

Synthesis of Single-Walled Carbon Nanotubes Over Co-Mo Catalysts Prepared by the Sol-Gel Method

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Introduction

The sol-gel method has been extensively used in the preparation of supported metal catalysts because it typically results in homogeneous materials with a high metal dispersion [1,2]. In particular, this method has been used to obtain active phases of Ni-Mo and Co-Mo [3] bimetallic catalysts supported on silica for the oxidative dehydrogenation of alkanes. It has been observed that catalysts prepared by the sol-gel method can stabilize the bimetallic active phases much more efficiently than those prepared by other methods. Therefore, sol-gel appears as a suitable method to produce Co-Mo/SiO₂ catalysts, which are highly selective towards for single-walled nanotubes (SWNT) when the gaseous feed is CO [4]. In this study, a series of silica-supported Co-Mo catalysts prepared by the sol-gel method has been prepared, varying the ratio of the added ammonium hydroxide to silica precursor (NH₄/TEOS). The concentration of ammonium hydroxide has an important effect on the rate of silica polymerization [5] and consequently, it is expected that changes in the NH₄/TEOS ratio will affect the resulting morphology and, consequently, the yield and structure of the SWNT that each catalyst produces. The carbon yield and structural characteristics of the nanotubes that result by varying the NH₄/TEOS ratio in the sol-gel process have been compared with the intention of drawing relationships between the catalyst structure and the catalytic performance.

Materials and Methods

In all the Co-Mo/SiO₂ catalysts prepared, the metal loading and Co/Mo molar ratio were kept constant at 9 wt% and 1:3, respectively. An aqueous solution of Co(NO₃)₂·6H₂O was combined with an isopropanol solution of MoCl₅; to this mixture, tetraethyl orthosilicate (TEOS) and ammonium hydroxide (28 %) solutions were added in different ratios. After aging for 20 hr, the gels were filtered and dried in air at 200 °C for 30 min, and further calcined at 650 °C for 150 min. Before the nanotube synthesis, the catalysts were pre-reduced at 500 °C for 30 min under H₂ (125 sccm) in a ½ inch vertical quartz reactor. When the reaction temperature (750 °C) was reached under He flow, the CO feed (250 sccm) started. After a growth period of 30 min, the system was cooled down in He flow. The catalysts and products were analyzed by Raman scattering, optical absorption, X-ray diffraction, temperature programmed oxidation and reduction, thermo gravimetric analysis, and transmission electron microscopy.

Results and Discussion

Table 1 summarizes the yield and SWNT selectivity data obtained over the different Co-Mo catalysts synthesized by varying the NH₄/TEOS ratio. As previously demonstrated the selectivity towards SWNT can be semiquantitatively estimated by the intensity ratio of the D and G bands in the Raman spectrum, the former due to disordered (sp³) carbon and the latter due to ordered graphene (sp²) in the SWNT structure. It is clear that the NH₄/TEOS ratio used

in the preparation has an optimum at intermediate values. Two factors seem to affect the quality and yield of SWNT, Co-Mo particle size and fraction of metal exposed (Figure 1). At high NH₄/TEOS ratios, the metal particle size is large and the fraction of metal exposed is low. On the other hand, at low NH₄/TEOS ratios, the metal particle size is large but the fraction of metal exposed is high.

Table 1. Carbon yield (%) and quality (D/G)

NH ₄ /TEOS ratio	1/6	2/6	4/6	6/6
Carbon yield (%)	4.2	13.5	9.6	3.4
D/G	0.081	0.046	0.049	0.068

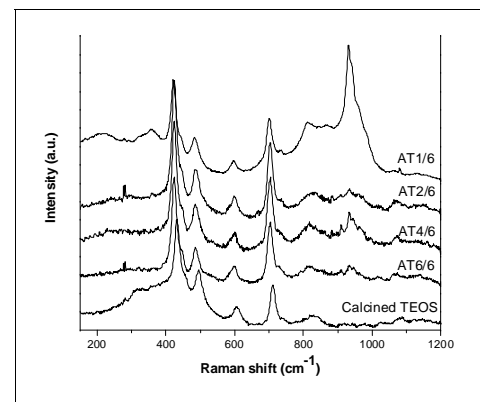


Figure 1. Raman scattering of the Co-Mo calcined catalysts with different NH₄/TEOS ratios (AT). The spectrum of the calcined support is also included (TEOS).

In addition to Raman, the four samples have been investigated with XPS, UV-Vis, TEM, and XRD to identify the types of CoMoO_x species stabilized in each case, and find a relationship between the different species that are present after the calcination step and the resulting SWNT product that is obtained (i.e. D/G ratio, and (n,m) nanotube type – chirality distribution).

References

1. Meille, V., *Appl Catal A*, 315, 1 (2006).
2. Samanta, S., Laha, S.C., Mal, N.K., and Bhaumik, K. *J. Mol. Catal. A*, 222, 235 (2004).
3. Maione, A., and Devillers, M., *J. Sol. State Chem.* 177, 2339 (2004).
4. Herrera, J.E., and Resasco, D.E., *J. Catal.* 221, 354 (2004).
5. Brinker, C.J., and Sherer, G.W. in "Sol-Gel science: The physics and chemistry of sol-gel processing" (Academic press Ed.), 1989.