Tailoring (n,m) SWNT distribution on CoMoCAT® catalysts

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Abstract
CoMo bimetallic catalysts have demonstrated excellent selectivity towards very narrow (n,m) distributions of SWNT. Different distributions can be obtained by changing the reaction temperature and/or changing the support used for the bimetallic catalyst.
An increase in synthesis temperature produce an increase in the mean diameter of the tubes shifting the (n,m) distribution towards higher indexes. This phenomenon can be explained by an increase in particle size of the Co clusters that are generated in situ during the reaction. Surprisingly, although the nanotubes produced at different temperatures show a big difference in diameter they show almost no difference in chiral angle. In three SWNT samples produced on a $CoMo/SiO_2$ catalyst at 750 °C, 850 °C and 950 °C the most abundant nanotubes were found to be (6,5), (7,6) and (8,7) respectively
The change of the catalyst support has more dramatic effects on the type of carbon species produced due to the complexity of the surface chemistry involved in the reaction. In a Co-Mo bimetallic system the interaction between the two metals is essential for the selective production of SWNT. Altering the surface chemistry can weaken or strengthen this interaction, changing the internal equilibrium of the catalyst. According to our model for the CoMo catalyst, the metal oxides are in a wafer-like microstructure. Molybdenum is highly dispersed on the surface and Co ions are stabilized in the Mo oxide structure in a form similar to $CoMoO_x$. Under reaction conditions, MoOx is reduced by CO and forms Mo_2C, while the Co ions migrate to the surface and get reduced forming small Co clusters that generate SWNT. Increasing the interaction between the support and the MoO_x (or the $CoMoO_x$) can change the subsequent carburization of the substrate and the release of Co. Moreover it can change the surface arrangement of the oxide or the released Co, which can lead to the production of nanotubes with different structure. Under similar reaction condition (e.g. same reaction temperature) using CoMo supported on SiO_2 or on MgO the mean diameter of the produced nanotubes is the same, but their chirality distribution is different. When SWNT are synthesized at 750 °C with a CoMo/ SiO_2 catalyst the chiral angle of the resulting nanotubes is high and the most abundant species is the (6,5). When a CoMo/MgO catalyst is used, the chiral angle of the produced nanotubes is lower and the most abundant nanotubes in this sample are the (7,5) and the (8,3)
Based on these results, it is clear that adjusting both the synthesis temperature and the support of the CoMoCAT catalyst can be used as a powerful tool to produce high quality SWNT with controlled (n,m) distribution.

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