Effects of Citric Acid Concentration and Activation Temperature on the Synthesis of Carbon Nanotubes

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Abstract: A series of Ni-La-Mg catalyst samples were prepared by citric acid complex method, and carbon nanotubes were synthesized by catalytic decomposition of CH\textsubscript{4} on these catalysts. The effects of the citric acid concentration and the activation temperature on catalytic activity were investigated by CO adsorption, TEM and XRD techniques. The experimental results showed that the particle size of the catalysts prepared through gel auto-combustion varied with the concentration of citric acid. Therefore carbon nanotubes with different diameters were obtained correspondingly. The effect of activation temperature on the activity of catalyst was negligible from 500 to 700 °C, but it became pronounced at lower or higher temperatures.

Key words: carbon nanotubes, preparation, citric acid complex, activation temperature, CH\textsubscript{4}

1. Introduction

With the discovery of carbon nanotubes (CNTs) in 1991, much attention has been focused on the preparation and application of carbon nanotubes in recent years. There are various ways for preparing CNTs in the laboratory including carbon-arc process \cite{1,2}, laser vaporization \cite{3,4} and catalytic chemical vapor deposition \cite{5,6} (CVD). The latter methods attracted more attention of scientists in the fields of materials, chemistry and physics because of low cost and industrial scale production of CNTs. Many catalysts \cite{7-8} have been employed to prepare CNTs. Liu and co-workers \cite{8} reported that CNTs were synthesized on LaCoO\textsubscript{3} catalyst. Chen et al \cite{5} reported that the decomposition of CH\textsubscript{4} was used to prepare CNTs on Ni-Mg catalyst. However, the effects of the concentration of citric acid and the pretreatment temperature of catalyst on the preparation of CNTs have not been determined yet. In this paper, CNTs were synthesized by catalytic decomposition of CH\textsubscript{4} on Ni-La-Mg which was prepared by citric acid complex method. The effects of citric acid concentration and activation temperature on the growth of CNTs were investigated.

2. Experimental

A series of citric acid solutions with the concentration of 0.06, 0.08, 0.10, 0.12, 0.14, 0.16 and 0.18 g/ml were prepared in advance.

2.1. Preparation of catalyst

A certain amount of Ni(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O, Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and La(NO\textsubscript{3})\textsubscript{3} were mixed thoroughly, then 10 ml of citric acid solution was added into the mixed solution under stirring. The solution was evaporated to form a gel, and the gel was taken rapidly to an oven and had been calcined at 200 °C for 15 min. Then a black and fluffy sample was obtained and subsequently calcined at 400, 500, 600, 700 and 800 °C,
respectively. Thus a series of catalyst precursors were obtained.

2.2. Preparation of carbon nanotubes

40 mg of the catalyst precursor was packed into a quartz reactor, and heated in a flow of H₂. The temperature was raised from room temperature to 700 °C, and then held constant for 30 min. Next, the catalyst was shifted into the feed gas of CH₄ after cooling down to reaction temperature. The raw CNTs were obtained after the reaction.

2.3. Purification of carbon nanotubes

The raw CNTs were purified by means of immersion in 4 M nitric acid solution to dissolve the catalyst particles attached on the ends of the nanotubes, followed by filtering, drying and weighing. The morphological characteristics of CNTs were observed by TEM.

2.4. Measurement of surface area of active nickel in catalyst

The surface area of active nickel on the catalyst was measured by CO chemisorption. 100 mg of sample was packed into a U-shape reactor and reduced in a flow of H₂ at certain temperature. After the reduction process was completed, temperature was dropped to room temperature in H₂ with flow rate of 60 ml/min. CO was injected into the reactor through a six-way valve until saturation. The number of pulses and the CO peak area were recorded and calculated.

The surface area of active nickel (S_{Ni}) was calculated as follows [9]:

\[ V = \frac{A \times n - \sum_{i=1}^{n} B}{A \times C \times V_1} \]

\[ S_{Ni} = \frac{V_0 \times N \times A_m}{W \times 2.24 \times 10^8} \]

A—peak area of adsorbed CO when CO adsorption is saturated, 
B—peak area of un-adsorbed CO when CO adsorption is unsaturated, 
\( n \)—number of pulses, 
C—concentration of CO, 
\( V_1 \)—volume of six-way valve (ml), 
\( V_0 \)—total adsorptive capacity at standard state (ml), 
\( N \)—Avogadro constant, 
\( A_m \)—effective cover area of adsorbent molecule of 13×10⁻¹⁶ cm² in value.

