

Review of Metal Supported on Mesoporous MCM41 as Catalyst for CNTs Growth

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Abstract. Carbon nanotubes (CNTs) is one of the most unique nanomaterials in the field of nanotechnology because of their high strength, stiffness and electrical conductivity. Growth CNTs through chemical vapour deposition (CVD) method offers controlled synthesis of ordered and aligned CNTs. Catalytic growth also can be designed CNTs in variety forms either straight filament, helically wound tubes and bent. Recently, transition metal incorporated Mobil Composition Matter (known as MCM41) molecular sieves as growth catalyst has been used for the production of CNTs. The invention of mesoporous molecular sieves by Mobil researchers in 1992 has given a new direction to the field of porous materials. MCM41 exhibit a good hexagonal arrangement, uniform channel structure, tuneable pore size (15-100 Å) and large surface area ($\approx 1200 \text{ m}^2\text{g}^{-1}$). Transition metal catalysts can be incorporated into the pore walls of the mesoporous molecular sieves and stabilizing the dispersed catalytic sites. The mesoporosity and the well-defined pore structure in combination with high surface area make MCM41 materials as promising candidates for the synthesis of CNTs. In this article, we review and discuss the role of catalyst and their catalyst support using MCM mesoporous material.

1. Introduction

Intensive research to produce high quality and high yield of CNTs have been attracted many researchers due to their unique properties. CNTs is a graphene layers that rolled up into cylinder and have special properties such as high surface area, high electrical and thermal conductivity, high mechanical properties and flexible [1]. The CVD method is currently used for the growth of CNTs due to simple method and can control the growth of CNTs during the growth process. Most of the CNTs synthesis techniques via CVD method require the introduction of catalyst either in the form of gas particulates or as a solid support. CVD method is also allowing the diameter of CNTs is controlled at certain range by modifying the size of catalyst nanoparticles [2].

The quality and yield of the growth of CNTs obtained depends on different parameters such as hydrocarbon sources, catalyst, and synthesis condition such as temperature, time and flow rate. By selecting proper conditions, the physical properties like length, shape, diameter and chemical properties



of CNTs can be controlled and designed. In this paper, we highlight about catalyst and it can be describe as a substance that increases the rate of reaction without itself being consumed [3]. But the main role of catalyst in CNTs growth is to decompose hydrocarbon molecules [4]. The catalyst materials may affect the CNTs growth in term of morphology, types of CNTs either single-walled carbon nanotubes (SWNT) or multi-walled carbon nanotubes (MWNTs), diameter and growth mechanism. Thus, catalyst material is very important for CNTs growth.

One of the most effective way to control the selectivity of CNTs with high yield is by using catalytic from mesoporous material. Mesoporous silica materials that have uniform pores and high specific areas have been used in numerous applications including catalysts, separation and adsorbent for large molecules [5]. These materials were first discovered by researchers at Mobil Research and Development Corporation in 1992 and known as the M41S family [6]. M41S family consist three members depends on their structure which has a hexagonal phase (MCM41), cubic phase (MCM48) and lamellar phase (MCM50). MCM41 has received most attention because of its simple structure, ease synthesis and good surface properties. The unique feature of MCM41 is the large uniform pore structure, large pore volume ($> 0.7 \text{ cm}^3/\text{g}$) and the pore can be tailored by several different strategies [7]. The unique feature of MCM41 is the large uniform pore structure and hence offered promising properties for both adsorption and catalysis [7].

However, purely siliceous MCM41 mesoporous materials have limited application, due to its lack of intrinsic acidity and ion exchange capacity. In order to utilize this material as efficient catalyst, it is necessary to generate the appropriate catalytically active sites to the silicate framework of MCM41. In previous study, different metal catalysts such as Cu, La, Gd, Ni, Co, Fe, Pd, Cr, Zn, Mn, Ti, Cd and Zr have been used to endow the properties of mesoporous materials [8]. It is because the structures and morphology can be influenced by particle size, metal content and the hollow pore structures of MCM41. But the most important property of the metals with regard to CNTs formation was their ability to catalytically decompose gaseous carbon-containing molecules [9]. The good thermal stability and high productivity of the MCM41 mesoporous molecular sieves could be a catalytic template for synthesizing CNTs. Most of the CNTs growth that we have performed in this paper so far used MCM41 supported with metal particles as growth catalyst. Due to MCM41 has high surface area that leads to high catalyst efficiency and high yield of CNTs. Therefore, we rely on the results obtained from previous study and discuss the performance of metal-MCM41 as catalyst to growth CNTs.

