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Relationship Between the Structure/Composition of Co-Mo Catalysts and their Ability to Produce Single-Walled Carbon Nanotubes by CO Disproportionation

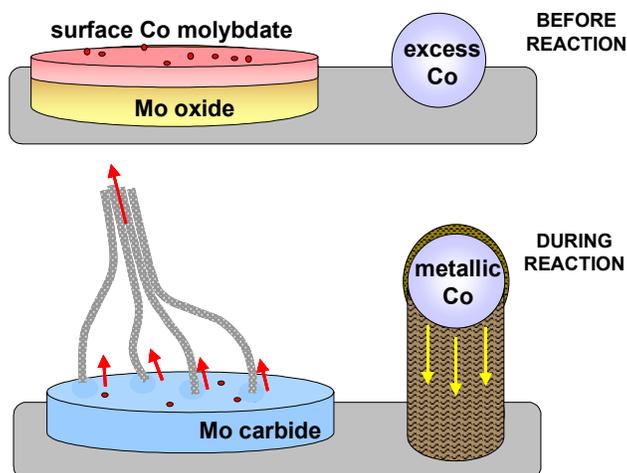
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Introduction: Existing SWNT synthesis methods are not easily scalable, operate under severe conditions, and involve high capital and operating costs. The current cost of SWNT is exceedingly high. A catalytic method of synthesis has been developed that has shown potential advantages over the existing methods. This method is based on a catalyst formulation that inhibits the formation of undesired forms of carbon; it can be scaled-up and may result in lower production costs. The single-wall carbon nanotubes (SWNT) exhibit exceptional chemical and physical properties that have opened a vast number of potential applications (). Among the various alternatives investigated in the last few years for production of SWNT, the catalytic decomposition of carbon-containing molecules appears as a promising technique since it has the potential to be scaled-up at a relatively low cost. A number of researchers have investigated different catalyst formulations and operating conditions for this process. Our group has focused on the disproportionation of CO on several bimetallic catalysts, which exhibited a high selectivity towards the production of SWNT at relatively low temperatures. Among the various formulations investigated, Co-Mo catalysts supported on silica gel and having low Co:Mo ratios exhibited the best performance.

Methods and Materials: X-ray absorption (XANES/EXAFS) has been used to fully characterize the structure and chemical state of Co-Mo/silica catalysts used for the production of single-walled carbon nanotubes (SWNT) by CO disproportionation at 700-850°C.

Results: The state of Co and Mo on a series of silica-supported catalysts was investigated after two sequential pre-treatments and after the production of SWNT under pure CO. It was found that the selectivity of the Co-Mo catalysts towards SWNT strongly depends on the stabilization of Co species in a non-metallic state before exposure to CO, which result from an interaction with Mo. The extent of this interaction is a function of the Co:Mo ratio and has different forms during the different stages of the catalyst life. From the detailed characterization conducted over the catalyst series it is concluded that after calcination, Mo is in the form of well dispersed Mo(6+) oxide while Co is either interacting with Mo in a superficial Co molybdate-like structure (at low Co:Mo ratios) or as a non-interacting Co_3O_4 phase (at high Co:Mo ratios). After a subsequent treatment in hydrogen, the non-interacting phase is reduced to metallic Co, while the Co molybdate-like species remain as well-dispersed Co(2+) ions. During the production of SWNT under pure CO, the Mo oxide species are converted into Mo carbide. This conversion disrupts the interaction between Co and Mo and results in the release of metallic Co in the form of extremely small clusters, which are responsible for the production of SWNT. By contrast, large Co clusters that are formed from the non-interacting Co phase, produce the non-selective forms of carbon (MWNT, filaments, graphite, etc.)



State of the catalyst components before and during the production of SWNT. The Co species stabilized by Mo resist reduction and sintering before the reaction. Under CO, Mo becomes carbide while Co becomes metallic and generates the SWNT. The excess Co, not-stabilized by Mo, produces MWNT and fibers.