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New carbon nanofiber/graphite felt composite for use as a catalyst support for hydrazine catalytic decomposition

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Graphite felt supporting 40 nm diameter carbon nanofibers was synthezised and successfully used as a support for a high loaded iridium catalyst (30 wt%) in the decomposition of hydrazine; a strong mechanical resistance and a high thermal conductivity led to a very efficient and stable catalyst as compared to that used industrially, iridium supported on a high surface area alumina.

Direct decomposition of hydrazine (N_2H_4) in microthrusters over iridium metal supported on stabilized γ-alumina catalyst (Shell 405, Shell Corporation Co.) is up to now the main way of providing propulsion power for satellite manoeuvring during path corrections.[1] The hydrazine decomposition pathway can be described as follows: part of the injected hydrazine is first catalytically decomposed into ammonia, nitrogen and hydrogen (eqns. (1) and (2)) over about 10 vol% of the catalyst bed, and thermal decomposition of the mixture subsequently occurs over the remainder of the catalyst bed (eqn. (3)).[2–4]

$$3\ N_2H_4 \rightarrow 4\ NH_3 + N_2 \qquad (1)$$

$$3\ N_2H_4 \rightarrow 3\ N_2 + 6\ H_2 \qquad (2)$$

$$4\ NH_3 + N_2H_4 \rightarrow 3\ N_2 + 8\ H_2 \qquad (3)$$

The extremely high exothermicity of the overall reaction leads to very hot gases and pressure release and provides the energy for the satellite propulsion. In addition, the reaction should take place in the millisecond range and is thus controlled by heat and mass diffusion processes: both the pressure and temperature of the catalyst bed instantaneously increase with hydrazine introduction, from atmospheric pressure and room temperature to respectively several dozens of atmospheres and about 800 °C. The catalyst efficiency under these extreme conditions of use is limited by several critical drawbacks due to the alumina support, such as a low thermal conductivity limiting heat diffusion leading to formation of hot spots on the catalyst surface, attrition problems resulting in the formation of fine powder and its structural instability at high temperature (γ to α phase transformation).

Carbon nanotubes and nanofibers have recently been reported to be suitable active phase supports for heterogeneous catalytic reactions, either in liquid or in gas phases.[5–7] Such new catalytic materials displayed unusual behaviours as compared to generally used supported catalysts, due to their peculiar interactions and/or their high external surface area. The aim of the present article is to report the synthesis and use of a new carbon nanofiber composite material, which combines the advantages due to carbon nanostructures and the easy handling of a macrostructured graphite felt and which will be used as a support for iridium metal for the catalytic decomposition of hydrazine. The catalytic performances are compared with those obtained on a commercially available high surface area alumina supported iridium catalyst (30 wt% and 110 m^2 g^{-1}).

The macroscopic graphite felt, supplied by Carbone Lorraine Co., was composed of entangled microfibers with a mean diameter of 10 μm and lengths up to several dozen millimeters. It had a non-microporous surface area of 1 m^2 g^{-1}. The nickel catalyst deposition (1 wt%) onto this felt was achieved by incipient impregnation with a nickel nitrate salt using ethanol as solvent. The solid was dried overnight at 110 °C and then calcined in air at 350 °C for 1 h to form the corresponding oxide. For the carbon nanofiber synthesis, 0.5 g of the graphite felt supported Ni catalyst was placed inside a quartz tube located in an electric furnace. After reduction of the material at 400 °C under hydrogen for 1 h, the hydrogen flow was replaced by a mixture of ethane and hydrogen with a molar ratio of 1 : 5 (total flow rate of 120 ml min^{-1}) and the carbon nanofibers were synthezised by catalytic hydrocarbon decomposition over the graphite felt supported nickel catalyst at 700 °C for 2 h. Fig. 1(a)–(d) show the structure of the graphite felt supported carbon nanofiber composite. Fig. 1(b) focuses on a naked part of the composite, showing the increase in diameter when the starting graphite microfibers forming the graphite felt were coated, after growth, by a several micrometer thick layer composed of entangled carbon nanofibers. It should be noted that very few microfibers or parts of microfibers remained naked after reaction. Fig. 1(c) shows the high density of the entangled synthesized nanofibers on the graphite felt support. Transmission electron microscopy also revealed the total selectivity towards nanofiber formation, since no amorphous carbon, onion-like carbon or nanoparticles were detected. The supported carbon nanofibers displayed the well known herring-

