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Performance comparison of Ir/CNF and Ir/Al_2O_3 catalysts in a 2 N hydrazine microthruster

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The aim of this work is to report the catalytic performances of iridium supported on carbon nanofibre (CNF) with macroscopic shaping in the catalytic decomposition of hydrazine. The performances obtained are compared to those of the commercial catalyst Shell 405. Catalytic experiments are carried out in a 2 N microthruster. The CNF-based catalyst shows better activity performances than the commercial one due to its high external surface area and its high thermal conductivity.

KEY WORDS: carbon nanofibres; catalytic support; hydrazine decomposition; microthruster; satellite propulsion.

1. Introduction

Today most of the satellites in orbit use monopropellant hydrazine as propulsion subsystem for orbit correction and positioning operations. The thrust is obtained by catalytic decomposition of the monopropellant on a highly loaded catalyst containing about 30–40% of iridium supported on alumina. Anhydrous hydrazine decomposition initially leads to nitrogen and ammonia and then ammonia is further decomposed into nitrogen and hydrogen [1]. The first decomposition is a structure-insensitive reaction, whereas ammonia decomposition is a structure-sensitive reaction, where the large iridium particles are more active than the small ones [2]. It is of interest to find a new catalytic system, which can provide high dispersion of the metal along with a macro- and meso-porous network in order to increase the active sites accessibility. Support with higher thermal conductivity is also needed in order to decrease hot spots formation. The support should also exhibit a high mechanical strength in order to survive the repeated chocks during operation.

Recently, several authors have reported the use of carbon nanofibres (CNFs) as support catalysts in gas and liquid phase processes [3–5]. The main advantages of these carbon supports are due to (i) its strong metal/support interaction caused by surface prismatic planes, (ii) its high specific surface area and (iii) the absence of pores reducing the diffusion phenomena. Nevertheless, the nanometric size of the CNFs can cause reactor loading problems and pressure drop, which render their use in a large-scale reactor configuration impossible. Supporting CNFs on a macroscopic host allows the conservation of their advantages, while diffusional phenomena can be suppressed [6]. CNFs composite supported on a macroscopic host, i.e., disc, cloth or foam, was synthesized through a chemical vapour deposition technique [7]. CNF composite impregnated with 30 wt% of iridium was successfully tested in the catalytic decomposition reaction of hydrazine in a micro-pilot plant under laboratory conditions [8]. The aim of the present work is to report the catalytic performance of the iridium supported CNFs composite catalyst in a bench scale set-up and compared with that of the commercial catalyst. The catalyst characteristics were investigated by means of scanning electron microscopy (SEM) and transmission electron microscopy.

2. Experimental

2.1. Preparation of the catalyst

The carbon felt (Carbone Lorraine Co.) with a specific surface area of 1 $m^2\ g^{-1}$ was impregnated with 1 wt.% of nickel and placed in a quartz tube located in a horizontal oven under hydrogen flow. After reduction at 400 °C for 2 h, the temperature was raised from 400 to 680 °C and hydrogen flow was replaced by the reaction mixture containing hydrogen and ethane with an appropriate molar ratio. The synthesis time was carried out at 680 °C for 2 h and the CNFs yield was amounted to about 100 wt% with respect to the initial catalyst weight [9]. The CNFs yield obtained in the present work was among the highest yield obtained today. This high performance was attributed to the existence of a peculiar

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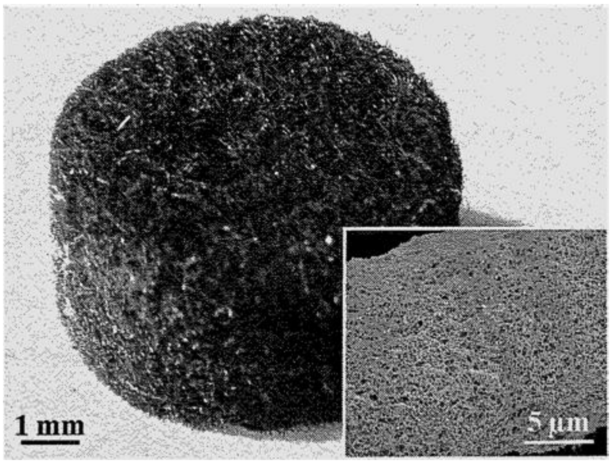

Figure 1. Photograph of a CNF composite. Inset:SEM image of a felt microfibre covered by CNFs.

