Effect of the surface oxidation of carbon nanotubes on the selective cyclization of citronellal

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ABSTRACT

Commercial carbon nanotubes have been oxidized with HNO_3, H_2O_2 and air and they have been tested on the cyclization of citronellal. The materials have been characterized by N_2 adsorption/desorption isotherms, transmission electron microscopy, X-ray diffraction, temperature programmed desorption, potentiometry titration and X-ray photoelectron spectroscopy. The HNO_3-treated samples displayed the largest concentration of carboxylic acids which increased by increasing the oxidation time and by a previous ball-milling treatment. The carboxylic acid groups were found to be the active groups on the reaction and the activity increased by increasing its content. The selectivity to isopulegols was higher (98%) over the most active samples (activity 0.20–0.68 mmol/g min), which has been explained by their smaller pore size caused by the oxidation treatment. The stability of the most active CNT sample was also proved by recycling the catalyst in 3 cycles.

1. Introduction

Citronellal is a renewable feedstock that can be naturally obtained from a great amount of natural essential oils such as *Cymbopogon nardus* or Java citronella, and it can be used in the chemical industry to replace petroleum in a wide variety of transformations. Among them, the cyclization of citronellal is a relevant reaction in fine chemistry industry as its product, isopulegol, is widely employed in flavor and perfume industry for the production of fragrances and manufacturing menthol, which is an important ingredient in perfumery and pharmaceuticals products [1].

Several heterogeneous catalysts have been studied for the cyclization of citronellal to substitute the environmentally unfriendly Lewis acids ($ZnCl_2$, $AlCl_3$, $SbCl_3$, etc.). Among them, several oxides (SiO_2–Al_2O_3, SiO_2) [2,3], zeolites containing Lewis acid centers, such as Sn and Zr atoms [4] and zirconia-based catalysts [1,5] have been found to be active and selective to certain extent for the reaction. Both Lewis and Brönsted acids have been identi-

fied as active sites and, although no precise correlation between acidity and catalytic performance has been established, it has been reported that a proper modulation of the acidity is needed to obtain an optimal activity while avoiding secondary reactions such as condensation, etherification or cracking [6]. Besides acidity, the catalytic performance depends largely on the textural properties of the catalyst and, for example, a comparison between different zeolites and mesoporous materials found that H-MCM-41 offered the best results [6].

In this context, carbon materials arise as excellent candidates given the possibility to control the surface acidity with relatively easy procedures. Moreover, they are chemically stable favouring the deposition of metal nanoparticles in acid and basic media. Their role in catalysis has extensively been reported both as a support and as catalyst its own [7,8]. They can react with multiple molecules to incorporate different heteroatoms (O, N, H, Cl, S, etc.), and the importance of their surface chemistry on a wide variety of reactions has been reviewed [9–11]. Besides the surface chemistry it has been proved that the morphology may affect the catalytic performance. Though most of the literature reports the use of activated carbon, mainly due to its high adsorption capacity, for liquid phase reactions a mesoporous material would offer additional advantages.

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In this sense, still few examples can be found in literature where carbon nanotubes have been used as catalyst its own [12–14].

The oxidation of carbon materials and CNT, in particular, has been performed employing several liquid and gas reagents such as H_2SO_4, H_2O_2, HNO_3, NaClO, HCl, ozone, air, etc [15,16]. The type and concentration of surface groups depend on the oxidizer and functionalization conditions [17–20]. Among the oxidizers, HNO_3 has proved to incorporate a high concentration of oxygen groups while preserving the CNT structure [21]. In general, the oxidation with HNO_3 and H_2O_2 produces acidic materials holding carboxylic acids and, to a smaller extent, lactones, anhydrides and phenol groups. Nonetheless, the obtained amount of oxygen functionalities is larger when HNO_3 is employed [22]. On the other hand, the treatment under air generates a larger proportion of carbonyl and ethers which are neutral or may form basic structures, such as quinone [23].

Therefore, we have explored the effect of different oxidation treatments (HNO_3, H_2O_2 and air) on the surface chemistry of CNT and studied their catalytic performance on the cyclization of racemic citronellal. The effect of the oxidation time with HNO_3 and the previous ball-milling treatment was also evaluated.

2. Experimental

2.1. Oxidation of the CNT

High purity multi-wall carbon nanotubes (i.d. 2–6 nm) were supplied by Nanocyl (Nanocyl 3100, > 95% purity) and submitted to different oxidation treatments. a) CNT were treated with 50 ml/g HNO_3 (65% wt) at 403 K, then they were washed with distilled water until pH ∼7 and dried at 333 K overnight. The oxidation was performed for 24, 16 and 8 h obtaining the samples labelled as CNToxn24, CNToxn16 and CNToxn8 respectively; b) CNToxa: oxidation of CNT under air flow (30 ml/min) at 673 K for 2 h; c) CNToxp: oxidation of CNT with H_2O_2 100 ml/g (30%), at 353 K for 24 h; d) The CNT were submitted to ball milling in a planetary stainless steel Spex 800 rpm for 1 h followed by oxidation as applied for CNToxn8 obtaining the sample CNTmox8; e) Two portions of the sample CNToxn24 were heat-treated in He (50 ml/min) with a heating ramp of 5 K min⁻¹ at 373 and 473 K for 1 h and they were labelled as CNToxn24-373 and CNToxn24-473.