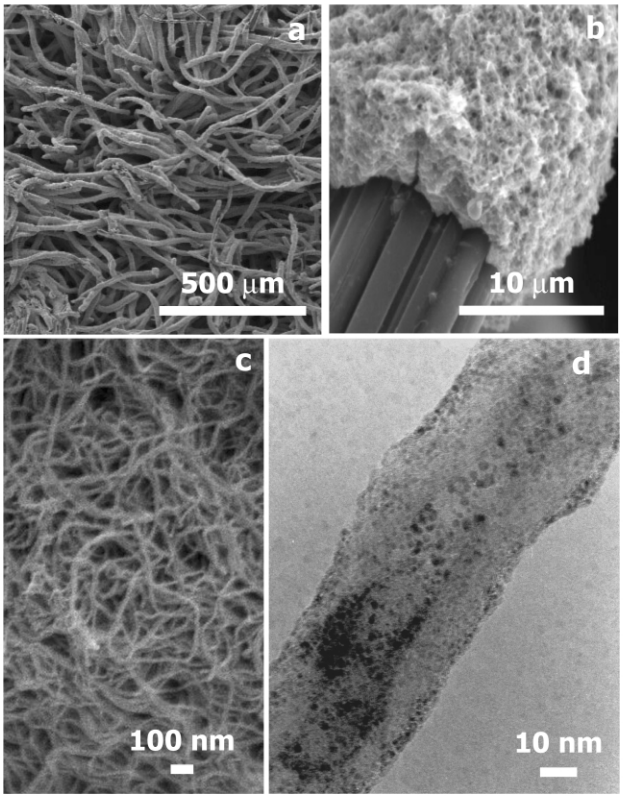

Fig. 1 (a)–(c) SEM images of the graphite felt supported carbon nanofiber composite. (d) TEM image of the composite supported iridium catalyst, showing the high dispersion of the iridium metal particles (narrow size distribution centered around 1.5 nm).

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bone structure, sometimes connecting in the middle of the fibers, according to the results reported in the literature for nickel-based catalysts.[8,9] These carbon nanofibers exhibited a mean diameter of 40 nm and lengths up to several micrometers. The iridium loaded catalyst (30 wt% of metal) was prepared by incipient wetness impregnation of the carbon composite felt with an iridium H_2IrCl_6 salt. After drying, oxidation in air at 350 °C for 2 h and final reduction in flowing hydrogen at 400 °C for 2 h, the catalyst exhibited a high metal dispersion onto the carbon nanofiber surface, with a narrow particle size distribution centered around 2 nm diameter (99% of the iridium particles with diameter lower than 5 nm), similar to that observed on the alumina supported catalyst (Fig. 1(d)). Such a high dispersion was attributed to the strong interaction between the iridium particles and the prismatic planes exposed by the carbon nanofibers and made of hydrophylic oxygenated surface groups.[9] These groups also allow an easy anchorage of the supported phases on the carbon support, as compared to what is observed with the less reactive basal planes of graphite or carbon nanotubes. The carbon nanofiber synthesis led to a large increase in the surface area of the material, from 1 up to 95 m^2 g^{-1}. The surface area was lower than that of pure carbon nanofibers,[9] because of the remaining low surface area graphite, located in the core of the composite. Such an increase could be explained by the presence of graphite prismatic edges, which could act as adsoprtion sites and also to the relatively low crystallinity along the nanofiber axis as compared to more ordered carbon nanotubes. The composite displayed a high mechanical resistance, neither soot formation nor nanofiber loss have ever been observed after sonication treatments. Such a high strength is required to resist the pressure shock inside the decomposition chamber.

The decomposition of hydrazine was carried out in a stainless steel reactor (13 mm i.d. and 30 mm length) using 100 mg of catalyst. 0.34 mL of liquid hydrazine ($>$99.99 vol%) was injected at atmospheric pressure into the decomposition chamber through an electronic valve with a short injection time (0.6 s), and the pressure increase inside the chamber was monitored by a Keller gauge, allowing pressure measurements within 0.1 s.

