Fe/Co SBA-15 materials for the dimensional control of carbon nanotubes

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Carbon nanotubes (CNTs), as a new form of carbon, are of great interest for many applications due to their nanometer size and interesting properties, such as high mechanical resistance and stability, good conductivity, gas adsorption capacities and capillarity.

Chemical Vapour Deposition (CVD) is the most common and cheapest method for the synthesis of large amounts of multi-walled carbon nanotubes, but normally the tube diameters obtained are bigger than those produced by arc-discharge or laser ablation methods. CNTs obtained by CVD over conventional Fe/Co supported catalysts are in the range of 50 nm, whereas for most of applications in catalysis and hydrogen storage, it could be useful to control the nanotubes diameter, decreasing in particular the diameter to values around 5 nm. A second problem connected with the CVD technique on conventional supported catalysts is the lack of control of growth defects. Although this aspect is often scarcely considered, it is of critical importance for the quality of the results.

The objective of this paper is to analyze how it is possible to control the characteristics of carbon nanotubes (diameter, defects) produced by CVD synthesis of propane or ethanol, by inclusion of Fe and Co metal particles in a mesoporous silica (SBA-15) matrix.

The SBA-15 support was synthesized by self-assembly using Pluronic P123 triblock polymer (EO_{20}-PO_{70}-EO_{20}, average molecular weight M_{av} = 1.100) as surfactant template and tetraethyl ortosilicate (TEOS) as silica source, according to the procedure reported by Zhao et al. [1]. In a typical run the copolymer was dissolved in a mixture of distilled water and hydrochloridric acid (HCl 37%) and stirred for 30 minutes at room temperature. To this polymer solution, tetraethyl orthosilicate (TEOS) was added with vigorous magnetic stirring and the resulting gel mixture was stirred for 20 h at 35°C and then heated for 21 h at 90°C. The solid product was filtered and dried for 6h at 80°C in an oven. The product was then slurried in ethanol under reflux conditions in order to remove the polymer, filtered and washed with ethanol and dried at 100°C overnight. The resulting white product was calcined at 500°C for 6h.

An amount of SBA-15 was contacted with an ethanolic solution of an appropriate concentration of $Fe(NO_3)_3$ and $Co(NO_3)_2$ precursors removing the solvent by rotavapor. The addition of iron and cobalt to SBA-15 was also carried out by incipient wetness impregnation [2] starting from the same metal precursors. In both cases the metal loading was 3% by weight either in Fe and Co.

Fe/Co SBA-15 catalysts were characterized by XRD, BET/porosity measurements, TEM and SEM.

XRD patterns of both catalysts showed at low angle a very intense diffraction peak and two weak peaks which are characteristic of 2D hexagonal structure (P6mm) with good textural uniformity. At higher angles no further peaks were detected, indicating the absence of formation of iron or cobalt oxides or similar phases within the instrumental sensitivity.

The isotherm of SBA-15, before and after the introduction of the metals, is of IV classification with the typical hysteresis loop of mesoporous materials. The decrease of the amount of adsorbed N_2 in the SBA-15 after the introduction of Fe and Co is due to the reduced pore volume and the condensation in adsorption branch, starting at lower temperature, is caused by the smaller pore size. The filling of the channels after the introduction of the metals accounts for the decrease of the pore volume, pore size and surface area. (Fig. 1)

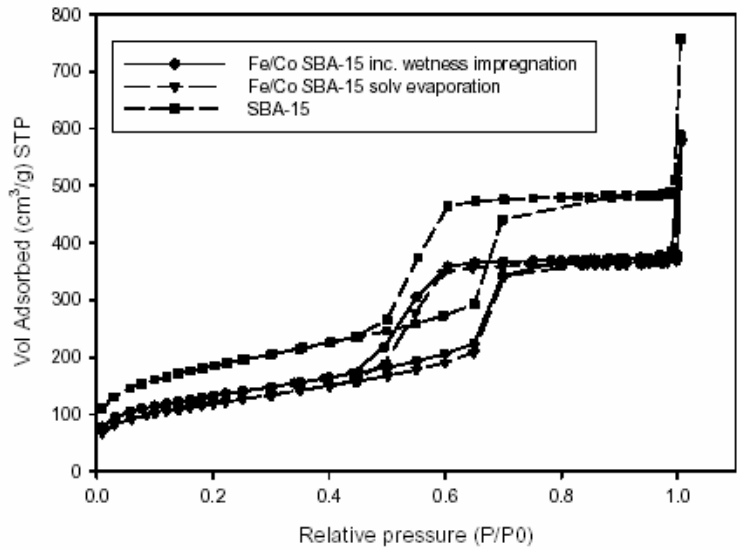

Figure 1. Comparison between N_2 adsorption-desorption isotherms for SBA-15 support and Fe/CoSBA-15 catalysts.

