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Carbon nanofibers as macro-structured catalytic support

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1. Introduction

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Since their discovery as a by-product of the arc-discharge process (Iijima, 1991), carbon nanotubes and their related materials, i.e. nanofibers and onion-like particles, have received an increasing academic and industrial interest due to their exceptional mechanical and electronic properties (Dresselhaus et al., 2001). Most commonly, carbon nanofilaments are produced by evaporating solid carbon in an arc discharge, by laser beams or by catalytic chemical vapour deposition (CCVD) of carbon-containing gases (Ebbesen, 1997). Depending on the nature of the metal catalyst, the composition of the carburizing mixture, and the synthesis temperature, carbon nanostructures with different shapes, i.e. nanotubes or nanofibers, can be prepared (de Jong & Geus, 2000). A carbon nanotube structure consists of cylindrical graphene layers with a hollow internal cavity, whilst a carbon nanofiber structure consists of a stacking of different graphite sheets oriented at an angle with respect to the fiber axis. The exposed surface of the carbon nanofibers mainly consists of prismatic planes with high surface reactivity when compared to the graphite basal planes of the carbon nanotubes.

Among the different potential applications of these materials, catalysis either within the gas or the liquid phase seems to be the most promising according to the results recently reported in literature (Salman et al., 1999). Metals supported on carbon nanofibers or nanotubes exhibit unusual catalytic activity and selectivity patterns when compared to those encountered with traditional catalyst supports such as alumina, silica or activated carbon. The extremely high external surface area displayed by these nanomaterials significantly reduce the mass transfer limitations, especially in liquid phase reactions (Pham-Huu et al., 2001), and the low interaction between the impregnated metallic phase and the exposed planes of the support which leads to the formation of active metallic faces (Rodriguez et al., 1994) were advanced to explain these catalytic behaviours.

However, these materials have only been synthesized in a powder form, making difficult their handling and large scale use, especially in a conventional fixed-bed catalytic reactor. The handling of the carbon nanostructures is hampered by the formation of dust and a severe pressure drop along the catalyst bed. It is of interest to find a method allowing *(i)* the synthesis of carbon nanostructures on a large scale and *(ii)* with a macroscopic shape in order for it to be used as a catalyst support. It is expected that the macroscopic shaping of

such nano-structured materials will open-up a real opportunity for their use as a catalyst support in relation to the traditional catalysts carriers (Vieira et al., 2004). The macroscopic support should also not change the physical properties of the carbon nanostructures deposited on it, i.e. high mechanical strength in order to avoid breaking and catalytic bed plugging, high specific volume in order to afford a high space velocity of the gaseous reactants, high thermal conductivity which is essential for catalysts operating in highly exothermic or endothermic reactions and finally, a high chemical resistance in order to be used in aggressive environments, i.e. highly acid or alkaline medium.

Macro-structured carbon nanofibers catalytic support was synthesized through a chemical vapour deposition technique described in next section, gowning carbon nanofibers on a macroscopic host, i.e. felt, cloth or foam, as well as the different applications of these new materials in the catalysis field.

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2. Carbon nanofibers synthesis

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The macroscopic host structures used in this work were mainly carbon felt or fabric, which was constituted of a dense entangled network of micrometer carbon fibers with a smooth surface. The starting graphite host had almost no porosity which was in good agreement with its extremely low specific surface area ($< 1m^2.g^{-1}$). These materials were cut into a pre-defined shape, in cylindrical tablets or disks with appropriate dimensions to the desirable application. The tablets/disks were further impregnated with 1wt.% of nickel using an alcoholic solution (50vol.% ethanol) of nickel nitrate. The solid was dried at room temperature overnight, then at 100°C for 2h and finally calcinated at 350°C for 2h. The sample was placed inside a quartz reactor inserted in a tubular electric oven. After 1h of *in situ* reduction at 400°C, the hydrogen flow was replaced by a mixture of hydrogen and ethane with a molar ratio of 5:1 ($H_2:C_2H_6$). The carbon nanofibers were obtained by catalytic hydrocarbon decomposition over the supported nickel particles at 680°C for 2h, resulting in a yield of 100wt.%. Figure 1A presents the surface of the felt completely covered by a layer of carbon nanofibers after its synthesis. The formation of the carbon nanofibers on the macroscopic carbon felt led to a significant increase in the specific surface area, i.e. $85m^2.g^{-1}$, of the final composite, taking into account the low surface area ($1m^2.g^{-1}$) of the starting felt. The surface area was measured using a Coulter SA-3100 sorptometer with nitrogen as adsorbant at liquid nitrogen temperature. Before measurements were taken, the samples were degassed at 200°C for 2h in order to desorb moisture and other weakly adsorbed residues.

