



Magnetic shepherding of nanocatalysts through hierarchically-assembled Fe-filled CNTs hybrids

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ABSTRACT

Mechanically robust, chemically stable and electronically active carbon nanotubes (CNTs) are widely used as supports in catalysis. Synergistic effects between CNT and the active phase critically depend on the homogeneity of the carbon/inorganic interface, whose assembly is difficult to achieve without admixtures of free-standing inorganic matrix. Here we show that Fe-filled CNTs, employed as nanocatalyst supports, allow a facile preparation of highly pure and uniform CNT/nanocatalyst materials, by taking advantage of magnetic separation from poorly-defined components (e.g. aggregates of inorganic nanocatalysts). The higher homogeneity translates into higher catalytic activity in two industrially important processes: the photocatalytic hydrogen production and the water-gas shift reaction, WGS (increase of ~48% activity for the former and up to ~45% for the latter as compared to catalysts isolated by standard filtration). In addition, the magnetic Fe core in the nanotubes enables effective separation and re-use of the nanocatalyst without loss of activity. This study demonstrates significant potential of magnetic CNTs as next generation of sustainable catalyst supports that can improve production of hydrogen and reduce the use of precious metals.

1. Introduction

The introduction of a precise hierarchical order in the assembly of nanostructured materials is nowadays considered as the latest frontier in heterogeneous catalysis. Energy-related applications have particularly profited from the use of this concept [1,2]. The structural interplay of hierarchically organized phases is often the key factor for the achievement of notable boosts of catalytic performance in several chemical transformations [3]. In many cases, such interplay crucially depends on the interface, in particular a tight contact between the different components, which secures an efficient electronic communication and also underpins an enhanced robustness of the catalytically active sites [3]. The assembly of metal/metal oxide core-shell systems, where metal nanoparticles are enveloped within a layer of metal oxide phase, is an excellent demonstration of this important concept, showing improved activity and stability, arising from the enhanced contact between the two components [4].

Carbon nanotubes represent a very useful scaffold in modern nanostructured catalysts [5], having been combined with a range of inorganic counterparts, resulting in hierarchical nanohybrids with intriguing catalytic features [6]. For example, in photocatalytic processes the presence of CNTs in tight contact with the photoactive phase retard the recombination of the photogenerated holes and electrons, thus generating longer lived charge separated states, thanks to the electron scavenging ability of the graphitic scaffold [7]. On the other hand, in the WGS, CNTs may help the electronic suppression of the deactivation pathway, with the catalytic performances depending on an optimum coverage of the carbon component with the active metal/metal oxide phase [8]. Many other examples are available where the beneficial role of CNTs is proven, and the critical importance of a close electronic crosstalk with the metal phase substantiated [9]. Despite the considerable advances in the preparation of CNT nanohybrids, a central and recurrent drawback lies in the generally poor control over the synthetic route to secure effective formation of a homogeneous

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nanohybrid. In fact, synthesized CNTs-inorganic hybrids generally present considerable amounts of free-standing inorganic phase that [10], possessing lower activity, diminishes the catalytic efficiency of the hybrid materials. An attempt to reduce the admixtures of metal phase by simply decreasing the metal loading is not viable, as the coverage of the CNTs and the isolated aggregates formation proceed in parallel, and a decrease of the metal loading also leads to partly bare CNTs with resulting lowering of catalytic activity [8,11]. The development of a general and efficient strategy to maximize the interfacing between the CNTs and the inorganic active components while reducing the total amount of the metal phase would guarantee a step forward for the definitive establishment of CNT-based hybrid nanocatalysts. We conjectured that the shepherding of the more active CNT/metal nanostructures, liberated from post-synthetic CNT-free aggregates, could be the winning strategy, maximizing the catalytic potential by full exploitation of the CNT-inorganic phase interaction.

For their part, magnetic nanocatalysts have become an appealing alternative to standard catalysts, as they bring the great advantage of avoiding cost- and time-consuming protocols for filtration, separation and isolation from by-products [12–14] and an extra asset in the ease of the post-catalytic recovery step [15]. Some of us have previously reported the synthesis and characterization of multi-walled CNTs (MWCNTs) filled with a magnetic Fe phase (Fe@CNTs) [16] for use in cancer treatment and cell shepherding [17,18] as well as in electrocatalytic O₂ reduction and H₂ evolution [19]. Building on these concepts, here we describe the hierarchical assembly of Fe@CNTs/Pd@MO₂ nanohybrid systems, integrating magnetic Fe@CNTs with an inorganic matrix made of Pd nanoparticles embedded within TiO₂ or CeO₂ nanocrystals. The magnetic Fe@CNTs core can harness a general and simple sieving process to obtain the most active CNT-based catalyst package as demonstrated by the measuring of the catalytic performances in two important energy-related processes: H₂ photocatalytic evolution and water-gas shift reaction (WGSR). Moreover, extension of the application of these nanohybrids to other chemical transformations may imply a direct involvement of the endohedral Fe phase, which can facilitate charge transfer pathways [20,21]. As a further asset of these new CNT-based hybrids, the recyclability of the catalyst can rely on the same simple principle of magnetic separation. We predict that the generality of our finding could spark new research on the use of a next generation of magnetic CNTs for heterogeneous catalytic applications.

