

Synthesis, Characterization and Stability of Fe-MCM-41 for Production of Carbon Nanotubes by Acetylene Pyrolysis

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Introduction

The use of mesoporous silica as a catalytic template for production of carbon nanotubes (CNTs) is gaining prominence because of the possibility of properly controlling the size of the metal nanoparticles [1]. The metal catalyst plays a key role during CNT growth. Several studies have revealed a direct relationship between the size of the metal particle and the eventual diameter of CNT [2]. To be able to control the physical properties (diameter and helicity) of CNTs, a thorough understanding of the microstructure, stability and chemical properties of the catalytic sites would be necessary.

In this study, different loadings of Fe-incorporated MCM-41 (ca. 1, 2 and 3 wt% Fe) were hydrothermally synthesized using different colloidal silica (HiSil-915 and Cab-O-Sil) and C16 surfactant. The synthesis procedure was adapted from a recipe previously reported for V-MCM-41 [2]. The catalysts were characterized using different techniques to determine their mesoporous structural integrity and the local environment of Fe in the silica framework. These materials were then used as catalytic templates for the production of CNTs by acetylene pyrolysis at atmospheric pressure. The results presented here reveals a strong correlation between Fe loading in MCM-41 and the type of carbon specie produced.

Experiments and Results

Fe loading in the catalytic templates (containing ca. 1, 2 and 3 wt% Fe) was verified by ICP. The following results were obtained: 0.99, 1.59 and 2.25 wt% Fe for samples synthesized from HiSil-915 while those synthesized from Cab-O-Sil were 0.99, 1.78 and 2.37 wt% Fe. N₂ physisorption and XRD studies carried out using calcined Fe-MCM-41 revealed a significant improvement in the mesoporous structural quality upon incorporation of ca. 1 wt% Fe, but a decrease is observed as Fe loading increases. Catalysts synthesized from Cab-O-Sil showed higher structural order in comparison to those synthesized from HiSil-915.

The local environment of Fe was characterized by UV-Vis, EPR and X-ray absorption spectroscopy. Fe³⁺ species in all the "as-synthesized" samples regardless of its loading were found in predominantly tetrahedral environment (framework). Upon calcination, dislodgement of some Fe³⁺ species to non-framework environment occurs and this phenomenon was more severe for catalysts containing ca. 2 and 3 wt% Fe. Generally, Fe³⁺ species occupying tetrahedral environment decreases with increasing Fe loading.

The pyrolytic decomposition of acetylene to produce CNTs was performed at 800 °C using a C₂H₂/N₂ (99% N₂ and 1% C₂H₂) flow rate of 200 sccm for 1 h over Fe-MCM-41. The above conditions were found to be optimal at atmospheric pressure. In a typical run, 0.5 g of the calcined catalyst was put into the cylindrical quartz reactor and heated to the reaction temperature in flowing He at 10 °C/min. At the reaction temperature, the gas flow was switched

to the reactant mixture and maintained under this condition for 1 h. It was then cooled to room temperature in flowing He at the end of each reaction.

Carbon deposited on the catalysts was characterized using a variety of techniques including thermogravimetry, Raman and HR-TEM. High carbon yields were observed for catalysts containing ca. 1 and 2 wt% Fe while catalysts with ca. 3 wt% Fe showed relatively lower activity for carbon formation. TEM images and Raman spectra indicate the presence of graphitic carbon and the absence of CNTs for reactions carried out over Fe-MCM-41 (ca. 1 wt%) while MWNT and graphitic carbon were mainly formed for Fe-MCM-41 (ca. 3 wt%), Fig. 1b. On the other hand, Fe-MCM-41 (ca. 2 wt%) showed high selectivity for CNTs production, especially SWNT, which were mostly in bundles as shown in Fig. 1a and Fig. 2. On the basis of TEM studies and Raman spectroscopy (low D/G band ratio), the CNTs synthesized in this study are of relatively high quality, with low amount of amorphous carbon. This work also reveals a relationship between the amount of Fe incorporated in MCM-41 and the carbon specie formed during acetylene pyrolysis.

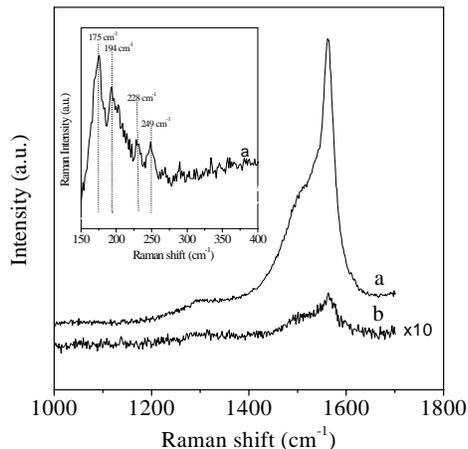


Fig. 1 Raman spectra of CNTs synthesized over catalysts containing ca. 2 wt% Fe (a) and ca. 3 wt% Fe (b)

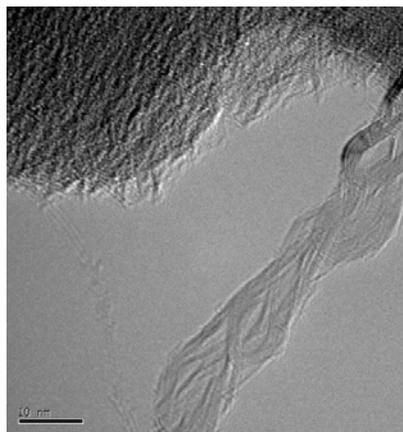


Fig. 2 Bundles of SWNTs synthesized over catalysts containing ca. 2 wt% Fe.

For Fe-MCM-41 to be used as a catalytic template to synthesize CNT, it is necessary that it shows high structural stability under harsh reaction conditions which include carbon deposition at high temperature and oxidation. The structural stability of Fe-MCM-41 after reaction and temperature-programmed oxidation was evaluated by N₂ physisorption. Catalysts synthesized from Cab-O-Sil were found to be more stable and maintained their high mesoporous structural quality better than those synthesized from HiSil-915, which is of lower purity than Cab-O-Sil.

To rationalize the differences observed in the selectivity of the catalysts for CNT production, the microstructure of the catalytic template after reaction was studied by X-band EPR spectroscopy. EPR results reveal that for catalysts containing ca. 1 wt% Fe, Fe³⁺ species remained mainly in the framework while for catalysts containing ca. 2 wt% Fe, Fe³⁺ species were well distributed in both framework and non-framework environment. Catalysts containing ca. 3 wt% Fe had Fe³⁺ species that were well reduced and were found in mainly non

framework location. The differences observed in the local environment of Fe have been hypothesized to be playing a key role in the selectivity for CNT production.

References

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