2.5. Characterization

X-ray diffraction (XRD) was performed on a D/max-IIIA polycrystalline X-ray instrument under the conditions: target of Cu, voltage of 30 kV, current of 30 mA, scan speed of 4°/min.

TEM observation was performed by using a Hitachi-600 transmission electron microscope.

3. Results and discussion

Generally, some other carbon materials including carbon fibers, carbon particles exist in the raw CNTs. In order to describe the activity of catalyst more accurately, the content of CNTs was used to measure the efficiency of catalyst besides carbon yield.

\[ \text{Carbon yield (\%) = } \frac{\text{amount of raw products} - \text{amount of catalyst}}{\text{amount of catalyst}} \]

\[ \text{Content of CNTs (\%) = } \frac{\text{amount of raw products} - \text{amount of catalyst}}{\text{amount of CNTs}} \]

3.1. Effect of citric acid concentration on growth of CNTs

The results in Table 1 showed that the carbon yield and the content of CNTs were the highest when the concentration of citric acid was 0.12 g/ml. Meanwhile the surface area of active nickel on catalyst was the largest, demonstrating that carbon yield and content of CNTs were in good correspondence with the surface area of active nickel on the catalyst. From the TEM Figures, it was found that the catalyst particle was on the top of CNTs. The larger the surface area of active nickel on catalysts, the more the active sites in catalysts, leading to higher content of CNTs, correspondingly.
Table 1. Effect of citric acid concentration on carbon yield, content of CNTs in the raw products and physico-chemical properties of active nickel on the catalyst

<table>
<thead>
<tr>
<th>Concentration (g/ml)</th>
<th>Carbon yield (g/g)</th>
<th>Content of CNTs (%)</th>
<th>$S_{NV}$ / (m²/g)</th>
<th>Size of Ni grains (nm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>5.21</td>
<td>54.6</td>
<td>9.02</td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td>5.44</td>
<td>79.1</td>
<td>8.50</td>
<td>40</td>
</tr>
<tr>
<td>0.10</td>
<td>6.68</td>
<td>80.0</td>
<td>11.45</td>
<td></td>
</tr>
<tr>
<td>0.12</td>
<td>6.90</td>
<td>81.9</td>
<td>21.65</td>
<td>20</td>
</tr>
<tr>
<td>0.14</td>
<td>5.90</td>
<td>80.5</td>
<td>11.73</td>
<td>32</td>
</tr>
<tr>
<td>0.16</td>
<td>5.75</td>
<td>70.0</td>
<td>11.30</td>
<td>33</td>
</tr>
</tbody>
</table>

* — obtained by XRD

The results of Table 1 also indicated that when the concentration of citric acid was 0.12 g/ml, the size of Ni grains was the smallest. In the process of preparing catalyst, the self-catalyzed oxidation-reduction reaction took place between citric acid and nitrate [10,11]. The catalyst particles with different diameters were obtained by mixing different concentration citric acid with nitrate. When the concentration of citric acid was 0.12 g/ml (the molar ratio of citric acid to nitrate was 5:4), the gel was totally combusted. Therefore the surface area of active nickel on catalyst with suitable size particles was the largest. In contrast, when the concentration of citric acid was lower than 0.12 g/ml, the gel was partially combusted and the oxidation-reduction reaction was incomplete. The unreduced nitrate was remained in the catalyst precursor, leading to the decrease of surface area of active nickel. When the concentration of citric acid was higher than 0.12 g/ml, the surface area of active nickel on catalyst was small too. It probably for the reason that the excess citric acid continue to decompose after the oxidation-reduction reaction between citric acid and nitrate, which made the particle size of catalyst smaller. Therefore the crystalline grain was easy to aggregate under calcination conditions.

The conformability between the content of CNTs and surface area of active nickel could be explained according to the growth process of CNTs. The first step in the process of growth was that the compound of NiC₃ was formed when carbon deposited on the surface of catalyst. Then carbon grains started to aggregate. The particle size of catalyst was large when the concentration of citric acid was higher or lower than 0.12 g/ml. This lengthened the distance for carbon to move and decreased its moving velocity, therefore the carbon grains could not spread in time and caused aggregation. Finally carbon fiber and carbon grain were formed. This was the reason that the diameter of carbon fiber was larger. Only when the concentration of citric acid was 0.12 g/ml, the catalyst was effectively
dispersed and moving velocity of carbon kept higher. Hence the carbon yield and content of CNTs were the largest under this condition.

