CATALYTIC GROWTH OF CARBON NANOTUBES ON ZEOLITES

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Abstract

Carbon nanotubes (CNTs) were synthesized by catalytic chemical vapor deposition (CCVD) of acetylene over Fe-supported Y zeolites in a fluidized bed (FB) reactor at 700°C. Iron catalyst on zeolite was prepared by metal organic chemical vapor deposition (FB-MOCVD) using [(1,3-Butadiene)(toluene)Fe(0)] complex as precursor. CVD in fluidized bed provides supported catalysts with high dispersion. The amount of the deposited iron (0.7-2.5 wt.%) was controlled by varying the duration of the deposition process. The metal-supported catalysts were characterized by ICP OES, SEM/EDX and nitrogen isothermal adsorption. The high specific surface area (700 m²/g) of the zeolite powder combined with the high dispersion of the Fe catalyst and its good contact with the acetylene gas due to its fluidization allow the growth of large quantities of carbon nanotubes. The influence of two process parameters such as iron amount and addition of hydrogen on the catalytic growth of CNTs was investigated. The produced carbon was characterized by Raman spectroscopy and scanning electron microscopy (SEM).

Introduction

Carbon nanotubes (CNTs) find a wide range of application due to their remarkable performances [Cabero, Mauron]. Compared to other synthesis methods, such as arc discharge and laser vaporization, the catalytic chemical vapor deposition (CCVD) techniques has the advantages of large yield of CNTs at low cost, lower reaction temperatures, high quality and high purity of the grown CNTs [Cabero, Mauron, Sinha, Lee]. Therefore, CVD is an attractive method for production of CNTs in industrial scale. Metals such as Fe, Ni and Co were found to be active in the catalytic growth of carbon nanotubes [Lee, Cabero]. The most metal-supported catalysts reported in the literature were prepared through wet impregnation, co-precipitation or ion exchange. Compared to these methods the metal organic chemical vapor deposition in a fluidized bed (FB-MOCVD) allows the preparation of high dispersed metal-supported catalyst with higher activity in one processing step [Xu, Michkova]. Therefore, an articulate low amount of metal is necessary for the carbon nanotubes synthesis. The fluidized bed system has also the advantage of providing good contact of the powder with the gas used as a carbon source resulting in large quantities of nanotubes produced [Mauron].

In the present paper, we have deposited iron on NaY zeolite in one step process using FB-MOCVD technique. Investigated was the influence of the iron concentration and the carbon source system: C₂H₂ or C₂H₂/H₂ on the yield and the microstructure of the resulting carbon nanotubes.

Experimental

Preparation of Fe catalysts by FB-MOCVD

The principle for the deposition of iron on zeolite is the same as described by [Michkova]. The schematic diagram of the apparatus used in this experiment is shown in Figure 1. The main body is a fluidized bed reactor of quartz glass in which middle a porous quartz plate is mounted. The zeolite powder was placed on it and was fluidized by helium flow saturated with iron precursor. Spray dried NaY zeolite (spNaY) was used as catalyst support. For each coating run, 2g of spNaY was calcined in a oven at 450°C for 2h. As iron precursor [(1,3-Butadiene)(toluene)Fe(0)] complex was used. The synthesis of this metal organic complex is reported by [Michkova]. For its evaporation a heat able Al-block was used.

The MOCVD experiments were carried out under atmospheric pressure of helium inert gas with an evaporator temperature of 70°C and a fluidized bed reactor temperature of 200°C. By varying the duration of the deposition process (15-360min) the amount of the deposited iron could be controlled.
Synthesis of carbon nanotubes by catalytic chemical vapor deposition (CCVD)

Carbon nanotubes were synthesized by catalytic decomposition of acetylene over iron-zeolite catalyst in a fluidized bed reactor at 700°C as shown in Figure 1. The only difference is that in the case of CNTs synthesis, the bubbler was omitted. All syntheses were carried out with 30mg of the Fe coated NaY zeolite, placed in the reactor. First the catalyst was heated from room temperature to 700°C in N₂/H₂ flow. At 700°C the reduced powder was heated 10 min longer. The CNTs synthesis was started with introduction of C₂H₂/N₂ or C₂H₂/H₂/N₂ flow for 30min. After this time the reactor was cooled to room temperature in a N₂ atmosphere. The final product was obtained as a lightweight and electrostatic black solid.

Characterization of the metal-supported catalysts and the carbon materials

The iron coated NaY zeolites produced by FB-MOCVD were investigated by SEM (scanning electron microscopy) and ICP OES (atom emission spectrometry with inductive coupled plasma). The SEM micrographs (Phillips XL 30) were used for a qualitative estimation of the iron distribution on the surface of the powder. ICP OES (Altamira, AMI-100) was used for quantitative determination of the iron mass fraction in the catalysts. To prove the existence of iron on the powder EDX (surface energy dispersed X-ray analysis, Phillips XL 30) was applied. Surface area of the zeolites was calculated by the conventional BET method, from the N₂ adsorption isotherms -196°C, determined using ASAP 2010.

