Introduction

The vast amount of research papers published in recent years on the preparation and characterisation of carbon nanotubes and carbon filaments is related with their possible interest for different several commercial applications [1 and references cited therein, 2]. It is believed that carbon nanotubes and filaments possess unique properties for many applications such as: storage of hydrogen, nanowires, components for nanoscale electronic devices and catalyst supports [1,2,3].

These carbon materials have been prepared by arc-method, laser evaporation and lately by CVD of hydrocarbons catalysed by different metals (Ni, Co, Fe). Depending on the preparation method, two types of carbon nanotubes can be obtained: single wall nanotubes (SWNT) and multi-wall nanotubes (MWNT). However, the large scale production of nanotubes is obtained from the catalytic decomposition of hydrocarbons, such as acetylene, propylene, methane or ethylene[4-7].

Depending on the chemical nature of the catalyst and the conditions of the CVD reaction, different nanostructures with various morphologies can be produced. The width of the nanofilament is directly related with that of the catalyst particle [8,9] and this parameter can be controlled during the catalyst preparation.

In the present work we investigated the effect of the catalyst, the hydrocarbon and temperature on the type of the material produced.

Experimental

Catalysts preparation

The preparation method of Ni supported on SiO$_2$ and Co supported on Al$_2$O$_3$ has been described elsewhere [10]. 15 g of Ni(NO$_3$)$_2$:6H$_2$O or Co(NO$_3$)$_2$:6H$_2$O were dissolved into 150 mL of water and 150 mL of ammonia solution (28wt%). While stirring, 10 g of γ alumina from Degussa (or SiO$_2$) were added to the solution. The contact time with the solution was 2 hours and the load obtained was 5.3% in Co.

After centrifugation, the catalyst precursors were washed and dried at 373 K a certain number of times. The Ni/Al$_2$O$_3$ catalyst was prepared by the incipient wetness method. 2 g of Al$_2$O$_3$ were dried under vacuum (2 hours) and then an aqueous solution of Ni(NO$_3$)$_2$ was added via a peristaltic pump to obtain a load of 5% in Ni. After impregnation, the sample was dried overnight at 373 K.

The Co/Al$_2$O$_3$ catalyst precursor obtained was reduced with a mixture of H$_2$ and N$_2$ (5% of H$_2$, total flow 75 mL) from room temperature to 973 K and then at 973 during 11 hours. The heating rate was 1.8 K/min.

The Ni/SiO$_2$ and Ni/Al$_2$O$_3$ catalyst precursors were reduced with a mixture of H$_2$ and N$_2$ (5% of H$_2$, total flow 75 mL) from room temperature to 673 K and then at 673 K during 4 hours. The heating rate was 5 K/min.

CVD of hydrocarbons

The CVD reactions were carried out in a vertical fixed-bed reactor in the temperature range 793-1073 K. 300 mg of catalyst (Ni/SiO$_2$, Ni/Al$_2$O$_3$ or Co/Al$_2$O$_3$) were placed in the reactor, reduced, and when the CVD temperature was obtained, a flow of 5% of propylene or ethylene in H$_2$ was added. The reaction time was 90 minutes and the cooling down was made under N$_2$. For calculation of carbon yield, the following formula was used:

\[ \text{Carbon yield (\%) = } \left( \frac{M_{\text{final}} - M_{\text{cat}}}{M_{\text{cat}}} \right) \times 100 \]

where $M_{\text{cat}}$ is the initial amount of catalyst and $M_{\text{final}}$ is the total weight after reaction.

The morphology of the carbon deposit was characterised by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). For TEM and HRTEM (high resolution transmission electron microscopy) the samples were dispersed into ethanol by ultrasonication and deposited on a copper grid covered with an amorphous carbon film.
Table 1- Experimental conditions for the preparation of carbon nanotubes and carbon filaments.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Catalyst</th>
<th>Hydrocarbon</th>
<th>CVD temperature (K)</th>
<th>Yield (%)</th>
<th>SEM and HRTEM observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>G8CoSupP</td>
<td>Co/Al₂O₃</td>
<td>Propylene</td>
<td>793</td>
<td>170</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>G14CoSupP</td>
<td>Co/Al₂O₃</td>
<td>Propylene</td>
<td>973</td>
<td>-</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>G6CoSupP</td>
<td>Co/Al₂O₃</td>
<td>Propylene</td>
<td>1023</td>
<td>5.3</td>
<td>Filaments; graphene layers parallel to the tube axis (nanotubes); see fig 3 and 4.</td>
</tr>
<tr>
<td>G15CoSupP</td>
<td>Co/Al₂O₃</td>
<td>Propylene</td>
<td>1073</td>
<td>13.3</td>
<td>Filaments; graphene layers parallel to the tube axis (nanotubes); see fig 3 and 4.</td>
</tr>
<tr>
<td>G12CoSupE</td>
<td>Co/Al₂O₃</td>
<td>Ethylene</td>
<td>1023</td>
<td>-</td>
<td>Filaments; graphene layers parallel to the tube axis (nanotubes); see fig 3 and 4.</td>
</tr>
<tr>
<td>G4FsupP</td>
<td>Ni/Al₂O₃</td>
<td>Propylene</td>
<td>1023</td>
<td>11.2</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>FniSupP</td>
<td>Ni/Al₂O₃</td>
<td>Propylene</td>
<td>923</td>
<td>35.1</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>G9NiSupE</td>
<td>Ni/Al₂O₃</td>
<td>Ethylene</td>
<td>923</td>
<td>4</td>
<td>Filaments; hollow filaments with the so-called “herringbone structure” evidencing a stacking of cone segment carbon layers.</td>
</tr>
<tr>
<td>G11NiSupE</td>
<td>Ni/Al₂O₃</td>
<td>Ethylene</td>
<td>1023</td>
<td>16.2</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>4Ni/SiO₂P</td>
<td>Ni/SiO₂</td>
<td>Propylene</td>
<td>1023</td>
<td>13</td>
<td>Filaments; graphene layers perpendicular to the tube axis; see fig. 6.</td>
</tr>
<tr>
<td>1Ni/SiO₂P</td>
<td>Ni/SiO₂</td>
<td>Propylene</td>
<td>923</td>
<td>-</td>
<td>Small amount of filaments</td>
</tr>
<tr>
<td>G10NiSiO₂E</td>
<td>Ni/SiO₂</td>
<td>Ethylene</td>
<td>923</td>
<td>-</td>
<td>Small amount of filaments</td>
</tr>
</tbody>
</table>