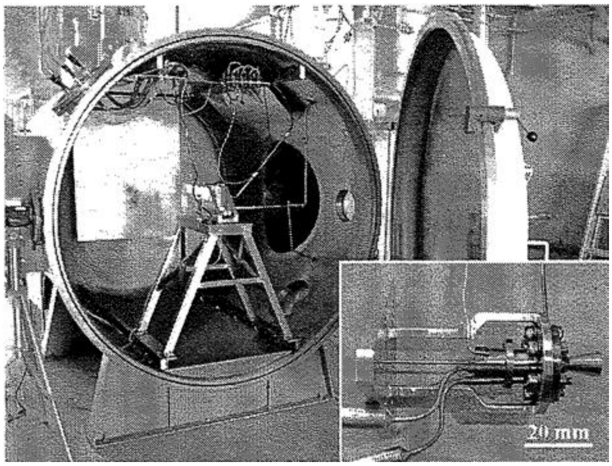

Figure 3. Photograph of the vacuum chamber of the Test Bench of the INPE. Inset: 2 N microthruster used during the tests.

interaction between the deposited nickel catalyst and the graphite surface of the macroscopic host leading to the formation of active nickel faces for hydrocarbon decomposition and CNFs secretion. SEM images obtained (figure 2) show that the CNFs grow from a single nickel centre with an homogeneous diameter, i.e. 30 nm, and with a length of several hundred nanometers.

The formation of CNFs significantly increases the specific surface area of the composite from 1 to 85 m^2 g^{-1}. The composite was cut in cylinder forms with 7 mm of diameter and 7 mm of height (figure 1).

These cylinders were impregnated with 30 wt% of iridium using a alcoholic solution of hexachloroiridic acid, and the resulting wet solid was dried at 100 °C for 2 h. The catalyst was reduced at 500 °C for 2 h followed by thermal treatment at 500 °C during 24 h (figure 2). This treatment had two objectives:first to eliminate chlorine remaining on the catalyst surface responsible for the non-desirable mobility of the metallic particles during the fire tests [10]; second to enlarge the particle sizes and consequently increase the catalyst selectivity in hydrogen.

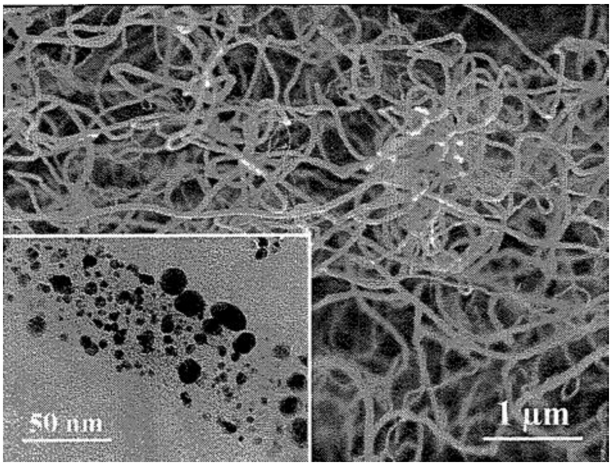

Figure 2. SEM image of CNFs. Inset: TEM image of a nanofibre covered by iridium particles.

2.2. Test conditions

The catalysts were tested in a bench scale fire tests (figure 3) constituted by a vacuum chamber that allowed to simulate the pressure conditions in space and an acquisition data system. The tests were carried out with a 2 N microthruster designed to operate with the commercial catalyst Shell 405. The dimensions of the microthruster reaction chamber were 6.7 mm diameter for 20 mm length. The microthruster was loaded with 1.14 g of the reference catalyst and with 0.15 g of the CNF-based catalyst.

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

Table 1
Operating conditions of the propellant valve

Test	P_{inj} (bar)	t_{on} (ms)	t_{off} (ms)
1	5.5	20	980
2	5.5	100	900
3	5.5	200	800
4	5.5	500	500
5	5.5	5000	–
6	22	20	980
7	22	100	900
8	22	200	800
9	22	500	500
10	22	5000	–

Note: P_{inj}, Propellant pressure injection; t_{on}, pulse-on; and t_{off}, pulse-off modes.

2.3. Performance evaluations

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

3. Results and discussion

Table 2 shows the thrust average values of a series of 100 pulses in different conditions of hydrazine injection.

The CNF-based catalyst showed superior thrust (F) performances than the reference catalyst. This better performance can be explained by the large metallic surface exposed on the CNF-based catalyst, despite the mass introduced in the microthruster, which is 10 times lower than the quantity used with the commercial catalyst. This performance can also be attributed to high external surface area of the support, which provides a high accessibility to the reactant. In this type of reaction, where the heat and mass transfers must be very fast, the reactant does not have time to penetrate the pores and the main reaction occurs on the external surface of the catalyst grains. This fact can be confirmed by the increase of the performance of the Shell 405 in relation to the Ir/CNF tested at 22 bar. The feed pressure increase allows the propellant to penetrate deeply inside the pores of the reference catalyst and, as a consequence, significantly increases the decomposition rate. The temperature values (T_c) showed in table 2 represent the maximum values measured on the external wall of the microthruster during each test of 100 consecutive pulses. The lower temperature value observed on the Ir/CNF catalyst compared to the one observed on the reference catalyst was due to the fact that carbon thermal conductivity is superior to alumina, leading a better evacuation of the heat generated during the decomposition reaction.