The nanofibers produced by this technique showed homogeneous diameters (around 30nm) and fishbone structure with exposed prismatic planes (Figure 1B). The images were taken by Scanning Electron Microscopy LEO model 440.
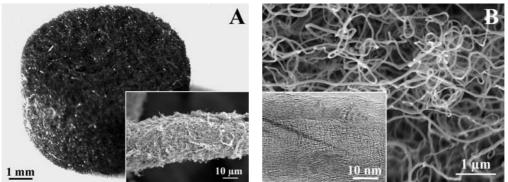
Fig. 1. (A) Image of a macro-structured carbon felt and detail of a fiber covered by carbon nanofibers; (B) Scanning Electron Microscopy image of carbon nanofibers with homogeneous diameters and detail of its fishbone structure.

The shape of this macro-structured material can be modified at will, depending on its required application (Figure 2). Thus, carbon nanofibers composites can be efficiently used as a catalytic support in reactions where diffusion phenomena of the reactants are essential, and in reactions with high mass and heat transfers. Moreover, the high thermal conductivity of this carbon based support allows a fast homogenization of the heat generated during the reaction throughout the catalyst body, preventing the formation of hot spots which are detrimental to the active phase dispersion and catalyst body conservation.
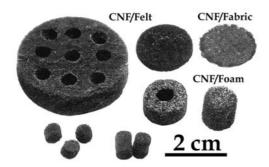

Fig. 2. Macro-structured carbon nanofibers with different shapes, sizes and micro-structures.

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3. Catalytic reactions using carbon nanofibers

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3.1 Catalytic hydrazine decomposition

Nowadays, most of the satellites in orbit use liquid monopropellant hydrazine in its propulsive subsystem for orbit correction and positioning operations. The thrust is obtained by catalytic decomposition of the monopropellant on a highly loaded catalyst containing about 30 to 40wt.% of iridium supported on alumina (traditional catalyst). This catalyst is mainly composed of macro and mesoporous network, in order to increase the active sites

accessibility. Macro-structured carbon nanofibers were proposed as an alternative catalytic support for the iridium in the hydrazine decomposition (Vieira et al., 2005). The composite was cut in cylinder forms and impregnated with 30wt.% of iridium from a solution of hexachloroiridic acid. The tests were carried out with a 2N microthruster designed to operate with the traditional catalyst, placed in a vacuum chamber, which allowed simulating the pressure conditions in space. The dimensions of the microthruster reaction chamber are 6.7mm in diameter and 20mm in length. The microthruster was loaded with 1.14g of the traditional catalyst and with 0.15g of the carbon nanofibers based catalyst, due the different densities of these materials.

The parameters of performance evaluations of the different catalysts in the microthruster used were the steady-state pressure chamber and the ignition time delay, the latter one being defined as the time response from the valve response to 90% of steady-state pressure chamber signal.

The tests were carried out under two level of hydrazine injection pressures, i.e., 22 and 5.5bar, thus simulating the real conditions of the propellant tank pressure at the beginning and the end of its lifespan. For each level of pressure 4 series of 100 short pulses and 1 duty cycle were performed. The catalyst bed was pre-heated at 120°C for all tests.

