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## **X-ray Absorption Study of the Effect of CO<sub>2</sub> on the Activity of a CoMo Catalyst Used for SWNT Production**

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Beamline(s): X18B

**Introduction:** Single-wall carbon nanotubes (SWNT) can be considered as one of the building blocks for nanoscale science and nanotechnology. The procedures used thus far for SWNT production include arc discharge, laser ablation and catalytic decomposition of a carbon-containing molecule (sometimes referred to as chemical vapor deposition) over a metal catalyst. The catalytic decomposition of carbon-containing molecules appears as a promising technique for scaling-up the production process at a relatively low cost. Yet, obtaining high quality SWNT has not been always possible with this method. We have developed a method based on the CO disproportionation over a CoMo catalyst (Boudouard reaction) at relative low temperatures. Based on a detailed characterization study we found that at the beginning of the reaction both Co and Mo are interacting intimately with each other forming a surface Co molybdate. This structure is the precursor of the active species that catalyze SWNT growth. The effect of the CO<sub>2</sub> formed during the reaction on the activity of the CoMo catalyst has been studied using X-ray absorption spectroscopy.

**Methods and Materials:** The ability of different catalysts to produce SWNT by CO disproportionation were tested by passing pure CO over the catalyst at 700°C. The characterization of the carbon deposits was done by Raman spectroscopy, TEM and TPO. The X-ray absorption data were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory, using beam line X-18B. The spent samples, were not exposed to air, but directly transferred from the reaction chamber to a He glove bag, where they were wrapped in Kapton tape and stored in He-purged sealed veils until analysis. The EXAFS experiments were conducted in a stainless steel sample cell at liquid nitrogen temperature. Six scans were recorded for each sample. To obtain structural parameters, theoretical references for Co-Co, Co-O, Mo-O, Mo-C, Mo-Mo and Co-Mo bonds were obtained by using the FEFF and FEFFIT fitting programs from the University of Washington. The spectra of Mo<sub>2</sub>C, and Co foils were also obtained at liquid nitrogen temperature and used as references.

**Results:** It was found that the inhibiting effect of the CO<sub>2</sub> is present even when there are no thermodynamic limitations to the overall Boudouard reaction, this effect was then related to the mechanism of the carbon formation over the Co:Mo/SiO<sub>2</sub> catalyst. In a previous work we have proposed that there are several steps involved in the SWNT production. Before the reaction begins, most of the Co present in the catalyst is stabilized by the Mo in a Co-Molybdate-like structure. When the reaction starts, Mo oxide is converted into Mo carbide and the Co-Molybdate-like structure is broken releasing the Co. Under these circumstances, the Co can be reduced by CO and form very small metal clusters that lead to the formation of SWNT. Under this scheme, the presence of CO<sub>2</sub> in the reaction system may affect in different ways, its effect was investigated analyzing the MoC<sub>2</sub> formation by EXAFS. Figure 1 shows the Fourier transforms for the K edge of Mo ( $E_0 = 20,000$  eV) for a selective catalyst after 10 min of reaction using 100% CO, 5% CO<sub>2</sub> in CO and 10% CO<sub>2</sub> in CO. The EXAFS data of MoC<sub>2</sub> is presented as a reference. Although there is not a clear change in the amount of Mo Carbide (peak at 2.8 Å) when the reaction is carried out using 5% CO<sub>2</sub> compared with that one carried using 100% CO, it can be observed that the presence of MoO<sub>3</sub> is higher in the first case (peak at 1.4 Å). When the presence of CO<sub>2</sub> is increased to 10% of the feed, not only an increase in the presence of MoO<sub>3</sub> is observed but also the peak that corresponds to MoC<sub>2</sub> decreases almost in half. This inhibiting effect on the reduction of Mo is extremely important since it prevents the release of the stabilized Co clusters that are necessary to produce SWNT. In the same way, the Co reduction can also be restricted by the thermodynamics. In order to follow the oxidic state of cobalt, XANES analyses were performed at the Co edge. Figure 2 compares the XANES spectra for the K-edge of Co ( $E_0 = 7709$ ) in the Co:Mo (1:3)/SiO<sub>2</sub> – 60 catalyst for different reaction times with 100% CO as the feed stream (A) and 5% CO<sub>2</sub> in CO as the feed stream (B). It can be clearly seen that the reduction of Co from Co<sup>+2</sup> to Co<sup>0</sup> as the reaction advances is remarkably lowered in the second case. Almost 100% of the cobalt becomes metallic after 10 hours of reaction with pure CO. By contrast, the amount of metallic Co after the same period of time when 5% CO<sub>2</sub> is used is comparable to that one present in the first case after only 3 minutes of reaction.