2. Catalyst

Catalyst is described as a substance that increases the rate of chemical reaction until approaches equilibrium without itself being involved in the reaction. Catalyst are used widely in the industry and played a major role in the publishing the economic strength of the chemical industry. According to Clark [10], the major goals of “Green Chemistry” and the use of efficient solid catalysts are to achieve these goals; a) to increase process selectivity; b) to maximize the use of starting materials; c) to replace stoichiometric reagents with catalyst; d) to facilitate easy separation of final reaction mixture and e) efficient recovery of the catalyst.

In CNTs growth, the most important property of catalyst regard to CNTs formation is their ability to catalytically decompose gaseous carbon-containing molecule. The catalyst used for the production of CNTs are usually transition metals supported on silica [11], mesoporous silica [12], zeolites [13], magnesium oxide and calcium carbonate. Therefore, the selection of metal and support material may affect the morphology and growth of CNTs. The most important function of support material is to

provide high surface area and porosity for the active component. The interaction between catalyst and support material affects the dispersion and morphology of catalyst. Huh et al [14] reported that controlled growth of carbon nanotubes (CNTs) has been achieved by CVD of acetylene gas over nanometer-sized cobalt particles. They found CNTs with well-aligned, uniform diameter and high purity is successfully synthesized over cobalt. Amama et al [15] studied the synthesis of SWNTs over Fe-MCM41 using acetylene as carbon source. They found SWNTs successfully synthesized and claimed the reduction of Fe by the hydrogen produced during acetylene decomposition was responsible for the formation of metallic Fe, which provided the growth of CNTs.

Previous study reported that large amounts of CNTs can be formed by CVD method using acetylene as carbon source and cobalt and iron catalyst supported on silica or zeolite as catalyst [16]. However, the CNTs were proposed to grow over the external surface of the support materials. Thus, the growth directions are still random and the pore sizes are not narrowly distributed. To solve this problem, the mesoporous molecular sieves such as M41S materials are a kind of new catalyst supports with many interesting properties such as high surface area and periodic arrays of uniform pores. It suggested that MCM41 can be used as synthesis template for CNTs with regular pore structure.

3. MCM41 as Support for Metal-MCM41 Catalyst

The most important function of support material is to provide high surface area and porosity for the active component. The interaction between catalyst and support material directly affect the dispersion and morphology of catalyst. In CNTs growth, the catalyst needs an appropriate support material for selective controlling the morphology and yield of CNTs. It has been found that a single metal and mixture of metals supported on oxides, clays or porous materials like zeolite and MCM41 have great contribution in growth CNTs [17]. Chai et al., (2006) studied the effects of different support materials on CoO catalyst. They investigated titania, silica, alumina, magnesia, zeolite and calcium oxide as support and methane as carbon precursor at 700°C. They found that the carbon capacity decreased in order of alumina > zeolite > silica > titania > calcium oxide > magnesia [18].

Another approach was synthesized CNTs on different support materials which are quartz, porous alumina, conductive glass and nickel plates, using Co and Fe as catalyst and ethanol as the carbon sources. The SWNTs successful synthesized on porous alumina and nickel plates and MWNTs on conducting glass [19]. Su et al., (2000) studied the synthesized CNTs using aerogel support and Fe/Mo catalyst. They found this method improved the CVD method for SWNT preparation and achieved high quality SWNTs [20].

Besides, the CNTs were proposed to grow over the external surface of the support materials. Thus the growth directions are still random and the pore sizes are not narrowly distributed. The limited number of applications is related to the lack of mesopores in the zeolite that only contain micropores with diameter less than 2 nm. Therefore, only a fraction of the active sites in the zeolites is effectively used for catalytic conversions. To solve this problem, the mesoporous molecular sieves such as M41S materials are a kind of new catalyst supports with many interesting properties. It has unique properties such as high surface area and periodic arrays of uniform pores and also can be used as synthesis template for CNTs with regular pore structure. Recently, there are several reports of production of CNTs using mesoporous MCM-41 materials [21-23]. Hernadi et al [24] reported the comparison performance of Fe or Co supported on zeolite and MCM-41 as catalyst for growth CNTs using acetylene as carbon source

at 700°C in 1 hour reaction by ion-exchange and impregnation method. From results, they found only a tiny CNTs formation was observed with ion-exchanged Co-MCM41.

However, pure siliceous mesoporous molecular sieves possess a neutral framework, which limits their applications. In order to provide molecular sieves with potential catalytic applications, it is possible to modify the nature of the framework by introduction of heteroatoms by hydrothermal methods. Besides, other elements can also be incorporated on the surface of the materials by grafting or impregnation. Recently, there are several reports of formation of carbon nanotubes over these mesoporous MCM41 materials [22, 23]. Table 1 shows the results obtained in in the previously reported work on various metal-MCM41 catalysts for CNTs production.