The carbon nanofibers based catalyst showed superior thrust performances than the traditional catalyst. The pressure chamber pulses delivered during the hydrazine decomposition over the Ir/CNF composite were invariably higher than those detected on the Ir/Al$_2$O$_3$ catalyst (Figure 3), regardless of the great difference between the iridium loading in the propulsion chamber with the traditional and carbon nanofiber based catalysts. The high performance of the Ir/CNF catalyst was attributed to the greater accessiblity of the reactant to the active sites, due to the open structure of the support, i.e. high external surface area and absence of ink-bottled pores. In this type of reaction, where the heat and mass transfers must be very fast, the reactant does not have time to penetrate into the pores, and the main reaction occurs on the external surface of the catalyst grains. In addiction, the high thermal conductivity of the carbon nanofibers also allowed a rapid homogenization of the temperature through the entire catalyst bed whereas on the alumina-based catalyst, due to its insulating character, especially during the continuous long duration tests, i.e., 5000ms.
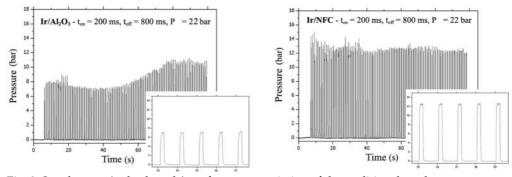

Fig. 3. Steady state (pulsed mode) performance variation of the traditional catalyst (Ir/Al$_2$O$_3$) and the carbon nanofibers based catalyst (Ir/CNF) from the chamber pressure curves of a series of 100 pulses t$_{on}$ 200ms and t$_{off}$ 800 ms.

The ignition time delay was 46ms for the Ir/CNF catalyst and 62ms for the Ir/Al$_2$O$_3$ catalyst both at 5.5bar, and 41ms for the Ir/CNF catalyst and 43ms for the Ir/Al$_2$O$_3$ catalyst at 22bar. The carbon nanofibers based catalyst presented a higher spontaneous restarting capability than the traditional catalyst under these tests.

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3.2 Styrene synthesis

The styrene synthesis is one of the ten largest industrial processes used nowadays. This monomer is involved in several polymer synthesis, and is industrially produced by the direct dehydrogenation of ethylbenzene at 600 - 680°C over potassium promoted iron oxide catalyst. This strongly endothermic process suffers from drawbacks such as: thermodynamic limitations, an irreversible catalyst deactivation and a relatively low yield (> 50%). Carbon is reported to be a catalytically active material for this reaction (Guerrero-Ruiz & Rodriguez-Ramos, 1994). It has been shown that high performances could be obtained over onion-like carbons and carbon nanotubes (Pereira et al., 2004). Such non-planar sp^2-nanocarbons are very active and promising alternative catalysts to the industrial catalyst, with a higher styrene yield and a lower reaction temperature.

Delgado et al. (2006) have shown that just carbon felt with its surface covered by carbon nanofibers is catalytically active in the oxidative dehydrogenation of the ethylbenzene under low temperatures, combining the properties of the nanostructures and the advantages of the macro-structured felt support. Figure 4 shows the performances obtained at temperatures ranging from 375 to 530°C for total flows of 30ml.min^{-1} and 8ml.min^{-1}. Under both conditions, increasing the temperature led to a slight decrease in the styrene selectivity. The selectivity was not strongly influenced by the space velocity. In contrast, this parameter strongly influenced the ethylbenzene conversion, especially at lower temperatures. This implies that operating a low temperature (440°C) and a low space velocity results in upper styrene yields (38%) with a high styrene selectivity (81%), so a low flow favouring reactant adsorption and a low temperature minimizing the combustion, could make such supported carbon nanofibers attractive for industrial applications. Whatever the reaction conditions, and in particular the space velocity, no pressure drop occurred in the reactor and the catalyst bed.
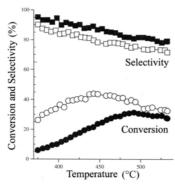

Fig. 4. Ethylbenzene conversion curve (○,●) and selectivity to styrene (□,■) on the macro-structured carbon nanofibers as a function of the reaction temperature in the range 375 – 530°C, using total flow rate of 30ml.min^{-1} (●,■) and 8ml.min^{-1} (○,□).

