Catalytic function of Mo/Ni/MgO for the synthesis of thin carbon nanotubes

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The functions and structures of Mo/Ni/MgO catalysts for the synthesis of carbon nanotubes (CNTs) have been investigated by TEM, XRD, XPS, and Raman spectroscopy.

As shown in Fig.1, thin 2 - 5 walled CNTs with high purities (over 90%) have been successfully synthesized by catalytic decomposition of CH_4 over Mo-Ni-MgO catalysts at 1073 K. Fig.2 shows the carbon yield as a function of the Ni mole fraction at the fixed Mo mole fractions of 0.01, 0.1 and 0.3, ($Mo_{0.01}Ni_xMg_{0.99-x}O$, $Mo_{0.1}Ni_xMg_{0.9-x}O$ and $Mo_{0.3}Ni_xMg_{0.7-x}O$). The carbon yield was always low for catalysts with Mo= 0.01 or 0 at any Ni mole fractions. This indicates that Ni/MgO is inactive for the carbon formation at our reaction conditions. However, at Mo= 0.1 and 0.3, the addition of Ni to Mo/MgO drastically promoted the carbon yield as shown in Fig.2. That is, the coexistence of Ni and Mo significantly promotes the formation of carbon. The optimal sum of Mo and Ni mole fractions is 0.3-0.4.

It has been found that the outer diameter and the thickness of CNTs well correlate with the contents of these three elements. As shown in Fig.3, the outer diameter of the CNTs and the thickness of graphene layers increase from 4 nm to 13 nm with increasing Mo content at a fixed Ni content, while the inner diameter is identical at 2-3 nm and regardless of the contents. Furthermore, the average of outer diameters is in good agreement with the average of the particle size of metal catalysts. That is, the thickness or the outer diameter can be controlled by selecting the composition of the Mo/Ni/MgO catalysts.

XRD analyses have shown that Mo and Ni form a Mo-Ni alloy before CNT synthesis, while the Mo-Ni alloy phase is separated into Mo carbide and Ni. These alloy particles are supported on MgO cubic particles with 15 to 20 nm width. It has been found that only small Mo-Ni alloy particles with the size of 2 nm to 16 nm catalyze the CNT synthesis, but the larger particles over 15 nm exhibit no activity. Mo carbide and Ni should play different roles to synthesize the thin CNTs. It is proposed that Ni is responsible for the dissociation of CH_4 into carbon and Mo carbide works as a reservoir of carbon.

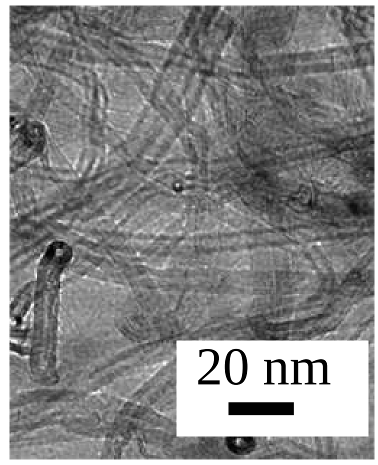

Fig.1 TEM images of as-grown carbon nanotubes produced from catalytic decomposition of CH_4 at 1073 K for 8 h over $Mo_{0.025}Ni_{0.05}Mg_{0.925}$ catalyst

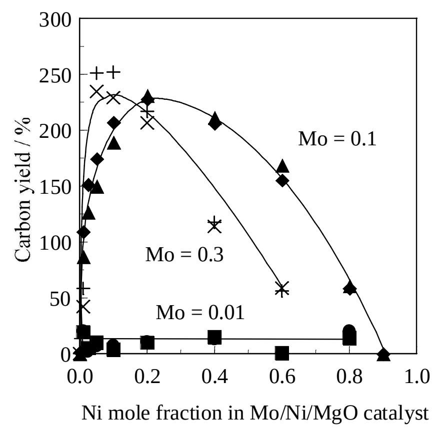

Fig. 2 Carbon yield on Mo/Ni/MgO catalysts as functions of the Ni mol ratio.

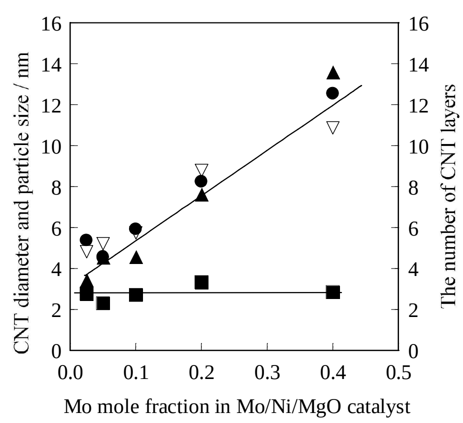

Fig. 3 Average size of CNTs and metal vs Mo mole fraction of $Mo_xNi_{0.05}Mg_{0.95-x}O$ catalyst. (■) inner diameter of CNTs, (●) outer diameter of CNTs, (▲) layers of CNTs, (□) metal particle size.