Cobalt Molybdenum Supported Catalysts Characterization for Methane Decomposition and Carbon Nanotube Growth

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Introduction
Many researchers [1-3] have studied different catalyst formulations and operating conditions for carbon nanotube (CNT) synthesis by chemical vapor deposition. Cobalt/molybdenum supported catalysts have shown high selectivity towards single walled carbon nanotube production. The nature and morphology of cobalt species affects the catalyst activity and selectivity for CNT production. Thus, it is important to understand the influence of the cobalt and molybdenum species on carbon nanotube production in order to develop a strategy to maximize the catalyst selectivity and activity. This work has focused on the characterization of the cobalt and molybdenum species present in CoMo/Al₂O₃ system for each step of CNT growth. The influence of such species in CNT synthesis was also investigated.

Materials and Methods
A series of monometallic Co and Mo catalysts and bimetallic Co-Mo catalysts supported on γ-Al₂O₃ were prepared by incipient wetness impregnation. Bimetallic catalysts were prepared by sequential impregnation. The Co solution was introduced first and, the catalysts were calcined at 550 °C. The chemical compositions of the samples were determined by EDX in vacuum using an EDX-720 Shimadzu apparatus. XPS experiments were performed with an ESCALAB 250Xi Thermo Scientific with monochromatic Al Kα X-rays. TPR experiments were performed in a reactor coupled to a quadrupole mass spectrometer (Omnistar, Balzers). The CNT were synthesized by methane CVD. Catalyst was heated under in H₂ flow from room temperature to 700 °C. Then, H₂ flow was switched to 200 mL min⁻¹ of methane for 30 min. The CNT were characterized by TPO and TEM images. TPO experiments were performed in the same apparatus described for the TPR experiments. TEM images were obtained in a FEI Tecnai F30 microscope.

Results and Discussion
The selectivity toward CNT depends on the cobalt particle size during de reaction step. For the Co-Mo catalyst, molybdenum can interact with cobalt resulting in small cobalt particles. The Co:Mo mass ratio of the catalysts were studied by EDX and XPS and the results are shown in Figure 1. The straight dash line represents the values where the Co:Mo mass in the bulk phase of the catalyst is equal to the respective Co:Mo mass ratio on the catalyst surface. The solid line represents the value of the Co:Mo mass ratio found by XPS analyses in relation to the values found by the EDX analyses. At high Co:Mo mass ratios, the concentration of cobalt on the surface is increased and the cobalt may exist as small cobalt oxide particles. However, at low Co:Mo mass ratios, cobalt particles may be covered by molybdenum moieties. The TPR data also show a strong influence of molybdenum on the reduction profile of cobalt precursor. While a significant fraction of the cobalt in the monometallic catalyst, 2Co/Al₂O₃, is reduced at temperature below 350 °C, almost no reduction occurs below 400 °C for the bimetallic catalyst. This shift to higher temperatures is more intense at low Co:Mo ratios. The reduction profile for the 1.4Co20Mo/Al₂O₃ catalyst is quite different from other bimetallic catalysts. It exhibits two main peaks at 570 and 680 °C, which can be ascribed to the reduction of MoO₂ in two steps and the reduction of CoMo/Al₂O₃ [1,4].

Table 1. Catalyst selectivity and yield for carbon nanotube reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amorphous</td>
<td>CNT</td>
</tr>
<tr>
<td>1.4Co7Mo</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>1.4Co20Mo</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>2Co4Mo</td>
<td>16</td>
<td>84</td>
</tr>
<tr>
<td>2Co5Mo</td>
<td>15</td>
<td>85</td>
</tr>
</tbody>
</table>

* The yield during the reaction step was defined as the mass of carbon deposited per mass of catalyst.

Significance
The introduction of molybdenum as promoter on cobalt catalyst can increase the selectivity towards CNT by improvement of the cobalt dispersion as shown by several authors. However, at low Co:Mo ratio, molybdenum may cover the cobalt particles decreasing the carbon yield.

References