Phase evolution and characterization of supported CoMo / SiO$_2$ catalyst used in single-walled nanotube production

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Introduction

Single-walled carbon nanotubes (SWNT) are one of the building blocks of the emerging nanotechnology. They have many applications that span from the micro-electronic industry, due to their unique electronic structure, to material technology, due to their unique strength, stiffness, Young's modulus and light weight that makes them suitable for composite materials [1]. One of the reasons for the delay in bringing these qualities to market is the limited availability of high-quality SWNTs. The material purchased from different suppliers many times behaves differently due to the different production methods and a definition of standard material is not yet available. Among the several production techniques, catalytic CVD appears as the most amenable to scale-up. Understanding the growth mechanisms and chemical modifications of the catalysts under reaction conditions is essential to improve the reproducibility and to control the type and quality of the material produced [2]. In this contribution we will study Co-Mo/SiO$_2$, a catalyst that is widely used for the production of SWNTs. We will explore the structural evolution during the several steps of the catalyst life and we will try to correlate these with the final product.

Materials and Methods

The catalyst life encompasses several stages: calcination, pre-reduction, re-heating and finally SWNT growth [3]. During these steps, the species present on the surface of the catalyst undergo several chemical and/or physical reactions, which alter their crystalline or even chemical structure. We employ surface and bulk spectroscopy methods like XPS, XRD, EXAFS, UV/VIS Diffusive Reflectance and Raman directly in situ (Raman and XRD) or ex situ, using glovebags, to study the evolution of the catalyst. Also temperature programmed techniques like TPD and TPR and imaging techniques like SEM and TEM are used. The final product of the reaction (SWNT) is also characterized to correlate the differences between the structure of the catalyst and the type of material produced. The main characterization techniques used to study the SWNT are Raman, TPO and optical absorption [2].

Results and Discussion

The initial structure of the supported CoMo/SiO$_2$ catalyst, which was prepared as described elsewhere [2], is expected and confirmed by XRD, to be CoMoO$_4$. This oxide, that is chemically stable, needs to be partially pre-reduced to generate some vacancies in the lattice and increase its reactivity. During this step the crystallinity is lost as shown by the disappearance of the XRD (figure 1) and the Raman bands characteristic of the latter specie. This reduction step of the catalyst is critical. While the lack of reduction results in inactivity; over-reduction segregates metallic Co, which sinter under reaction conditions and produce MWNT and fibers [2]. During the following re-heating step, an annealing of the crystalline structure is possible. This results in segregation of a Mo-rich phase that reduces at higher
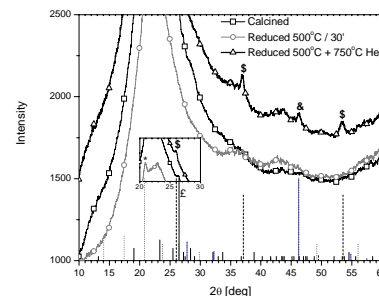
Figure 1. XRD spectra of the catalyst. The strong lines are corresponding to: * SiO$_2$; £ CoMoO$_4$; $ MoO$_2$; & Mo$_3$O
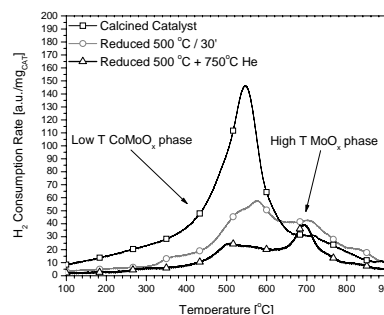
temperature (Figure 2). The XRD profile shows that these species are mainly composed of MoO$_2$. We observed that this annealing is directly related to the selectivity of the catalyst towards SWNT. When the initial particle size is large, for example when the catalyst metal loading is higher, the interaction of the Mo species with the support [4] is weakened and this rearrangement inside the particles is favored. This results in an unselective catalyst. The presence of segregated Mo sub-oxidic phases will increase the amount of available free Co (corresponding to an effective increase of the Co/Mo ratio) resulting in sintering and growth of the Co

particles. In the optimal case, the annealing does not produce the segregation of a MoO$_2$ phase that cannot stabilize the Co. The Co is kept inside the MoO$_x$ lattice and is released only in the final step, where the MoO$_x$ is converted to Mo$_2$C and metallic Co can nucleate on its surface starting the SWNT growth. Only the catalyst with the right Mo-support interaction will result in high quality SWNT.

Significance

The catalyst studied in this contribution is used for the production of SWNT by CO disproportionation. The scale-up of the process will ultimately bring forward a continuous fluidized bed reactor, so furthering the knowledge of the catalyst transformation under pretreatment and reaction is necessary to produce high quality SWNT. Moreover, as we shown in a previous contribution [2], it will help in the control of the (n,m) distribution, necessary for the use of SWNT in the electronic industry.

Figure 2. TPR profile of the catalyst

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