2. Experimental

2.1. Synthesis of Fe@CNTs

The preparation of Fe@CNTs followed the procedure previously developed [19]. In detail: in a 180 cm long quartz tube of a furnace setup, a 10 cm long quartz substrate was introduced in the temperature region around 900 °C and a constant flow of 0.2 m³ h⁻¹ of argon was used to purge the system of remaining air. Under this flux, ferrocene (5 g) was introduced in a boat and placed in a region close to 550 °C. Toluene vapour was then flown into the quartz tube of the furnace by the argon purge of 0.2 m³ h⁻¹ for 15 min. The toluene flow is then turned off and the quartz substrate is moved to a cool zone of the 180 cm long quartz tube to allow the sample to cool down to room temperature under an argon flux of 0.2 m³ h⁻¹. The black material is then washed with ethanol to remove any residual ferrocene to obtain pristine Fe@CNTs (about 2.3 g). The material was then subjected to HCl washing in order to remove any external Fe or Fe oxide. As produced Fe@MWCNTs (250 mg) was introduced into a 1 L round-bottomed flask with methanol (375 mL). The reacting mixture was sonicated for 10 min, an aqueous HCl solution (4 M, 125 mL) was added and the mixture was sonicated for 10 min and stirred for 24 h at room temperature. Water (375 mL) was added and the mixture filtered through a 0.45 μm hydrophobic polytetrafluoroethylene filter. The precipitate was redispersed by 10 min of sonication in 100 mL of methanol, filtered

through the same filter and washed with water (100 mL). This procedure was repeated twice. The precipitate obtained was then washed with methanol (few mL). A black powder (about 220 mg) was finally recovered.

2.2. Functionalization of Fe@CNTs with benzoic acid (*f*-Fe@CNTs)

Fe@CNTs (100 mg) were placed in a 500 mL round bottomed flask and N-methyl-2-pyrrolidone (NMP, 67 mL) was added. The solution was sonicated for 20 min and *p*-amino-benzoic acid (675 mg) was introduced, the solution was sonicated for another 10 min and diisopropylethylamine (DIPEA, 40 μL) was added. After 10 min of further sonication, isoamyl nitrite (1.5 mL) was added slowly and the reaction mixture was stirred at 90 °C for 20 h. The dispersion was cooled to room temperature and was filtered through 0.45 μm hydrophobic polytetrafluoroethylene filters. The precipitate was redispersed by 10 min of sonication in 100 mL of ethyl acetate and filtered through the same filter. This step was reproduced two additional times and the final precipitate was dispersed in 100 mL methanol by 10 min sonication, water (200 mL) was added and the suspension was filtered through the same filter. Two additional washings with water (50 mL) were also realized. The precipitate was finally washed with few mL of methanol to facilitate drying. About 85 mg of black powder (*f*-Fe@CNTs) were thus recovered.

2.3. Synthesis of Fe@CNTs/Pd@TiO₂-filt and Fe@CNTs/Pd@TiO₂-magn

The precursor Pd-MUA (MUA = mercapto-undecanoic acid) was prepared according to a previous procedure [22]. The *f*-Fe@CNTs were dispersed in absolute ethanol (EtOH mL/*f*-Fe@CNTs mg ratio: 2.5) by sonication for 30 min meanwhile a Pd-MUA THF solution (containing 1.5 mg of Pd) was slowly added to a THF solution of Ti(OBu)₄ (containing nominal 88.5 mg of TiO₂ respectively). Then the Pd@TiO₂ precursor solution was slowly added under sonication to the *f*-Fe@CNTs dispersion and the mixture was further sonicated for 30 min. Finally a 10% solution of H₂O in EtOH (Ti(OBu)₄/H₂O molar ratio: 1/120) was dropped and the mixture sonicated for 30 min. The materials were collected by either magnetic separation (Fe@CNTs/PdTiO₂-magn) or by filtration (Fe@CNTs/PdTiO₂-filt). For the former, the dispersion was left in a vial close to a NdFeB magnet (purchased by www.supermagnete.it) for 3 h, the liquid phase was then discarded. This operation was repeated twice redispersing the material in fresh EtOH. The solid was then recovered and left to dry. For the filtration method, the dispersion was filtered on a 0.45 μm polytetrafluoroethylene Millipore membrane, washed with ethanol and dried overnight at 80 °C. The solids were thermally treated under a flow of H₂ (10%) in Argon (total flow 220 mL min⁻¹) for 5 h at 450 °C.

2.4. Synthesis of Fe@CNTs/Pd@CeO₂-filt and Fe@CNTs/Pd@CeO₂-magn

The synthesis was similar to the previous one used for TiO₂, with the exception that the Ce precursor was Ce(ODe)₄ (ODe = decyloxyde), prepared according to a previously developed procedure [23]. In this case the thermal treatment was made in situ before the WGSR tests. The materials were treated under H₂ (10%) in Argon (total flow 49 mL min⁻¹) for 1 h at 250 °C.

The relative percentage of Pd@MO₂ (M = Ti or Ce) was calculated based on TGA data. In particular, the Fe:CNT ratio was first evaluated and it was assumed that such ratio remains constant after hybridization with the Pd@MO₂. After observing the CNT% in the final hybrid, the Fe proportion could therefore be calculated and the amount of Pd@MO₂ evaluated by difference between the total inorganic residue and the Fe.

2.5. Characterization

Thermogravimetric analyses (TGA) of approximately 1 mg of each

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