Scanning electron microscopy evidenced the typical wheat-like morphology of SBA-15 with a crystal size in the range of 1-2 micron.

TEM analysis showed the highly ordered mesoporous structure of SBA-15 which remains after the introduction of the metals. Furthermore, it was evidenced that the metal particles are inside the channels of SBA-15 for the catalyst prepared by solvent evaporation even if some metal conglomerate are present on the surface. Whereas the sample synthesized by incipient wetness impregnation showed a more uniform distribution of the metal particles inside the channels. In both cases, the high ordered mesoporous structure of the host silica imposes the size of the guest metal particles by the dimension of the channels.

For the synthesis of CNTs, these Fe/Co SBA-15 materials were deposited in a ceramic boat and inserted into a quartz tube located in a horizontal electrical furnace. After reduction at 400°C by H_2 for 45 minutes, the hydrogen flow was replaced with a mixture of hydrogen and propane (Φ_{H2}=60 ml/min, Φ_{C3H8}=60 ml/min) or helium and ethanol (Φ_{He}=50 ml/min, Φ_{C2H5OH}=0.05 ml/min) and the temperature was rapidly increased to 750°C.

When CNTs were grown on Fe/Co SBA-15 prepared by the solvent evaporation method, TEM images of the samples obtained by CVD using ethanol as the carbon source, evidenced the presence of CNTs with different diameter (in the range of 10-40 nm), whereas for samples prepared by propane CVD on the same Fe/Co catalyst, the formed nanotubes have a narrower diameter distribution (in the range of 10-20 nm).

On the other hand, TEM images evidenced that, if the introduction of the metal particles in the SBA-15 is more controlled, as by careful incipient wetness impregnation, it is possible to obtain CNTs with homogeneous distribution of diameter centred at around 5 nm, which corresponds to the SBA-15 diameter dimension (Fig. 2).

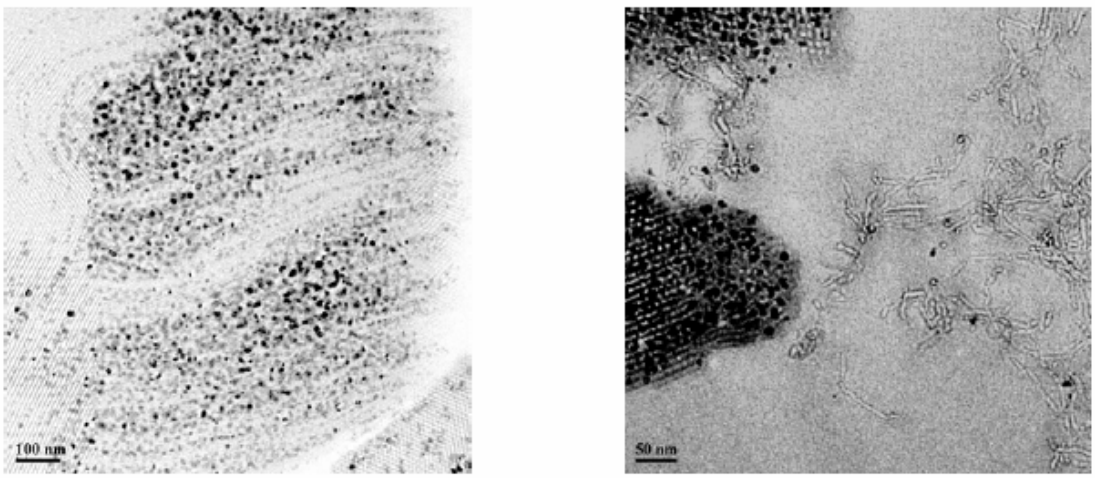

Figure 2. TEM images of Fe/Co SBA-15 catalyst prepared by incipient wetness impregnation before (left) and after carbon nanotubes growth (right)

In addition, high resolution TEM images evidenced also that carbon nanotubes with larger diameter (and thicker walls) are also more defective.

In conclusion carbon nanotubes coming up from the metal particles located in the SBA-15 maintain the channel dimension, whereas those which eventually grow from few metal particles on the external surface are not under dimensional control and their diameter is around 50 nm.

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