2.2. Characterization

Conventional TEM analysis was carried out with a JOEL model JEM-210 electron microscope working at 200 kV and equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey-carbon film support.

X-ray powder diffraction patterns were recorded on a Rigaku diffractometer equipped with a nickel-filtered CuKα1 radiation (λ = 1.5418°A), using a 2° min⁻¹ scanning rate. N_2 adsorption-desorption analysis was performed at 77 K on a Micromeritics ASAP 2010 apparatus. Specific surface areas were determined via the BET (Brunauer–Emmett–Teller) equation, using adsorption data in the relative pressure range of 0.05–0.3, and pore size distributions were estimated using the BJH model.

The thermogravimetric analyses were performed with a Mettler Toledo Thermogravimetric TGA/SDTA 851 system. The sample was treated under flowing He for 2 h and then heated with a heating rate of 10 K min⁻¹ rate up to 1123 K.

Temperature-programmed desorption (TPD) experiments were carried out in a vertical tube furnace with He as the carrier gas to thermally decompose the stable surface oxygen complexes. 100 mg sample was placed in a quartz tube and heated to 383 K for 1 h, and then the temperature was raised to 1000 K at 10 K min⁻¹.

Acid site concentrations and acid strength measurements of the materials were determined using a potentiometric method [24], whereby a suspension in acetonitrile (Merck, 99.9%) was titrated with n-butylamine (Merck, 99%). The variation in electric potential was registered on a Denver Instrument UltraBasic pH/mV meter.

Photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer equipped with a hemispherical analyser and using non-monochromatic Mg K X-ray radiation (h = 1253.6 eV). The surface O/C atomic ratios were estimated from the integrated intensities of C 1 s and O 1 s lines after background subtraction and correction by the atomic sensitivity factors. The spectra were fitted to a combination of Gaussian–Lorentzian lines of variable proportions.

2.3. Reaction

The catalytic performance was tested in a 100 ml stainless steel Parr- type reactor lined with glass at 363 K and 10 bar of He with a stirring speed of 700 r.p.m. For each reaction 50 mg of catalyst, 30 ml of toluene and 0.16 M of racemic citronellal (Sigma Aldrich ≥ 98.0%) were employed. For the recycling studies, 75 mg was initially employed keeping the same reactant concentration and substrate/catalyst ratio. The catalysts were recovered by filtration, extensively washed with acetone and dried under vacuum at 323 K for 6 h and the amounts of reactant and solvent recalculated according to the catalyst mass recovery. Analyses of reactants and products were followed by gas chromatography mass spectrometry using a GC–MS instrument (Shimadzu GCMS-QP5050) with chiral-Dex 225, a 30-m column (Supelco), and helium as the carrier gas. Small aliquots of sample were taken for analysis by gas chromatography (GC). The activity was calculated as mol converted per minute at 50% conversion and the selectivity was estimated as the
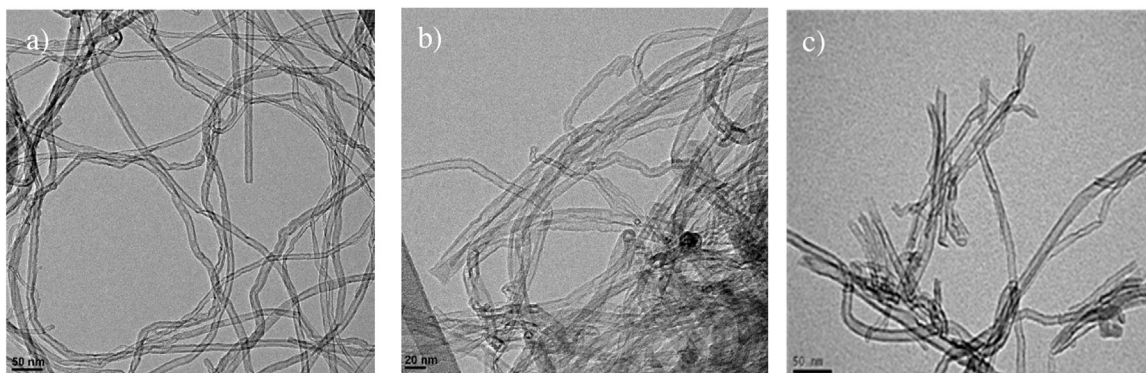

Fig. 1. TEM micrographs of a) CNT, b) CNToxn24, c) CNTmox8.