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3.3 H_2S oxidation into elemental sulfur

Over the last few decades, sulfur recovery from the H_2S-containing acid gases have become more and more important due to the ever increasing standards of efficiency required by environmental protection measures. The general trend is to selectively transform H_2S into elemental sulfur which is a valuable product, by the modified Claus process. However, due to thermodynamic limitations of the Claus equilibrium reaction, typical sulfur recovery efficiencies are only 90–96% for a two stage reactor plant and 95–98% for a three stage reactor plant (Wieckowska, 1995).

Ledoux et al. (2000) have shown the high activity and selectivity of the NiS_2/β-SiC catalyst in the direct oxidation of the H_2S into elemental sulfur at a low reaction temperature (60°C). The catalytic desulfurization reaction conditions were: H_2S 2500ppm, O_2 5000ppm, H_2O 30vol.% and balance He, which is typically the industrial working concentrations in a discontinuous mode. The total selectivity for sulfur was attributed to the absence of micropores in the support. The heterogeneous nature of the support surface (hydrophilic and hydrophobic areas) could explain the important role played by water to maintain a high and stable H_2S conversion level. The catalyst was submitted at frequently regenerations cycles due to the sulfur fouling of the catalyst surface. Later, Nhut et al. (2004) have studied the use of NiS_2 nanoparticles encapsulated inside multi-walled carbon nanotubes for the trickle-bed oxidation of H_2S into sulfur at 60°C. The use of carbon nanotubes led to a significant increase in the overall catalytic performance, both in terms of desulfurization activity and resistance to the solid sulfur deposition onto the material, as compared to the reference catalyst supported on macroscopic SiC grains. The high capacity of solid sulfur storage on the carbon nanotubes compared to that of macroscopic SiC grains was thus attributed to the large void volume outside the nanotubes available for the sulfur storage.

Recently, we studied macro-structured carbon nanofibers as support for the catalytic selective oxidation of H_2S into elemental sulfur at low temperatures (Coelho, 2009). The catalyst was NiS_2 with a metal loading of 15wt.% and the reaction conditions were: H_2S 1000ppm, O_2 1000 to 4000ppm, H_2O 30vol.% and balance He. The results showed that the stoichiometric O_2/H_2S ratio did not significantly the reaction yield, suggesting that the partial order for O_2 is zero. The H_2S conversion at 120°C without water addition was complete during the first 390min (Figure 5A). The deactivation after this period of time was attributed to the encapsulation of the active sites by solid sulfur deposition, i.e. the absence of liquid water hindered the sulfur removal from the active sites; whereas at 180°C, the sulfur liquefaction allowed the maintenance of activity for an additional time (700min).

The water plays a special role of mechanical transport in this reaction. The reaction performed at 60°C with the addition of 30wt.% of water vapour, it was observed 100% of conversion and selectivity in sulfur, even after 288h. Despite these preliminary results, we notice that the sulfur is continuously removed outside of the composite by water added due the hydrophobicity of nanofibers (Figure 5B), letting the active sites exposed for a longer period of time.
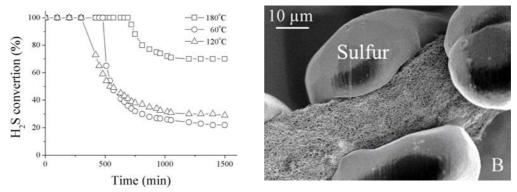
Fig. 5. (A) H_2S conversion as a function of time on 15% NiS_2/CNF catalyst at different temperatures. (B) SEM micrograph of the particular mode of sulfur deposition on carbon nanofibers.

3.4 Fuel cells electrodes

Fuel cells have received considerable interests because of its potential for power generation efficiency and a low pollutant emission. Among them, polymer electrolyte membrane (PEM) fuel cells are the most promising, particular for mobile applications.

