

# Role of the Mo local structure in the CoMoCAT® SWNT catalyst

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## Abstract

CoMo bimetallic catalysts have demonstrated excellent performance in large-scale synthesis of single-walled carbon nanotube (SWNT). This performance is attributed to the reciprocal stabilization of both metals. Tuning this interaction by changing the surface chemistry of the system, can help understanding the complex role of the two metals involved. This knowledge could ultimately lead to the development of a new family of catalysts specifically designed for the selective production of SWNT with a specific (n,m) distribution of nanotubes. In this work, catalysts over different supports (SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, doped and undoped with La) have been systematically studied by TPR (temperature-programmed reduction), Raman scattering, UV diffusive reflectance, XPS, TEM/SEM imaging and EXAFS/XANES (x-ray absorption techniques).

It was found that due to the strong CoMo-Al<sub>2</sub>O<sub>3</sub> interaction, the evolution of the surface species on alumina is much more complex than that on silica.

Although the small metallic Co clusters are the catalytic active species for the carbon nanotube growth, the structure of Mo is essential for the performance of the catalyst. It stabilizes the Co in an oxidized form during the pretreatment and, under reaction conditions, it allows for the slow release of the small Co clusters. This process is controlled by the carburization of MoO<sub>3</sub> to form Mo<sub>2</sub>C. The ability of Molybdenum to become a carbide is essential for releasing the Co ions that otherwise will be trapped inside the CoMo structure. MoO<sub>3</sub> clusters that are too small or too stable resulted in inactive or unselective catalysts for SWNT synthesis. For this reason, it is important not to consider Molybdenum just a promoter of the Co catalyst, but a species that participates actively and dynamically in the SWNT production process.

A strong interacting support can lead to a different surface structure (highly disordered monolayer or distorted octahedral cluster) that can react differently with the carbonaceous gas. However, when a new catalyst based on a different support is developed, it is important to keep and preserve the ability of Mo to transform from its oxide form to its carbide form. If a support interacts strongly with MoO<sub>3</sub>, Co ions will be released at a lower rate, which may result in the formation of different Co clusters on the surface. Thus, changing the catalyst support can be an effective way to change the catalyst selectivity towards a specific (n,m) distribution of tubes.

## Acknowledgements

This research was conducted with financial support from the Department of Energy, Office of Basic Energy Sciences (grant No. DE-FG03-02ER15345). We also thank the technical support of the personnel at NSLS, Brookhaven National Laboratory, for the X-ray absorption experiments.