Figure 4 shows the evolution of the pressure generated in the reaction chamber during the hydrazine decomposition. Both catalysts did not show instability superior to 10% and spiking superior to 50% of the steady state pressure.

The pressure response time is considered as the time required to reach 90% of the steady-state chamber pressure. The Ir/CNF and Shell 405 catalysts showed an ignition delay of 46 and 62 ms at 5.5 bar respectively. In the tests at 22 bar, both catalysts presented similar performances, the ignition delay were of 41 and 43 ms for the Ir/CNF and Shell 405 catalysts. In the lower pressure level, the CNF catalyst has a more spontaneous restarting capability than the Shell 405. The performance of the Shell catalyst increases with the propellant

Table 2

Catalytic performance comparison between Ir/CNF and Shell 405 catalysts:thrust (F) and temperature chamber (T_c)

	P_{inj} (bar)	$t_{on}20/t_{off}980$		$t_{on}100/t_{off}900$		$t_{on}200/t_{off}800$		$t_{on}500/t_{off}500$	
		F (N)	T_c(°C)	F (N)	T_c(°C)	F (N)	T_c (°C)	F (N)	T_c(°C)
Shell 405	5.5	0.34	380	0.56	550	0.63	610	0.66	680
Ir/CNF	5.5	0.40	340	0.55	520	0.85	610	0.75	660
Shell 405	22	0.44	440	2.25	580	2.25	730	2.25	780
Ir/CNF	22	1.20	420	2.25	530	2.65	560	2.20	640

The tests were carried out in a 2 N microthruster under different propellant injection pressures (P_{inj}) and pulses mode (t_{on}/t_{off} in ms).

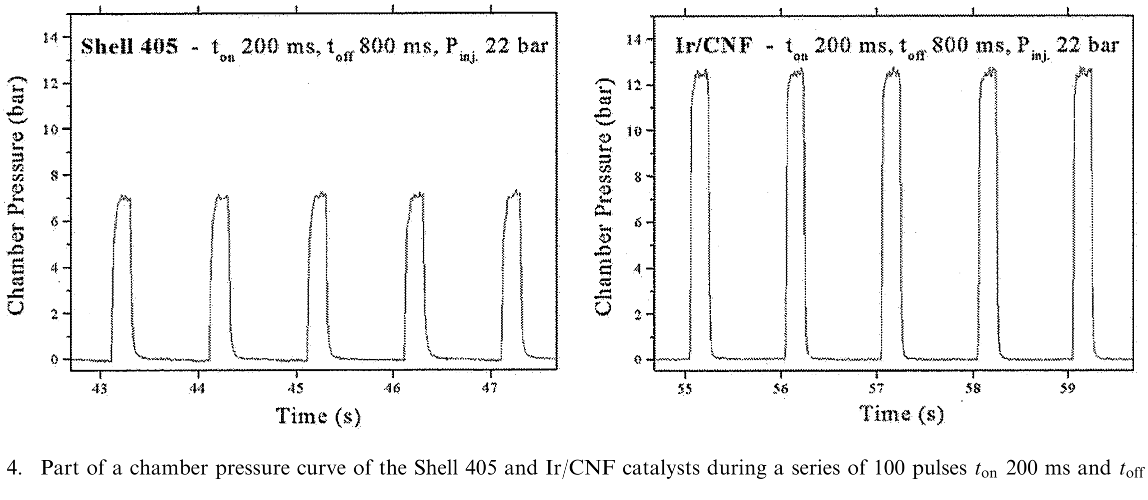

Figure 4. Part of a chamber pressure curve of the Shell 405 and Ir/CNF catalysts during a series of 100 pulses t_{on} 200 ms and t_{off} 800 ms.

injection pressure due to a better penetration of the propellant in the pores of the catalyst, allowing the active sites, located in the interior of the pores, to participate in the reaction.

4. Conclusion

The results show that for the decomposition reaction of hydrazine iridium catalyst deposited on CNF composite has a better performance than a commercial catalyst supported on alumina. This better performance is attributed to the high external surface area of CNFs, which facilitates the monopropellant diffusion in the catalyst. Moreover, the high thermal conductivity of the 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 and catalyst body conservation. The performance of the commercial catalyst increases with the rise of the propellant injection pressure, which provided a deeper penetration of the hydrazine in the catalyst pores. Finally, the CNFs composite can also be used efficiently as catalytic support in liquid phase reactions, where diffusional phenomena of the reactants are essential and in reactions that present high mass and heat transfers.

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