

Comparative Study on Effect of Iron Oxide Doped Alumina-Based Catalysts via Sol-Gel and LFS Methods on CNTs Growth by Methane Decomposition

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Abstract

By using the sol-gel technique and the liquid flame spray method (LFS), three different iron oxide doped alumina-based catalysts (Catalysts A, B and C) were prepared by using iron nitrate and ferrocene as the iron source. Multiwalled carbon nanotubes were obtained by a decomposition of methane gas over Catalysts A and C, but not over Catalyst B. X-ray diffraction, transmission electron microscopy and the nitrogen adsorption /desorption test were used to compare the three different catalysts and discuss the influence of the different catalysts on the formation of the multiwalled carbon nanotubes.

Keywords: Sol-gel, Liquid flame spraying, Catalyst, Nanotubes

PORÓWNAWCZE BADANIA NAD WPŁYWEM KATALIZATORÓW OPARTYCH NA TLENKU GLINU, DOMIESZKOWANYCH TLENKIEM ŻELAZA, OTRZYMANÝCH METODAMI ZOL-ŻEL I LFS NA WZROST NANORUREK WĘGLOWYCH Z ROZKŁADU METANU

Wykorzystując technikę zol-żel i metodę rozpylania cieczy w płomieniu (*liquid flame spraying*, LFS) przygotowano trzy różne katalizatory (Catalyst A, B i C) oparte na tlenku glinu(III) i domieszkowane tlenkiem żelaza(III), przy czym jako źródło żelaza zastosowano azotan żelaza(III) i ferrocen. Poprzez rozkład metanu na katalizatorach Catalyst A i Catalyst C otrzymano wielościennie nanorurki węglowe, natomiast w przypadku katalizatora Catalyst B nanorurki nie powstały. Aby porównać trzy różne katalizatory i przedyskutować ich wpływ na proces powstawania wielościennych nanorurek węglowych wykorzystano rentgenowską analizę dyfrakcyjną, elektronową mikroskopię transmisyjną i badania adsorpcji/desorpcji azotu.

Słowa kluczowe: zol-żel, rozpylanie cieczy w płomieniu, katalizator, nanorurki

1. Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention in both academic and industrial sectors due to their promising structural, electronic, mechanical and chemical properties, which lead to numerous potential applications in various technology fields [1-8]. In order to implement the commercial applications, different synthesis methods have been studied to produce carbon nanotubes such as arc discharge [1], laser ablation [2], plasma-enhanced [3] and thermal [4] chemical vapor deposition, *etc.* Of these, the chemical catalytic vapor deposition (CCVD) process was considered to be the most suitable method for the large scale production of carbon nanotubes by decomposition of various hydrocarbons over different catalysts [5]. Iron-, cobalt- and nickel-containing catalysts on different supporting oxides such as alumina have been widely studied [5-8]. The catalysts made by different ways are critical on the formation of CNTs.

The sol-gel method normally involves the use of metal alkoxides or inorganic salts as starting materials. Several different metal alkoxides or inorganic salts can be added into the same precursor solution with controllable amounts.

Hydrolysis, condensation and polycondensation reactions occur when the metal alkoxides or inorganic salts are mixed with water and solvents [9]. The sol-gel method allows one to design the material (particle size, morphology, surface area, pore diameter, *etc.*) by controlling the conditions of the process (temperature, precursor, concentration of reagents, amount of water, drying methodologies, *etc.*) [10]. The sol-gel method has the advantages of high chemical purity, high chemical homogeneity, lower calcining temperatures and good control of the particle size [11]. On the other hand, the liquid flame spray (LFS) method also involves a precursor solution with controllable amounts of starting materials [12]. The precursor solution is fed into a high-velocity high-temperature flame where the liquid precursor evaporates, decomposes, reacts and finally nucleates to form nanoparticles [13].

In this study, we prepared three different iron oxide doped alumina-based catalysts (Catalysts A, B and C) from the sol-gel technique and the liquid flame spray method by using different iron source compounds of iron nitrate and ferrocene. After the treatment with the methane gas, MWCNTs were found over Catalysts A and C, but not over Catalyst B. The catalysts were characterized by XRD, TEM as well as the

nitrogen adsorption/desorption test, and compared to discuss the influence of the catalysts made by different ways on the formation of the MWCNTs.