The nature of the conductive macroscopic carbon support and a high surface area are fundamental, and conductivity is essential for good electrocatalytic performances. The peculiar electronic, adsorption, mechanical and thermal properties suggest that carbon nanotubes are a suitable material for electrodes and catalysts support in PEM fuel cells (Yu et al., 2002). It should also be noted that the good and reversible hydrogen storage capacity of carbon nanotube materials is very interesting for application in the PEM fuel cell. Recently, Gangeri et al. (2005) evaluated the electrocatalytic performance of platinum supported on felt covered with carbon nanofibers (Pt/CNF/felt) and fabric (Pt/CNF/fabric) as alternative electrodes for PEM fuel cells. The authors compared the performance of these new macro-structured platinum/carbon materials with those of a commercial Pt-carbon black on carbon cloth electrode (E-TEK Inc.) in a 1cm² fuel cell working at room temperature. The analysis of polarization curves (Figure 6) indicated that both carbon nanofibers composites (Pt/CNF/felt and Pt/CNF/fabric) are better electrocatalysts than commercial ones, and the Pt/CNF/fabric gives the lowest ohmic losses while Pt/CNF/felt materials give the lowest mass transfer losses. Further studies of a better membrane and electrodes assembly engineering are necessary to validate the results, but these preliminary analysis, indicate that new electrode material based both on carbon macro-structured composite could be very interesting for fuel cells applications.
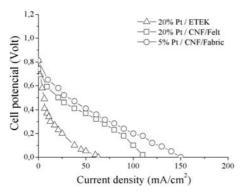
Fig. 6. Polarization curves for the different classes of electrodes.

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3.5 Ammonia decomposition

The catalytic decomposition of ammonia appears to be an appealing process for clean hydrogen production. Ammonia decomposition for production of hydrogen in large-scale, would seem pointless, as ammonia itself is produced from hydrogen, but it appears to be promising from the point of view of specific fuel cell applications, because it can produce CO_x-free hydrogen. Recently, Yin et al. (2004) have reported that very small ruthenium nanoparticles on carbon nanotubes (CNT) present a high activity in ammonia catalytic decomposition. The good performances of Ru/CNT and K-Ru/CNT were related to the high dispersion of the metal and to the high graphitization and purity of carbon nanotubes. The authors have investigated also the influence of the support in catalyst activity. Moreover, the order of ammonia conversion was ranked as Ru/CNT > Ru/MgO > Ru/TiO$_2$ > Ru/Al$_2$O$_3$ > Ru/ZrO$_2$. Among the reported transition metals, ruthenium is the most active in ammonia catalytic decomposition. Various materials have been found to be effective supports for loading of ruthenium metal, but the carbon nanotubes was presented as the better performance as support for ammonia decomposition.

We used carbon nanofibers composite as a support for ruthenium for the catalytic decomposition of ammonia (Furtado et al., 2008). Macro-structured carbon nanofibers with a specific surface area of 85m^2.g^{-1} were prepared using nickel catalyst impregnated onto macroscopic carbon felt. Carbon nanotubes in powder form were deployed as reference support. The above powder was prepared by vapour deposition using 20% Fe/Al$_2$O$_3$ as catalyst, under a reaction mixture of ethane and hydrogen with a molar ratio of 1:1 at 650°C for 2h. The carbon nanotube with a specific surface area of 220m^2.g^{-1} was purified by refluxing in 5M HNO$_3$ solution for 2h, followed by exhaustive washing. Thereafter, the material was refluxed in 1M KOH solution for 2h, followed by washing, drying and calcination at 350°C. The ruthenium loaded catalyst (5wt.% metal) was prepared by incipient wetness impregnation of the carbon nanofibers composite and the carbon nanotubes powder with RuCl$_3$ using ethanol as solvent, followed by drying at 100°C for 12h and calcination at 350°C for 2h.

Catalytic testing was carried out in 10mm inner diameter continuous flow quartz reactor, loaded with 100mg of catalyst, under pure ammonia atmosphere at flow rate 50ml.min^{-1}. Prior to the reaction, the metal catalyst was reduced *in situ* at 500°C for 2h under hydrogen.