Results and Discussion

Different supports and two different preparation methods were used in order to find catalysts which are more effective for carbon nanotube formation. The experimental conditions used and some results are summarised in table 1. Ni/SiO₂ and Ni/Al₂O₃ prepared by different methods (ammonia method and incipient wetness method) were found to be inactive for the formation of carbon nanotubes. With these two catalysts, and for both hydrocarbons (propylene and ethylene), only filaments were obtained in the temperature range used (figure 1). The carbon deposit showed some inhomogeneity. We can find thick filaments having a diameter of 70 nm and filaments having a diameter of 10 nm (figure 2). This inhomogeneity is probably related to the catalyst dispersion and to the size of the Ni particles after reduction.

With the Ni/Al₂O₃ catalyst, the nature of the hydrocarbon had a noticeable effect on the carbon morphology. Thus ethylene produced hollow filaments with the graphene layers inclined to the tube axis.

The Ni/SiO₂ catalyst was prepared by the ammonia method, and this method of preparation has been used for preparing well-dispersed catalysts [10]. But with this catalyst, for all the conditions tested, we obtained only a small yield of carbon. TEM observation demonstrated that it consisted only of filaments.

The Co/Al₂O₃ catalyst has been successful in the production of carbon nanotubes from the carbon monoxide disproportionation reaction [9,11].

By using this catalyst in the CVD of propylene and ethylene, it was found that in the temperature range 793-973 K the product consisted mostly of carbon filaments, and HRTEM observation demonstrated that the graphene layers were perpendicular or inclined relative to the tube axis. At higher temperatures (1023 K) the carbon product consisted mostly of nanotubes, with the graphene layers parallel to the tube axis (figures 3 and 4). These HRTEM micrographs show multiwalled nanotubes with a cobalt nanoparticle trapped in the inner cavity of the nanotube. Similar results were obtained with both hydrocarbons. The presence of some spiral nanotubes was also observed (figure 5).
The existence of these helices has already been described using supported Co/silica catalysts [12]. The presence of filaments with the carbon layers perpendicular to the tube axis was also observed (figure 6). Increasing the reaction temperature favoured the formation of carbon nanotubes, but the carbon yield decreased to a great extent. At higher temperatures, no carbon deposit could be determined for some experiments.

The results obtained with the three different catalysts indicate that the metal-support interaction at CVD reaction conditions plays an important role in the structure of the carbon deposits. The effect of temperature in the carbon morphology obtained with the Co/Al$_2$O$_3$ catalyst must be related to this interaction. Therefore, it seems that controlling the size of the catalyst particles is not enough to prepare carbon nanotubes. Further insights may be obtained by studying the metal-support interaction under reaction conditions.

**Conclusions**

This study has demonstrated that the Co/Al$_2$O$_3$ catalyst is effective for the production of carbon nanotubes under certain CVD reaction conditions. A similar Ni catalyst, prepared by the same method but supported on SiO$_2$ and a Ni/Al$_2$O$_3$ catalyst prepared by the incipient wetness method, were ineffective for the production of carbon nanotubes, and the carbon deposit obtained consisted only of carbon filaments.

**Acknowledgments**

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**References**

Figure 1- SEM of carbon deposit from CVD of propylene at 1023 K over Ni/Al₂O₃.

Figure 2- SEM of carbon deposit from CVD of ethylene at 1023 K over Ni/Al₂O₃.

Figure 3- HRTEM of carbon deposit from CVD of propylene at 1023 K over Co/Al₂O₃.

Figure 4- HRTEM of carbon deposit from CVD of propylene at 1073 K over Co/Al₂O₃.
Figure 5- HRTEM of a helix-shaped nanotube (sample G6CoSupP).

Figure 6- HRTEM of a carbon filament (sample G15CoSupP).