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Carbon Nanotubes for Methane Tri-reforming

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Highlights

- Synthesis of Fe, Co and Cu nanoparticles on multi-walled carbon nanotube nanocomposites.
- Efficient method for insertion of nanoparticles in CNTs with a mean diameter for less than 10 nm.
- The controlling incorporation of Fe in the carbon nanotubes.
- Activity tests of tri-reforming processes on Fe@MWCNT/Cu-Co catalysts presented high conversions.

1. Introduction

Carbon deposition is the major disadvantage of catalysts process, indicating that development of a material that minimizes carbon formation is a key research priority. Ways of suppressing carbon formation during the catalytic reaction include (1) better dispersion of the active metal on the surface support, (2) use of high surface areas supports/carriers, (3) increasing the basicity of the catalysts, and (4) incorporation of the active metal in the support structure with high oxygen mobility. For this reason, the search for materials that play a fundamental role as a support in heterogeneous catalysis, in particular carbon nanotubes (CNTs) has been the subject of many studies. Several procedures have been implemented to embed a variety of substances into CNTs and, depending on the final result, there are different techniques based on low-pressure vapour deposition [1], capillarity wetting [2], electrochemical processes and the use of supercritical fluids [3]. Furthermore, some efforts have been reported in producing CNTs with the desired filling material directly during the nanotube growth. However, these methods cannot control the amount of the filling material inside the nanotube cavity. Moreover, as far as the authors know, a specific method suitable to remove the filling material deposited on the external CNT walls has not been reported. In 2009, Tessonier et al. [4] described a general method for deposition of metallic nanoparticles selectively, either inside or outside of carbon nanotubes (CNTs). The method is based on the difference in the interface energies of organic and aqueous solutions with the CNT surface. This work aims to insert Fe nanoparticles in to the multi-walled carbon nanotubes having inner diameter smaller than 10 nm and to deposit Co and Cu nanoparticles over the external surface. Iron NPs, CoO_2 and CuO_2 are, respectively, the active phase and the promoters, which are very important for the methane oxidation or tri-reforming processes, due to its high storage capacity and promoting effect. The degree of exposed and inserted NPs is characterized by different methods and the activity of the catalysts synthesized was tested through the tri-reforming reaction of methane to produce synthesis gas at various temperatures and atmospheric pressure.

2. Methods

Catalyst Synthesis: The products and solvents used in this synthesis were: i) solid salt of – Iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), Copper(II) nitrate trihydrate ($Cu(NO_3)_2$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), from Aldrich; ii) the solvents: ethylene glycol, ethanol and nitric acid (Aldrich).; iii) the multi-walled carbon nanotubes (MWCNTs) functionalized with carboxylic acid (mean diameter of 9.5 nm) (Aldrich). The catalyst was prepared (5wt%Fe@MWCNT/5wt%Co10wt%Cu) using the method proposed by Tessonier et al [4].

Catalytic Activity Tests: Experiments were conducted in a temperature controlled quartz packed bed reactor, where the effluent gas concentrations were measured with online gas chromatography (Clarus 500, Perkin Elmer). 80 mg of 5wt%Fe@MWCNT/5wt%Co10wt%Cu were used in all experiments. The catalysts were pretreated in-situ by heating to 400°C and reducing in H_2 (99.999%, Air Products) for 120 min. The reactor was flushed with He (99.999%, Air Products) and heating to 500°C, where the catalyst was exposed to tri-reform reaction conditions for 2 h, then the temperature was gradually raised to 700°C.

3. Results and discussion

The transmission electron microscopy (TEM) images showed filamentous carbon in the sample, and allowed the calculation of internal and external diameters, number of walls and spacing interlayers. Figure 1 shows the image of the carbon nanotube functionalized with carboxylic acid and the EDX spectrum.

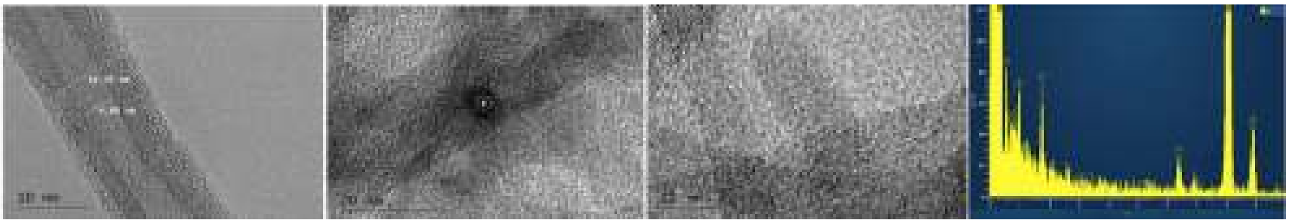

Figure 1. Image Transmission Electron Microscopy (TEM) and EDX spectrum of the MWCNT_acc.

The internal and external diameters were 4.6nm 14.3nm, respectively in Figure 1. It was also possible to determine the number of walls (13), the spacing (0.37nm), and identify the metals present in the sample. The EDX spectrum of an individual nanoparticles shows copper, silicon, iron and carbon. The copper grid, carbon of the nanotube, causes the copper peak while silicon and iron were detected as impurities in the carbon nanotubes. The figure to the right of the EDX spectrum is characteristic of a closed end carbon nanotube and, therefore, this one needs a treatment to open its in order to allow to deposit nanoparticles in its interior.

4. Conclusions

The synthesis method using a combination of organic and aqueous solvents during the incorporation of Fe nanoparticles inside the carbon nanotubes was successful and selective. The functionalization of the CNT sample with nitric acid only once was important for creating oxygen-containing groups, reducing the hydrophobic character of the surface of the carbon nanotubes and allowing the introduction of both organic and aqueous solvents. Insertion of Fe particles inside the wall nanotubes and Co-Cu outside the nanotubes for CNTs with diameters below 30 nm was obtained. The incorporation of Fe nanoparticles based on the pore volume of the carbon nanotubes allowed to control the size of the inserted particle. The catalytic tests for methane tri-reforming showed that the Fe@MWCNT/Co-Cu catalysts presented high conversions at different temperatures.

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Keywords
Functionalization of CNT; Iron; Cobalt; Copper; methane tri-reforming; nanoparticles.