Activity and Selectivity of Co-Mo Catalysts Supported on Different Silicas for the Synthesis of Single-Walled Carbon Nanotubes

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Introduction

Previous studies by our group [1-3] have demonstrated that Co-Mo/silica catalysts exhibit high selectivity to the growth of single-walled carbon nanotubes (SWNT) by CO disproportionation. The effect of parameters such as the extent of interaction of different Co-Mo species with the support, metal loading, Co:Mo molar ratio, and reaction conditions on the yield and structural properties of SWNT were analyzed. In this context, the present study focuses on the potential effects that using silica supports of varying surface properties (surface area, point of zero charge, residual impurities, particle size, crystallinity, etc.) may have on the yield and quality of the nanotube product. A number of silica supports synthesized by different methods (precipitation, flame hydrolysis, etc.) with varying surface properties have been compared. The carbon yield and structural characteristics of the resulting nanotubes from using the various silica supports have been compared with the aim of obtaining structure/properties relationships for this interesting application of heterogeneous catalysts.

Materials and Methods

Bimetallic Co-Mo catalysts supported on different silicas were prepared by incipient wetness co-impregnation of aqueous $(NH_4)_6Mo_7O_{24}.4H_2O$ and $Co(NO_3)_2.6H_2O$ solutions, keeping a Co:Mo molar ratio of 1:3. Before the SWNT synthesis, the catalysts were calcined in air and pre-reduced in H_2. When the reaction temperature (750 ºC) was reached under He flow, the CO feed (250 sccm) was started. After a growth period of 30 min, the system was cooled down in He. The catalysts and products were analyzed by Raman spectroscopy, optical absorption, TEM, TGA, TPO and X-Ray diffraction.

Results and Discussion

As illustrated in Table 1, significant variations in carbon yield and SWNT selectivity are observed on the products obtained over the different silicas. The carbon yield is measured by TPO. The SWNT selectivity is assessed from Raman and TGA analysis. Among the four silicas included in Table 1, the precipitated HiSil 210 results in the highest yield and highest selectivity in the product (i.e. lowest D/G Raman ratio, whereas the D band corresponds to disordered carbon (sp3) and the G band to ordered graphene (sp2)). It is apparent that the nature of the silica support has an effect on the type and domain size of the Co-Mo species stabilized during the calcination step. Depending on the nature and state of dispersion of these species, the carbon yield and SWNT selectivity vary widely.

Interestingly, while UV-Vis spectroscopy (see Fig.1, right) of the calcined catalysts indicate that all samples have at least a fraction of Co in the octahedral configuration, which is typical of Co molybdate, almost equally good samples (e.g. HS210 and HS915) exhibit very different fractions of Co in octahedral and tetrahedral configurations. On the other hand, Raman analyses (see Fig. 1, left) of the calcined samples suggest that the domain size of the molybdate is the parameter that determines the performance of the catalyst. For example, absence of bands in the 930-970 cm^{-1} region (e.g. HS190), indicative of a very high dispersion results in low SWNT yield. At the other extreme, large molybdate crystallites are not desirable either. Samples such as that supported on silica gel displayed high intensities in this range and high intensity ratio between the 948 cm^{-1} and 958 cm^{-1} bands ($CoMoO_4$ to Mo oxides) [4], indicating the presence of large $CoMoO_4$ crystallites. Such samples have low activity and low selectivity, consistent with the poor performance of unsupported $CoMoO_4$.

Table 1. Carbon yield and SWNT selectivity of the nanotube product

Catalyst	Silica gel	Hisil 190	Hisil 210	Hisil 915
Carbon yield (%)	1.21	0.78	3.33	1.17
D/G Raman ratio	0.225	0.100	0.040	0.100

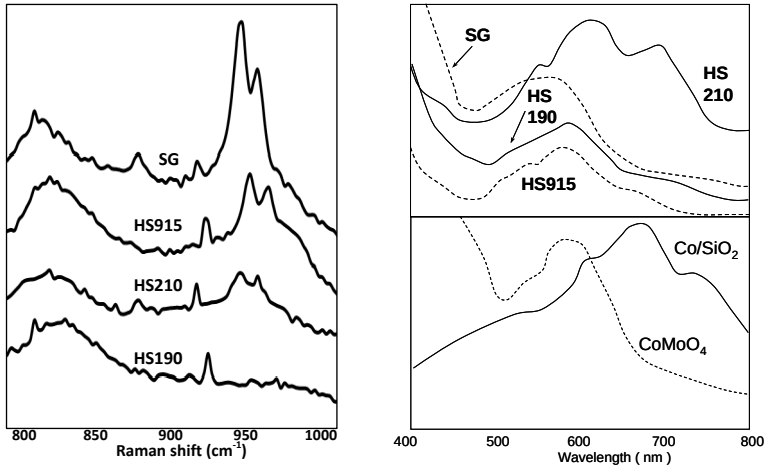

Figure 1. Raman (left) and UV-VIS (right) spectra of calcined Co-Mo catalysts supported on different silicas, as well as two reference compounds, monometallic Co/SiO_2 and $CoMoO_4$.

References

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