2. Experimental

2.1. Catalysts A and B: Iron oxide doped alumina by sol-gel technique

Two sol-gel precursor solutions were prepared from aluminium tri-sec-butoxide ($C_{12}H_{27}AlO_3$), isopropyl alcohol (C_3H_7OH) and ethyl acetoacetate ($C_6H_{10}O_3$), iron(III) nitrate ($FeN_3O_9 \cdot 9H_2O$) and ferrocene ($(C_5H_5)_2Fe$). Iron nitrate and ferrocene were used as an iron source. The molar ratio of the iron source compound to $C_{12}H_{27}AlO_3$ was 9.1 %. The two sol-gel precursors were dried at 120°C into fine powders which were then reacted with boiling water for 10 min. After that the suspensions were dried at 120°C to obtain fine powders which were heat-treated at 600°C. The heat-treatment was performed to form alumina and iron oxide. Catalyst A is referred to the iron oxide doped alumina by using iron nitrate, while Catalyst B to the iron oxide doped alumina by using ferrocene.

2.2. Catalyst C: Iron oxide doped alumina-zirconia by liquid flame spray (LFS) method

The LFS method was used to produce the iron oxide doped alumina-zirconia nanoparticles. The precursor solution was made from aluminium isopropoxide ($C_9H_{21}AlO_3$), zirconium(IV) n-propoxide ($Zr[O(CH_2)_2CH_3]_4$), ferrocene ($(C_5H_5)_2Fe$) and p-xylene (C_8H_{10}). The molar ratio of ferrocene to aluminium isopropoxide was 14.3 %. The precursor solution was fed into a turbulent, high-temperature ($T_{max} = \sim 2727^\circ C$) H_2 - O_2 flame. The feed rate was 30 ml/min with gas flows of 150 l/min for H_2 and 25 l/min for O_2 . The particles were collected by a cylindrical electrostatic precipitator, by using a voltage of 6.0 kV on the central rod, and a current of 0.3 mA from the central rod to the ground cylinder. The collected iron oxide doped alumina-zirconia powder is named Catalyst C.

2.3. MWCNTs growth over catalysts A, B and C by decomposition of methane gas

The beforehand prepared Catalysts A, B and C were then placed in a tubular furnace, which was evacuated and heated to 800°C with a heating rate of 60°C/min. After that the methane gas was fed into the tubular furnace until atmospheric pressure was reached. During 1 hour carbon nanotubes were grown over the catalyst and after that the furnace was cooled down to room temperature.

2.4. Characterizations

The crystalline phase composition was determined by X-ray diffraction (XRD, Kristalloflex D-500, Siemens) by using $CuK\alpha$ radiation and the morphology was examined with a transmission electron microscope (TEM, Jeol JEM 2010). The specific surface areas were calculated from N_2 adsorption/desorption isotherms (Coulter Omnisorp 100 CX,

Beckman Coulter Inc.) by a Coulter SA-reports™ software based on the Brunauer-Emmett-Teller (BET) equation using the data in a p/p_0 range of 0.05-0.4.

3. Results and discussion

The XRD patterns of Catalysts A and B from sol-gel technique are shown in Fig. 1, which also shows the XRD pattern of Catalyst C by the liquid flame spray method. The XRD pattern of Catalyst A suggests that Catalyst A is amorphous. The diffraction peaks in the XRD pattern of Catalysts B show great broadness, indicating the formation of nanocrystallites. The XRD patterns in (b) can be indexed to be γ -alumina. On the other hand, all the diffraction peaks of Catalyst C in (c) are due to the tetragonal phase of zirconia. No peaks of alumina are seen, probably due to its amorphous or nanocrystalline nature, so that the signal is submerged by zirconia. Besides, in all the three XRD patterns, no peaks of iron oxides or iron hydroxides are observed, probably due to the reasons that iron oxides were not formed, or the iron oxides or iron hydroxides are highly dispersed on the surface of the catalyst powders and their amounts are too small to be detected or the particles are of amorphous nature.

The morphology of Catalysts A and B from sol-gel technique are shown in Fig. 2 and 3. The two catalysts have similar morphology of nanoneedles. The nanoneedles in Catalyst A as shown in Fig. 2 are longer than those in Catalyst B in Fig. 3.

The BET specific surface area of Catalyst A is 261 m^2/g , and that of Catalyst B is 297 m^2/g . The values of the specific surface area agree well with the results shown from the XRD patterns and the TEM images. On the other hand, Catalyst C has the morphology of nanoparticles with the diameters of 5 nm - 30 nm, as shown in Fig. 4. Catalyst C has a BET specific surface area of 22 m^2/g , indicating that larger particles exist in Catalyst C than in Catalysts A and B.

