Growth of Single-Walled Carbon Nanotubes by Disproportionation of CO Over Co-Re/SiO₂ Catalysts

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ABSTRACT

In this work, a series of silica supported Co-Re catalysts was prepared and tested for the synthesis of single-walled carbon nanotubes (SWNT) by carbon monoxide disproportionation at 750 – 950 °C. The catalysts were characterized by temperature-programmed reduction (TPR). To follow nature and quality of the SWNT formed, Raman spectroscopy, temperature programmed oxidation (TPO) and transmission electron microscope (TEM) were used. The effects of reaction parameters such as molar ratio of Co to Re, reduction temperature, and reaction temperature were investigated and found that the synergism of Co and Re in the catalytic production of SWNT leads to the growth of SWNT with high selectivity in the range of studied temperatures.

KEYWORDS
Single-walled carbon nanotubes, cobalt, rhenium, carbon monoxide

INTRODUCTION

Single-walled carbon nanotubes (SWNT) (Iijima et al., 1993, and Bethune et al., 1993) have been the subject of interest from numerous researchers in various fields due to their exceptional physical and chemical properties, both theoretically predicted and experimentally investigated, that can be extended to several potential applications (Yakobson, et al., 1997). The extensive development of SWNT synthesis is now focused on large-scale manufacture at a relatively low cost. Among the various methods for SWNT synthesis, the catalytic decomposition of carbon-containing molecules is now become dominant in the mass production of SWNT.

In the production of SWNT by disproportionation of carbon monoxide, it has been found that Co is an active species but the presence of Co alone on silica support is not selective (Kitiyanan, et al., 2000). When Co and Mo are simultaneously present, particularly when the Mo is in excess, the selectivity toward SWNT is significantly enhanced. In addition, it has been found that the interaction of Co and Mo is critical for a good catalyst performance, because the role of Mo is the stabilization of Co²⁺ ions in the form of a superficial Co molybdate-like structure. Therefore, the well-dispersed Co²⁺ species are not reduced to form larger metallic Co clusters during the reduction treatment of the catalyst (Herrera et al., 2001). Recently, the stabilization of Co²⁺ ions in a Co tungstate-like phase has been observed on the silica-supported Co-W catalyst for the SWNT synthesis (Herrera, et al., 2003). From the successful combination of Co-Mo and Co-W system, it has been proposed that the SWNT selectivity strongly depends on the stabilization of Co species in a non-metallic state before exposed to CO. In other applications, the Co-based catalysts are commonly employed in the Fisher-Tropsch synthesis (the conversion of CO and H₂ into hydrocarbons and water). However, the addition of Re as a promoter to the Fisher-Tropsch catalyst exhibits the improvement on the formation of long-chain n-paraffins, but the synergism between Co and Re is still unclear (Martinez, et al., 2003, and Guczi et al., 2003).
In this contribution, the use of silica-supported Co-Re catalytic system for the production of SWNT by disproportionation of CO has been investigated. The catalysts were characterized by temperature-programmed reduction (TPR). The effects of pretreatment, reaction conditions, and catalyst formulations on the yield and selectivity toward SWNT were observed by using Raman spectroscopy, temperature programmed oxidation (TPO), and transmission electron microscope (TEM).

**MATERIALS AND METHODS**

The Co, Re, and Co-Re catalysts supported on silica gel were prepared by impregnation of aqueous cobalt nitrate and ammonium perrhenate solutions to obtain the bi- or monometallic catalysts. In the series of bimetallic catalysts, the amount of Co was kept constant at 1 wt %, while the amount of Re was varied to obtain the Co:Re ratios of 2:1, 1:1, and 1:4. Two monometallic catalysts were prepared at the metal loadings of 1 wt % Co and 3.2 wt % Re. The silica support obtained from Aldrich had the particle sizes in the range of 70-230 mesh (62 – 210 µm), average pore diameter of 6 nm, BET surface area 480 m²/g, and pore volume 0.75 cm³/g. The SiO₂ support was impregnated using a liquid/solid ratio of 0.6 cm³/g which is corresponding to the incipient-wetness conditions of this support. After impregnation, the samples were first dried in air at room temperature, then dried overnight in oven at 120 °C, and finally calcined in the flow of dry-air at 500 °C.