Table 1 Previously reported metal supported on mesoporous as growth catalyst for CNTs production

Catalyst	Reaction condition	Type of CNTs	CNTs size	References
Fe ₂ O ₃ -mesoporous	Carbon source : acetylene, CVD, 800°C	MWCNTs	5-15 nm	[25]
Ni-SBA15	Carbon source : acetylene, CVD, 850°C	Carbon sphres and filaments	0.5-0.8 μm	[26]
Ni-APTES-MCM41	Carbon source : acetylene, CVD, 600-800°C	MWCNTs	3-8 nm	[27]
Fe-Co-MCM41	Carbon source : acetylene, CVD, 750°C	SWCNTs	0.78-1.35nm	[22]
Fe/Co-Zeolite	Carbon source : ethane, pyrolysis, 850°C	MWCNTs	0.3-1.5nm	[28]

MWCNTs = multi-walled carbon nanotubes, SWCNTs = single-walled carbon nanotubes

Numerous studies had been reported that the presence of SWNTs is evidenced via Raman spectroscopy by observing the radial breathing modes (RBM) peak in the range 100 cm⁻¹ to 350 cm⁻¹ [29]. Meanwhile, the absence of RBM peaks indicates the CNTs produced is multi-walled type [30]. The two peaks were detected at ~1340 cm⁻¹ (known as D band) and ~1580 cm⁻¹ (known as G band) corresponding to the vibration of sp² bonded carbon atoms in a 2D hexagonal lattice, and the vibration of carbon atom with dangling bond in the plane, respectively [31]. Figure 1 shows the Raman spectra of single-walled and multi-walled, respectively [32]. Chen et al [33] found the SWNTs with low defects and uniform diameter was obtained by using Co-MCM41 as growth catalyst.

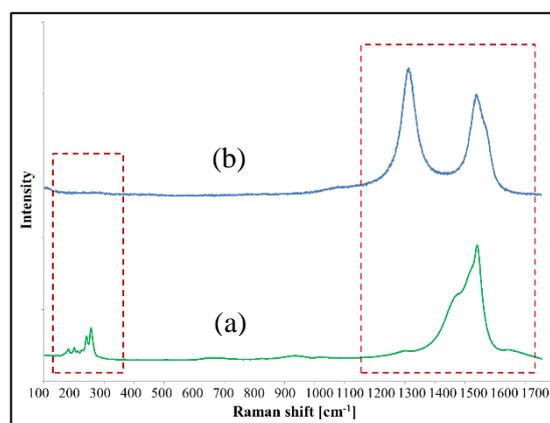


Figure 1. Raman spectra of (a) SWCNTs and (b) MWCNTs.

Urban et al [34] have reported TEM results show the diameter distribution of CNT formed was very narrow in between 5 to 6 nm in diameter and 200 nm in length. The quality of CNTs proved to be high, since their length exceeds 200 nm and had a narrow diameter distribution. Ahmad et al. [27, 32] reported that SEM and TEM images show the CNTs grown on Ni-MCM41 appearing looks like as a hair-like structure with the diameter in between 2 to 5 nm and a few hundred nanometres in lengths, as shown in Figure 2 [35]. Duxiao et al [36] reported the catalytic formation of CNTs on Fe-loading hexagonal mesoporous and microporous molecular sieves. The results confirmed that CNTs were grown inside the channel of mesoporous molecular sieves and on the external surface of microporous molecular sieves. The diameter of SWNTs formed was in the range 1 to 3 nm.

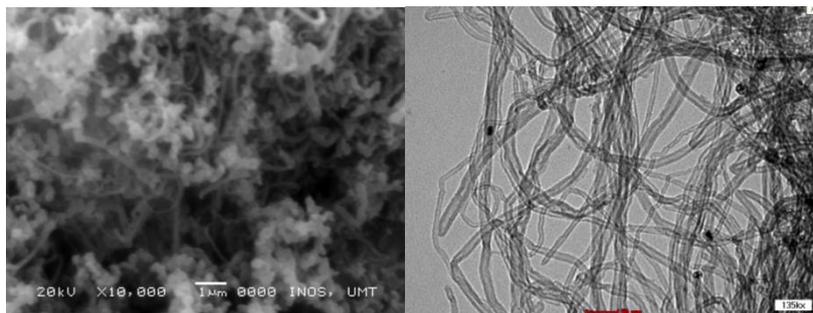


Figure 2. SEM and TEM images of MWCNTs grown on Ni-MCM41 catalyst

4. Conclusions

For commercial applications, the production of CNTs in high yield at low cost is importance and CVD method using growth catalyst has all the advantages in comparison with the other known method. Mesoporous MCM41 materials are considered as convenient candidates for the formation of carbon nanotubes. It is confirmed that MCM41 material with the incorporation of transition metals are considered to form better quality CNTs with high yield.

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