**Conclusions:** It was found that the carbon deposition reaction is limited by the presence of CO<sub>2</sub> even in small concentrations. The relationship of this phenomenon with the reaction mechanism and the deactivation was investigated. Using high space velocities in order to avoid CO<sub>2</sub> build up resulted in significant increased of the SWNT yield.

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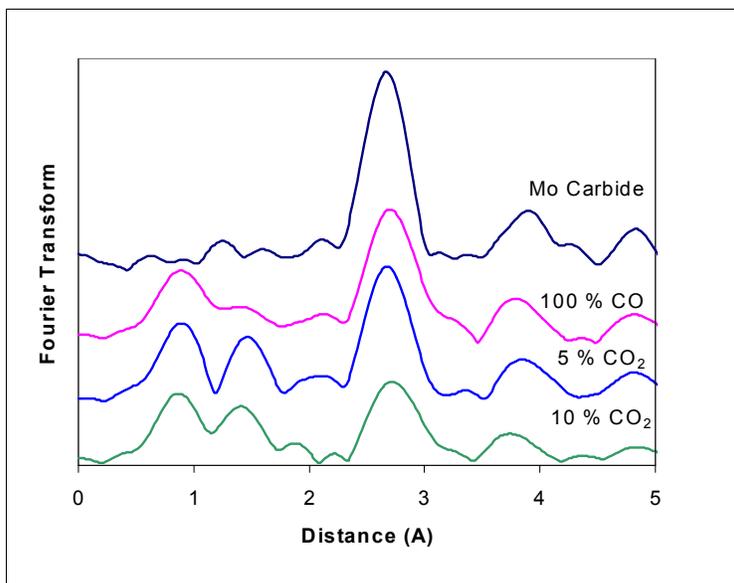


Figure 1 – Fourier Transforms of the k3 EXAFS data obtained for the K-edge of Mo for a Co:Mo catalyst after reaction during 10 min at 750°C for different feed compositions (100 % CO, 10 % CO<sub>2</sub> in CO and 5 % CO<sub>2</sub> in CO). The data of MoC<sub>2</sub> are included for comparison.

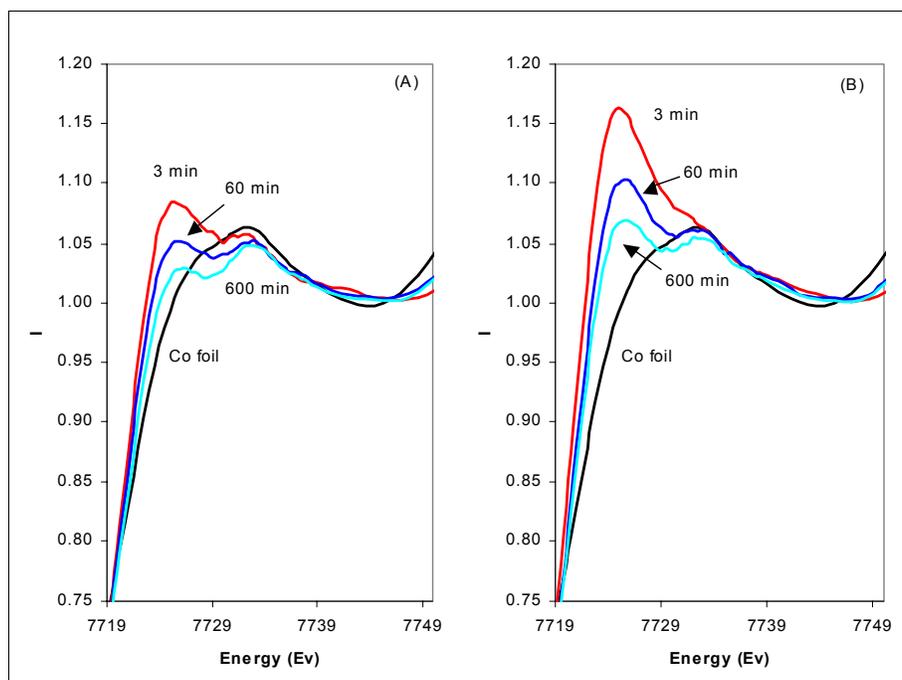


Figure 2 – Co K edge XANES of a Co:Mo(1:3)/SiO<sub>2</sub> – 60 catalyst after reaction at 750 °C for 3 min, 60 min and 600 min and 2 different feed compositions: A) 100 % CO B) 5 % CO<sub>2</sub> in CO. The data of Co foil are included for comparison.