The temperature-programmed reduction (TPR) experiments on the calcined catalysts were conducted on a Thermo Finnigan TPDRO 1100 equipped with a thermal conductivity detector. The system was operated by passing a continuous flow of 2% H₂ in N₂ over approximately 50 mg of the calcined catalysts, while the temperature was linearly increased at a rate of 10 °C/min.

The Raman spectra of nanotubes were recorded in a Jobin Yvon Horiba LabRam 800 equipped with a CCD detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser), 514, and 488 nm (Ar laser). The Raman spectra were obtained by using 3.0-5.0 mW laser power; 15 sec integration times for each spectrum; and ten Raman spectra were averaged for each sample.

For the production of nanotubes, 0.5 g of calcined catalyst was placed in a horizontal quartz tubular reactor, heated in 50 sec/min H₂ at different temperatures in the range of 500-900 °C, and then in 50 sec/min He up to the specific reaction temperature which ranged from 750 to 950 °C. Subsequently, 99.5% purity CO was introduced at a flow rate of 850 cm³/min at 5 atm for 1 h. At the end of each run, the system was cooled under the flow of He. The deposited carbon from the reaction was characterized by temperature-programmed oxidation (TPO) following the method described elsewhere (Kitiyanan et al., 2000), Raman spectroscopy, and transmission electron microscopy (TEM). The TEM images were obtained in a JEOL JEM-2000FX at 200 kV.

![Figure 1. Temperature-programmed oxidation (TPO) of the carbon deposits by CO disproportionation at 850 °C over the CoRe(1:4)/SiO₂ catalysts after prereduction at different temperatures](image-url)
RESULTS AND DISCUSSION

Effect of reduction temperature

To investigate the effect of varying the reduction temperature on the yield and selectivity to SWNT, the experiments were conducted by pretreatment with H\textsubscript{2} at 500, 600, 700, 800, and 900 °C before decomposition of CO over CoRe(1:4)/SiO\textsubscript{2} at 850 °C for 1 h. The normalized TPO profiles of the nanotubes samples obtained from different reduction temperatures are illustrated in Figure 1. In each sample, total area under the normalized TPO profiles are converted to the yield of carbon product, which is defined as a weight percentage of carbon deposited per total catalyst weight.

As shown in the TPOs of Figure 1, the amount of carbon deposited on the CoRe(1:4) catalyst increased with increasing reduction temperature from 600 °C to 800 °C. The maximum carbon yield of 5.8 wt % is obtained at 800 °C. However, when using reduction temperature at 900 °C, carbon yield is dramatically dropped to 2.8 wt % which may be due to the agglomeration to large metallic Co particles. In addition to TPO, the Raman spectroscopy provides useful information on the structure of carbon nanotubes. The information on tubes diameter of SWNT can be directly obtained from the analysis of radial A\textsubscript{1g} breathing mode which occurs below 300 cm\textsuperscript{-1} (Rao et al., 1997). The information on the electronic properties of the nanotubes can be obtained from the investigation of the graphite-like tangential mode (G band) ranging from 1400 to 1700 cm\textsuperscript{-1}. Moreover, the indication on the level of disordered carbon can be obtained from the analysis of the D band at around 1350 cm\textsuperscript{-1}. From the Raman spectra, qualitative measurement on the formation of undesirable forms of carbon can be estimated by comparing the size of the D band to the G band at around 1590 cm\textsuperscript{-1} (Bandow et al., 1998). In this work, a quality parameter \( \frac{G}{D+G} \times 100 \) has been defined and used as an indicator for the quality of carbon products, where

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![Figure 2. Raman spectra of the carbon deposits by CO disproportionation at 850 °C over the CoRe(1:4)/SiO\textsubscript{2} catalysts after pre-reduction at different temperatures](image1)