The reaction temperature range was 300 to 500°C. Ammonia decomposition rate over carbon nanofibers based composite was about 30% higher than on carbon nanotubes powder support for reactions above 400°C. Figure 7 shows the better performance of the carbon nanofibers based support, due to its opened structure, thus reducing the diffusion problems.
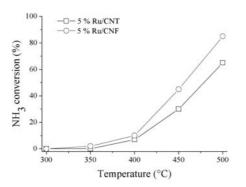

Fig. 7. Curve of ammonia conversion in function of the temperature on the 5% Ru/CNF (○) and 5% Ru/CNT catalyst (□).

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3.6 Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis is a process to convert syngas (CO + H_2) to a cleaner fuel. The nature of its products depends on the catalysts used (Fe, Co, Ni, Ru…), the temperature and the reaction pressure. Diffusion problems of the reactants and products within the catalytic bed are frequent, causing the deactivation of the catalysts by pore obstruction of oxide-based support, consequently affecting the reaction selectivity. As this reaction is highly exothermic, it is necessary to release the heat generated to avoid an eventual sintering of the active phase. Thus, we studied the activity and selectivity of the Co/CNF catalyst in the CO hydrogenation reaction (Furtado, 2009). A central composite design combined with response surface methodology was applied to determine the optimum operating condition on the production of diesel from Fischer-Tropsch synthesis. The variables used in this study were reaction pressure (8 to 22bar), temperature (194 to 236°C), contact time (1 to 7s) and concentration of the active phase (8 to 22%). The response chosen was the CO conversion and hydrocarbons yield. In all experiments the molar ratio CO/H_2 was kept equal to 2. It was verified that high temperatures and pressures, large contact time and metal loading favour the CO conversion. The subsequent figures show that the gasoline (C8-C13) yield is improved mainly by high temperature and cobalt loading, and moderate contact times (around 4s). On the other hand, the pressure has little influence on the gasoline yield. However, diesel (C14-C19) is enhanced by high temperature and pressure, cobalt loading over 15% and moderate contact times.
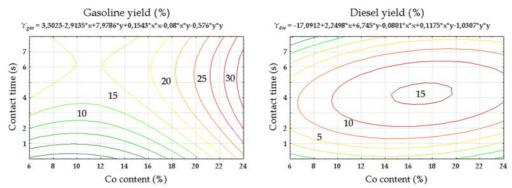
Fig. 8. Contour plot of the relationship: gasoline and diesel yield with contact time and Co content at fixed temperature of 215°C and pressure of 15bar.
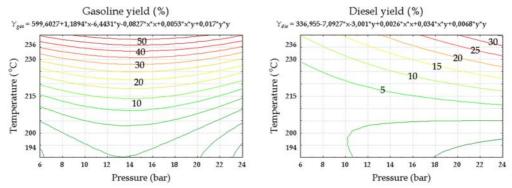

Fig. 9. Contour plot of the relationship: gasoline and diesel yield with temperature and reaction pressure at fixed contact time of 4s and Co content of 20wt.%.

No deactivation was observed with the Co/CNF catalyst over 75h of reaction. A previous comparative study was done with 15% Co/CNF and 15% Co/Al$_2$O$_3$ catalysts, maintaining the best reaction conditions for the first catalyst. It was observed that the Co/CNF catalyst presented a CO conversion (30%) of about tree times higher than that of the Co/Al$_2$O$_3$ catalyst. The good results obtained from this work are attributed to the high thermal conductivity and specific area, chemical inertia, absence of ink-bottle pores and carbon nanofibers hydrophobicity.

4. Conclusion

In summary, macro-structured carbon nanofibers can be efficiently employed as a new class of catalyst support which exhibits a high catalytic activity along with peculiar product selectivity when compared to those observed using traditional catalysts. The high catalytic performances of the carbon nanofibers based catalyst were mainly attributed to (i) the high external surface area and morphology of the support which allows rapid access of the

reactants to the active sites and (ii) the high thermal conductibility of the support which allows the rapid evacuation of the heat formed during the reaction and favours the temperature homogenization throughout the catalyst bed. Finally, it should be noted that the complete absence of bottled pores allows the rapid 3D access of the entire volume of the catalyst to the reactants and also for the rapid evacuation of the products which significantly lowers secondary reactions.

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5. References
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