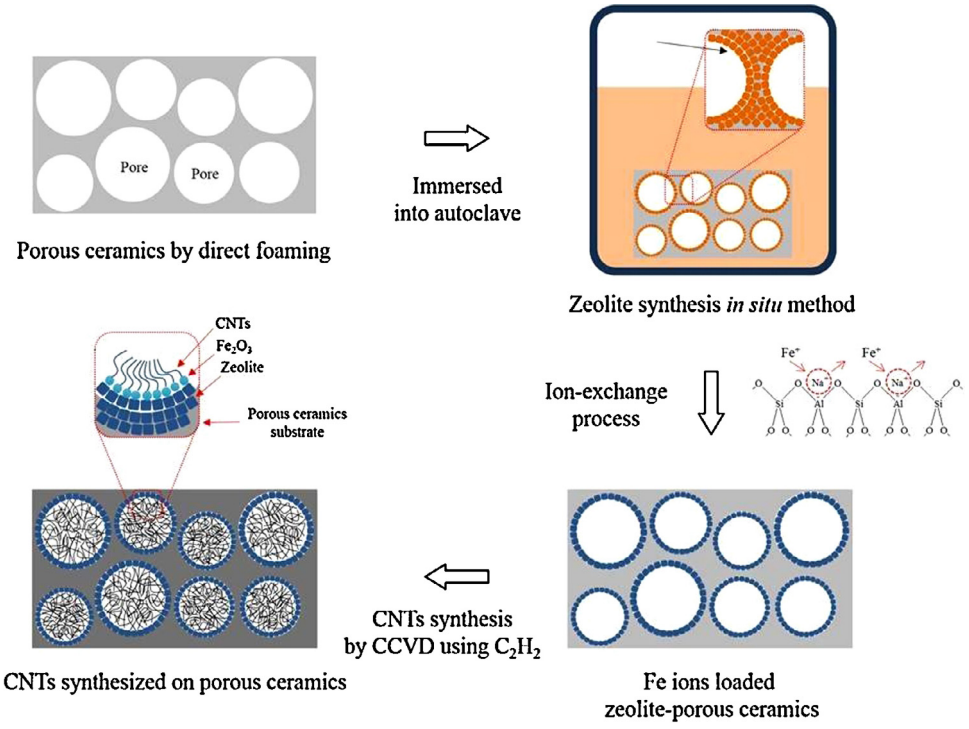

Figure 1. Schematic diagram for CNTs synthesized on Fe ions loaded zeolites coated porous ceramics.