![Figure 3. Temperature-programmed reduction (TPR) of the mono- and bimetallic cobalt/rhenium catalyst](image2)
D and G are integrated areas of the D and G bands, respectively. A quality parameter approaching 100 represents a high-quality product. Figure 2 shows the Raman spectra of the carbon deposited on the spent CoRe(1:4)/SiO$_2$ catalysts under different reduction temperatures. In combination with TPO results, the optimum reduction temperature seems to be 800 °C where the quality parameter is 85. As the reduction temperature was preceded to 900 °C, the quality parameter drastically dropped to 53. However, the TPR results of both mono- and bimetallic catalysts (Figure 3) demonstrated that complete reduction of all bimetallic CoRe catalysts occurred before 600 °C. As a result, the optimum prereduction at 800 °C may lead to the conversion of Co-Re-oxide into Co-Re alloy with an appropriate interaction that is necessary for the growth of nanotubes. From this observation, the stabilization of Co species is occurred in the Co-Re alloy phase, which is different from what was observed on the CoMo/SiO$_2$ catalyst as previously described.

![Figure 4. Temperature-programmed oxidation (TPO) of the carbon deposits by CO disproportionation at different reaction temperatures over the CoRe(1:4)/SiO$_2$ catalyst](image4)

![Figure 5. Temperature-programmed oxidation (TPO) of the carbon deposits by CO disproportionation at 850 °C over several bimetallic CoRe/SiO$_2$ catalysts](image5)

![Figure 6. TEM image showing SWNT produced by CO disproportionation at 850 °C over CoRe(1:4)/SiO$_2$ catalyst](image6)
Effect of reaction temperature

The CoRe(1:4)/SiO₂ catalyst was selected to study the effect of reaction temperature on the carbon yield. In this study, the catalysts were pretreatment in H₂ at 800 °C before the reaction at three different reaction temperatures: 750, 850, and 950 °C. The normalized TPO profiles obtained from these samples are illustrated in Figure 4. As the reaction temperature varied from 750 °C to 950 °C, the maximum carbon yield (5.6 wt %) was observed at reaction temperature of 850 °C. At the higher or lower reaction temperature, the larger amount of either disordered carbon (oxidation peak < 400 °C) or graphitic carbon such as multi-walled carbon nanotubes (oxidation peak > 600 °C) were formed. However, in case of 950 °C reaction temperature, MWNT were increased due to the rapid agglomeration of Co metallic particles to larger clusters.

Effect of Co:Re ratio

It is interesting to compare the amount of carbon deposited on the CoRe catalysts operated under the best observed conditions: prereduction at 800 °C and reaction at 850 °C. These values for CoRe(2:1), CoRe(1:1), and CoRe(1:4) obtained from the TPO profiles (Figure 5) are 2.6, 3.5, and 5.8 wt %, respectively. At this condition, a small amount of disordered carbon generated during the reaction period was observed on each catalyst. Furthermore, it is obvious that the ratio of Co to Re exhibits the less effect on the amount of disorder carbon, while both carbon yield and selectivity toward SWNT are improved when using a low ratio of Co-to-Re catalyst.

The high-magnification TEM image of a fraction of deposited carbon obtained on a CoRe(1:4)/SiO₂ sample after prereduction at 800 °C and reaction at 850 °C is shown in Figure 6. From several observations around the sample, the forms of deposited carbon are mainly presented as small bundles of SWNT, while undesired forms of carbon such as disordered carbon, MWNT, and graphitic carbon appeared in small quantities. It is interesting to note that most of the SWNT produced at 850 °C with Co-Re catalyst are 0.7-nm tubes. The average bundle diameter is about 6 nm which is closed to the pore size of silica support.

CONCLUSIONS

Silica-supported Co-Re catalysts have been studied for SWNT synthesis by CO disproportionation. The yield and selectivity toward SWNT of Co-Re catalysts are strongly depended on the reduction temperature. The highest yield and selectivity were achieved with the CoRe(1:4)/SiO₂ when the catalyst is pretreated in H₂ at 800 °C then follows by reaction at 850 °C. The SWNT obtained are mostly 0.7-nm tubes which is the smallest diameter expected for capped SWNT. At the optimum reduction temperature, all Co and Re oxides are completely reduced to metallic state at which the nanotubes are formed. However, the stabilization of Co species is occurred in the Co-Re alloy phase, which is different from what was observed in the CoMo/SiO₂ catalyst. To predict the mechanism on the CoRe/SiO₂ catalyst, more investigations will be proceeded to follow the interaction of Co and Re that are responsible for the nanotubes growth.

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