The resulting CNTs samples were characterized by SEM and Raman spectroscopy (dilor ISA, Labram HR, excited at 514nm). The carbon yield was calculated according to the following equation:

\[
\text{carbon yield} = \frac{m_{\text{Carbon}}}{m_{\text{Fe}}}
\]

where \(m_{\text{carbon}}\) = mass of carbon deposit, g
\(m_{\text{Fe}}\) = mass of the Fe catalyst, g

Results and discussion

Catalyst characterization

The spray drying process causes the formation of approximately equally shaped spheres which can be easy fluidized in the reactor. Some of the spheres have holes because of the preparation process. This can be clearly shown in the Figure 2. The changes in the iron amount by the untreated and coated samples can be seen in the EDX spectrums.
Figure 2. SEM and EDX images for the untreated and coated NaY zeolites with various iron content a),b) untreated spNaY zeolite (wFe=0.5%); c),d) Fe/spNaY (wFe=0.7%); e),f) Fe/spNaY (wFe=2.5%)

The results of the ICP analyses and the specific surface area (SSA) for the untreated and iron coated zeolites are presented in Table 1. The calcination of the initial spNaY zeolite in an oven, increases the specific surface area. On the other hand rising the amount of deposited iron leads to a decrease of its value.

Table 1. Specific surface area (SSA) of untreated and Fe coated zeolites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Time [min]</th>
<th>wFe [%]</th>
<th>SSA [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>spNaY untreated</td>
<td>-</td>
<td>0.5</td>
<td>557</td>
</tr>
<tr>
<td>spNaY calc.</td>
<td>-</td>
<td>0.5</td>
<td>702</td>
</tr>
<tr>
<td>Fe0.7/spNaY</td>
<td>15</td>
<td>0.7</td>
<td>717</td>
</tr>
<tr>
<td>Fe2.5/spNaY</td>
<td>360</td>
<td>2.5</td>
<td>534</td>
</tr>
</tbody>
</table>

Characterization of carbon deposit

Carbon yield at different Fe content and composition of the reaction gas is presented in Table 2. It is clearly to be seen, that the amount of the grown carbon is only slightly affected by the catalyst concentration. A possible explanation is that at lower Fe concentrations a higher dispersion of the catalytic active Fe particles could be achieved, thus improving the carbon growth. Addition of hydrogen to the acetylene causes reduction of the carbon yield because of inhibiting its decomposition resulting is slower growth rate of carbon.
Table 2. Influence of Fe content and addition of hydrogen to the acetylene on the carbon yield

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe [%]</th>
<th>Reaction system</th>
<th>Carbon yield [g C/g Fe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe0.7/spNaY</td>
<td>0.7</td>
<td>C2H2/N2</td>
<td>22</td>
</tr>
<tr>
<td>Fe0.7/spNaY</td>
<td>0.7</td>
<td>C2H2/N2/H2</td>
<td>12</td>
</tr>
<tr>
<td>Fe2.5/spNaY</td>
<td>2.5</td>
<td>C2H2/N2</td>
<td>25</td>
</tr>
</tbody>
</table>

The microstructure of the carbon deposit was investigated by Raman spectroscopy. The Raman spectrum (Figure 3.) of the three carbon samples shows two main peaks at approximately 1350 cm\(^{-1}\) (D-band) and 1600 cm\(^{-1}\) (G-band). The D-band represent the disorder structures inside the carbon layers, including the lattice defects or poly-microcrystalline of carbon. The G-band means the graphitization of CNTs [Weizhong, Mauron]. These peaks are characteristic for the graphite structure of MWNTs and carbon nanofibres (CNFs). The absence of peaks below 300 cm\(^{-1}\) (low frequency Raman spectrum) reveals the absence of single-wall carbon nanotubes [Mitri]. The relative peak intensity of the D-band to the G-band for all samples is about 0.8 independent of the iron amount. It reveals that the degree of crystalline perfection of the carbon materials is high.

The SEM analyses for all the catalyst samples after the CCVD of acetylene in a fluidized bed reactor confirm the formation of carbon nano structures. Figure 4 illustrates the SEM images for the synthesized carbons after FB-CVD of C2H2/N2 and C2H2/N2/H2 on Fe0.7/spNaY and Fe2.5/spNaY catalysts for 30 min at 700°C.

Carbon nano structures like nanotubes and/or nanofibers were found. It is also shown that the use of hydrogen (Figure 4. c)) leads to formation of finer carbon structures with identical thickness of 10nm compared to the sample in Figure 4. b)) with equal iron amount synthesized without hydrogen. At the sample with higher iron amount (Figure 4. a)) nano structures with bigger diameter of approximately 30nm have been observed.
Figure 4. SEM images of CNTs and CNFs formed by the decomposition of C$_2$H$_2$ at 700°C for 30min
a) Fe$_{2.5}$/spNaY with C$_2$H$_2$/N$_2$; b) Fe$_{0.7}$/spNaY with C$_2$H$_2$/N$_2$; c) Fe$_{0.5}$/spNaY with C$_2$H$_2$/N$_2$/H$_2$
Conclusion

Carbon nano structures in form of nanotubes and/or nanofibers were deposited by FB-CVD onto iron coated NaY zeolites. Due to the high dispersion of the iron on the zeolite support achieved by FB-MOCVD it was possible to synthesizes carbon structures applying very low amount of iron $w_{Fe}=0.7\%$ compared to the other methods used in the literature for preparation of metal-supported catalysts. We found that the amount of the grown carbon is only slightly affected by the catalyst concentration because of the higher dispersion of the catalytic active Fe particle at low concentrations. Addition of hydrogen to the acetylene causes reduction of the carbon yield because of its inhibiting effect on the decomposition, resulting in slower growth rate of carbon. However, with hydrogen addition nano structures with smaller diameter have been observed.

References