After the three catalysts (Catalysts A, B and C) were treated with the methane gas, multiwalled carbon nanotubes (MWCNTs) were found over Catalysts A and C. However, there was no growth of CNTs on Catalyst B. The growth of the MWCNTs was determined by Raman Spectroscopy and FESEM, according to other studies [14-16]. It is commonly

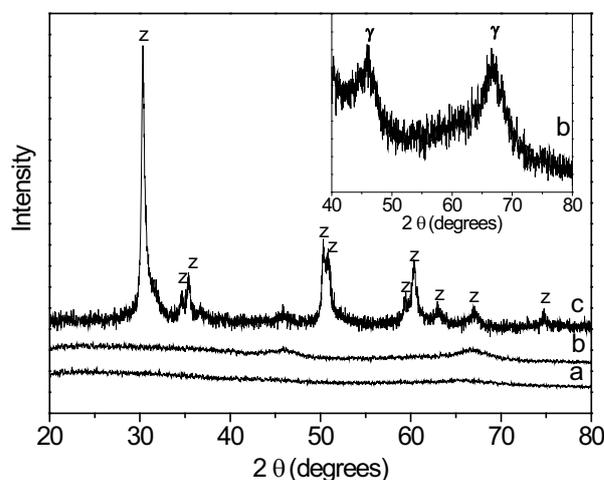


Fig. 1. XRD patterns of studied catalysts: a) Catalyst A, b) Catalyst B, c) Catalyst C; γ and z represents γ -alumina and zirconia, respectively. Inset shows the pattern b with higher magnification.

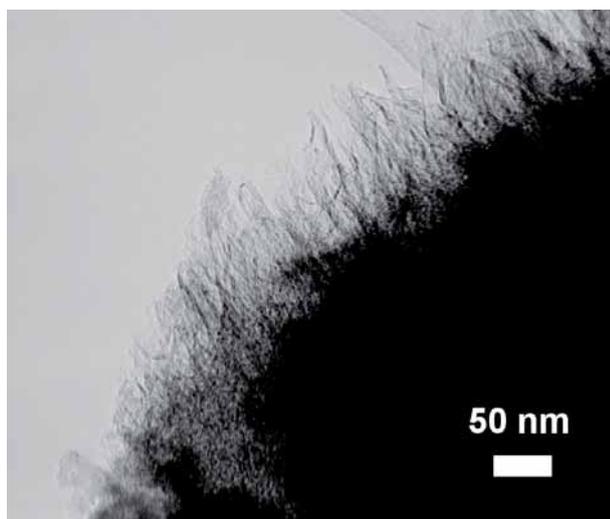


Fig. 2. TEM image of Catalyst A.

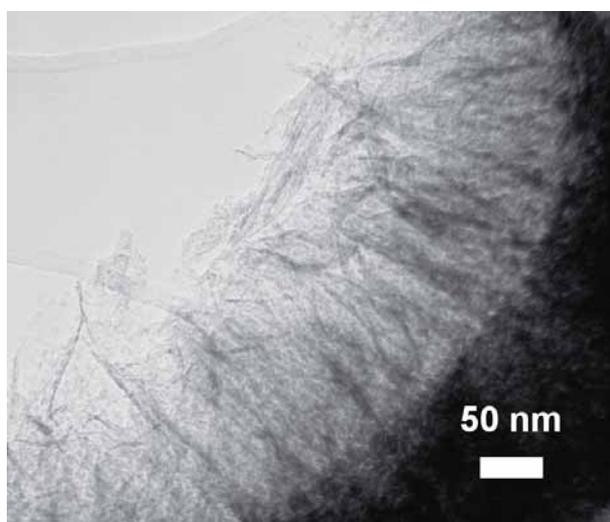


Fig. 3. TEM image of Catalyst B.