According to TEM observation (Figure 3), the higher the concentration of citric acid, the more even the distribution of CNTs diameter. When the concentration was 0.18 g/ml, the diameter of CNTs was very even with the outer diameter of 35 nm (Figure 3(c)). When the concentration is 0.06 g/ml, the diameter of CNTs was uneven and differed from 10 to 40 nm, with 20 nm or so in most of CNTs. (Figure 3(b)). No matter what citric acid was used, 0.18 or 0.06 g/ml, the CNTs synthesized was not ideal. The wall of CNTs was very thick (the ratio of inner to outer diameter was 1:8) and was mixed with a few carbon fibers. When the concentration was 0.12 g/ml, CNTs was ideal (Figure 3(a)) with thinner wall of CNTs (the ratio of inner to outer diameter was about 1:3).

Figure 3. TEM of carbon nanotubes synthesized on Ni-La-Mg catalyst after different treatments
Citric acid concentration and catalyst activation temperature: (a) 0.12 g/ml, 600 °C; (b) 0.06 g/ml, 700 °C; (c) 0.18 g/ml, 700 °C; (d) 0.12 g/ml, 800 °C respectively
3.2. Effect of activation temperature on growth of CNTs

3.2.1. Effect of activation temperature on the surface area of active nickel in catalyst

The results of Table 2 showed that the surface area of active nickel was the largest when the activation temperature was 600 °C. It meant that the particle size of catalyst was suitable and the active nickel could well dispersed under this condition. At higher activation temperature (such as at 800 °C), the surface area of active nickel decreased obviously. The reason was that high temperature led to aggregation, resulted in the agglomeration of catalyst grains, hence the active nickel dispersed poorly and the catalytic activity decreased distinctly. When the activation temperature was above 600 °C, the surface area of active nickel decreased rapidly. From Figure 4, it was found that the crystalline phase of catalyst changed at higher temperature. The peak of 1, 2 and 3 disappeared when the activation temperature of the catalyst was 700 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$S_{Ni}$ / (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>29.6</td>
</tr>
<tr>
<td>500</td>
<td>34.3</td>
</tr>
<tr>
<td>600</td>
<td>36.6</td>
</tr>
<tr>
<td>700</td>
<td>21.6</td>
</tr>
<tr>
<td>800</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Table 2. The surface area of active nickel on catalyst at different calcination temperature

The concentration of citric acid is 0.12 g/ml

Figure 4. XRD patterns of catalysts calcined at different temperatures

(a) 500 °C, (b) 600 °C, (c) 700 °C

3.2.2. Effect of activation temperature on carbon yield and content of CNTs

The results of experiment demonstrate that the carbon yield and the content of CNTs were near to the highest value when the activation temperature was 600 °C (see Figures 1 and 2). This result was in agreement with the result of surface area of active nickel. When the activation temperature was above 600 °C, the catalytic activity of catalyst decreased with the increase of activation temperature. When the activation temperature was 800 °C, the catalytic activity of catalyst decreased rapidly. The catalyst precursor became gray, implying that catalyst was agglomerated and the crystalline structure of the catalyst was destroyed. When the activation temperature was raised to 900 °C, the catalyst lost its activity. When the activation temperature varied from 500 to 700 °C, the catalytic activity of catalyst kept at the same level.

From the TEM observation (Figure 3(a) and Figure 3(d)), it was found that the diameter of CNTs was uneven and a large number of carbon fibers coexisted with CNTs when the catalyst was activated at 800 °C. Whereas CNTs synthesized was even in diameter and showed good properties when the activation temperature was 600 °C, and no carbon fiber was found on the surface of CNTs.

4. Conclusions

(1) When citric acid solutions of different concentrations were used to prepare the catalyst, catalyst samples with different grain sizes were obtained because of the difference in self-combustion extent of the gel. As a result of this, it was found that the catalysts with different surface areas of active nickel were obtained which influenced the growth and morphology of CNTs. When the concentration of citric acid was 0.12 g/ml, the CNTs synthesized showed better properties.

(2) Within a suitable temperature range (from 500 to 700 °C), the catalytic activity was not obviously affected by the activation temperature. However, the influence of activation temperature on catalytic activity was distinct at lower or higher temperatures, and the optimum activation temperatures was 600 °C.

References


