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Synthesis and physico-chemical properties of multiwall carbon nanotubes doped with transition metals.

Abstract

The carbon nanotubes are materials exhibiting interesting properties [1] could being applied in numerous fields, including catalysis [2]. However, most of the times it is necessary to increase the reactivity of the surface of these materials by functionalization with groups of acid character, which can serve as anchoring groups for metals or other functionalities. Our research group has recently prepared doped alkaline multiwall carbon nanotubes, which have resulted to be efficient catalysts in the Knoevenagel condensation [3].

In this paper we show the synthesis and characterization of multiwall carbon nanotubes (CNT) doped with different transition metals, M-CNT (with M= V, Cr, Mo, Ni). The goal is to obtain acid catalysts active for the synthesis of Fine Chemicals. Other carbonaceous materials containing those metals, in particular, carbon xerogels, were tested in the synthesis of chalcones, resulting as active catalysts [4]. The solids have been prepared by treatment of commercial multiwall carbon nanotubes with nitric acid (CNTO) and subsequent doping with the metals by ionic exchange of the corresponding salts under ultrasonic activation. The materials thus obtained were dried at 60 º C and pyrolyzed at 500 º C to decompose the salts. A reference solid without metal was also prepared (CNTOp).

The analysis by different techniques shows that the doping of the CNT with the metals has been produced. Thus, FTIR-ATR spectra show the disappearing of the bands assigned to the carboxylic groups and the appearing of new bands. The TG curves in air of the pyrolyzed samples lead to a higher residue than that for CNTOp, following the V > Cr > Ni > Mo order. The thermal stability of C=C bonds of the skeleton of nanotubes functionalized with nitric acid (CNTO) increases with respect to commercial nanotubes; however, in samples doped the temperature of decomposition of nanotubes is lowered in approximately 100ºC, with respect to that of CNTOp. This fact indicates that the metallic phases contribute to the destabilization of the nanotubes, promoting their oxidation. The exception is the Mo-CNT sample, whose TG curve is not altered with respect to that for CNTOp, the final residue being almost the same for both samples. Therefore, in the case of sample containing Mo, the doping has been produced in a less extent than for the rest of metals.

XRD patterns of samples show the formation of vanadium pentoxide in the V-CNT sample, whereas no crystalline phase is detected for the rest of samples, indicating a higher dispersion of the metals in the carbon nanotubes.

The commercial carbon nanotubes are mesoporous solids. The oxidation causes a decrease in S_{BET} and the pore volume due to the pore blockage by oxygenated functionalities, which are partially removed during pyrolysis. The value of the BET areas also decreases in nanotubes doped with the transition metals, due to the blockage of micropores and small mesopores by the metals.

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