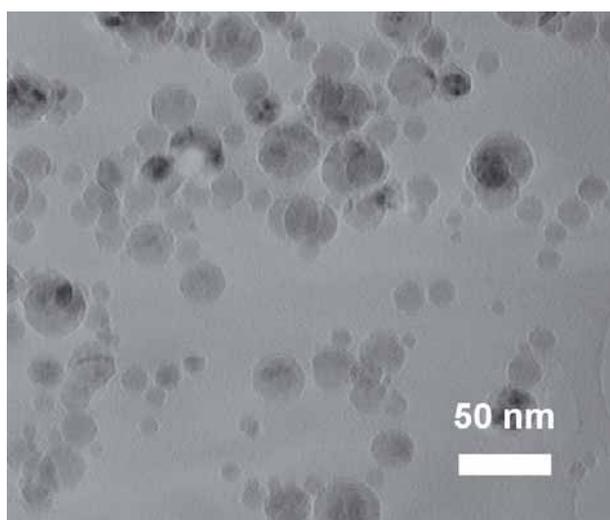


Fig. 4. TEM image of Catalyst C.

suggested that the growth of CNTs follows a tip growth mode [17]. The methane gas is decomposed into carbon and hydrogen at 800°C. The carbon is then dissolved into the particles of the iron oxide (possibly also the reduced iron oxide Fe_xO_y), oversaturated by diffusion and precipitated on the rear surface of the iron oxide particles, leading to the

formation of CNTs [18]. Over Catalyst A, FESEM suggested that the MWCNTs have two typical outer diameters of 50 nm and 15 nm, with varying lengths of over many microns. The Raman spectra reveal that the diameter of the inner tube is estimated to be 1.25 nm. While over Catalyst C, the outer diameter of the MWCNTs is about 10 nm with an estimated diameter of the inner tube of 1.24 nm.

Clearly the iron oxide doped alumina-based catalysts made by different methods by using different iron source compounds have a large effect on the formation of the MWCNTs. A detailed comparison of the different iron oxide doped alumina-based catalysts (Catalysts A, B and C) used in this study is given in Table 1. It is interesting to see that Catalyst B did not work to grow CNTs while Catalyst A could. The only difference between Catalysts A and B is that the different iron source compound was used, *i.e.*, iron nitrate was used in Catalyst A and ferrocene in Catalyst B. However, CNTs were grown also over Catalyst C where ferrocene was used by LFS method. Therefore we cannot say that the iron source compound is the only factor to the growth of the CNTs.

The ferrocene used in the process to obtain Catalyst C had experienced the high temperature treatment at about 2727°C in the flame, yet the ferrocene used in for Catalyst B had been only heated at 800°C. It is possible that the heat-treatment of 800°C is not high enough to form the catalytic iron oxide on Catalyst B. While the heat-treatment of 800°C led to the formation of iron oxide, iron nitrate was used to produce Catalyst A. Therefore, with Catalyst B, without the presence of iron oxide, CNTs were not formed after the decomposition of methane. In our study, we do see the possibility of growing CNTs on different catalysts made by different methods by using different iron source compounds, only when the right parameters and conditions are to be fulfilled. A combination role of the crystalline phase of the supporting material, iron source compound, the amount of iron oxide, particle size, morphology, processing method *etc.*, needs to be considered as a whole.

4. Conclusions

Three different iron oxide doped alumina-based catalysts (Catalysts A, B and C) were prepared by the sol-gel technique and the liquid flame spray (LFS) method by using iron nitrate and ferrocene. After treated with the methane gas at 800°C in the same conditions, MWCNTs were obtained over Catalysts A and C, but not over Catalyst B. The only difference in Catalysts A and B is that iron nitrate was used in Catalyst A and ferrocene in Catalyst B. Ferrocene, however, was also used in Catalyst C. Therefore, the growth of CNTs depends on a combination of many factors, such as iron source compound, processing methods, and so on. The right parameters and conditions have to be found to obtain CNTs successfully.

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Table 1. Comparison of the iron oxide doped alumina-based catalysts (Catalysts A, B and C) on the growth of MWCNTs.

	Crystalline phase of the supporting material	Iron source compound	Molar ratio of Fe to Al [%]	Processing method	Morphology of the iron oxide doped catalyst	S_{BET} [m ² /g]	Formation of MWCNT
Catalyst A	Amorphous	Iron nitrate	9.1	Sol-gel	Nanoneedles (length ~100 nm)	261	Yes Diameters of outer tubes 50 nm and 15 nm, Diameter of inner tubes 1.25 nm
Catalyst B	Nanocrystalline γ -alumina	Ferrocene	9.1	Sol-gel	Nanoneedles (length ~200 nm)	297	No
Catalyst C	Amorphous or nanocrystalline alumina + tetragonal zirconia	Ferrocene	14.3	LFS	Nanoparticles (diameter ~30 nm)	22	Yes Diameter of outer tubes 10 nm, Diameter of inner tubes 1.25 nm

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