The high performance of the carbon composite felt as compared to the commercial alumina-based catalyst is reported in Fig. 2. The use of the carbon composite felt supported iridium as a catalyst led to a pressure increase from atmospheric pressure up to 15 bar whereas the peak pressure generated on the alumina-based catalyst was limited to 5 bar. It cannot be excluded that part of the injected hydrazine was trapped inside the micropores of alumina containing no iridium particles, and thus could not be decomposed. The absence of any detrimental microporosity in the carbon composite supported iridium catalyst is therefore of great interest. The strong interaction between the exposed prismatic planes of the carbon nanofibers and the iridium particles could provide particles exposing peculiar faces, and/or also developing specific electronic and adsorption properties, similar to those reported by other groups to explain very unusual catalytic behaviours.[8] The high performance for the catalytic decomposition of hydrazine over the iridium/carbon composite catalyst was also attributed to the extremely high external surface area of the composite support, which induces a high dispersion of the active phase. This high external surface area was observed because of the entangled carbon nanofiber structure.

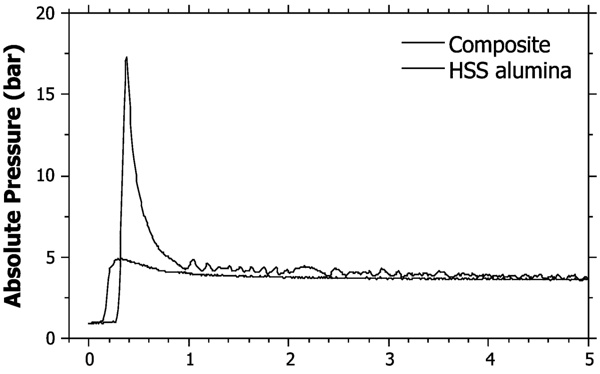

Fig. 2 Performance obtained on the graphite felt supported carbon nanofiber composite catalyst for hydrazine decomposition as compared to the high specific surface area alumina-based catalyst (HSS alumina).

It is worth noting that formation of fine powder occured when using the alumina-based catalyst which, after performing several successive catalytic shoots, led to a complete destruction of the material, probably due to the sudden pressure increase inside the pore network. No structural modification could be observed on the spent carbon composite as compared to the fresh material. This mechanical strength was assigned to the high mechanical stability provided by the graphite felt, which limited friction phenomena between the carbon nanofibers during the high pressure increase. The strong elasticity of the graphite felt support probably contributed to absorb the energy during the pressure shock inside the decomposition chamber. The high thermal conductivity of the carbon composite also led to a rapid and homogeneous dispersion of the heat across the overall material, whereas hot spots should occur on the insulator alumina-based catalyst. This probably contributed to the fragilization of the alumina catalyst. In addition, the iridium particles completely sintered after a series of runs on the alumina-based catalyst, giving the surface a molten aspect, whereas, only a slight sintering of the iridium particles, *i.e.* 3 nm instead of 2 nm after a dozen of hydrazine decomposition cycles, was observed on the carbon composite and the homogeneous dispersion of the metal phase was left quite unchanged. The pressure generation during the catalytic decomposition of hydrazine remained almost unchanged after a dozen injections evidencing the high mechanical stability of the composite-based catalyst. A more erratic behaviour in the catalytic decomposition of hydrazine has been observed on the alumina-based catalyst, probably due to the beginning of the catalyst body breaking as reported above.

In conclusion, a pre-shaped carbon nanofiber supported iridium catalyst can be prepared, conserving the macrostructural and mechanical flexibility properties of the graphite felt precursor. The graphite felt supported carbon nanofiber composite can be efficiently used as a catalyst support for the decomposition of hydrazine with higher performance as compared to the industrial catalyst, due to the high external surface area, providing a close contact between the reactant and the active phase. This new catalyst is resistant to the great increase in pressure which occurs inside the decomposition chamber. The macroscopic design of such a composite could open new routes for feasible industrial uses of carbon nanostructures, which remained problematic up to now, due to the powder form of the primary structure.

Notes and references

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