Aerospace Science and Technology 46 (2015) 197–203

Contents lists available at ScienceDirect

Aerospace Science and Technology

www.elsevier.com/locate/aescte

Lanthanum doping for longevity of alumina catalyst bed in hydrogen peroxide thruster

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ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 19 May 2015
Accepted 7 July 2015
Available online 13 July 2015

Keywords:
Lanthanum doped alumina
Hydrogen peroxide
Thruster
Catalyst longevity
Endurance test

ABSTRACT

The effects of doping alumina catalyst supports with lanthanum were investigated in terms of catalyst performance in a high concentration hydrogen peroxide monopropellant thruster. The catalyst support was doped with lanthanum by wet impregnation method in different conditions and characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and bulk crushing strength (BCS) test. XRD showed adequate crystal structure by doping lanthanum on alumina and BET analysis demonstrated that the reduction of active surface area was modest, even though the catalyst was cured at a temperature higher than the phase transition temperature of alumina. The BCS test exhibited a 57.75% increase in the mechanical strength of the lanthanum doped alumina compared to pure γ-alumina. A 50 N monopropellant thruster was built and firing tests were conducted to examine the longevity of manganese oxide lanthanum doped alumina catalyst. The catalyst pellets were removed from the thruster and analyzed. The experimental results have shown significant improvements in the longevity of the catalyst. The firing tests have shown significant improvement in catalyst volume loss, along with characteristic velocity efficiency higher than 98%. The catalyst with lanthanum doped alumina has also shown better pressure stability and a steady pressure drop across the catalyst bed.

1. Introduction

Monopropellant thrusters have been extensively used for the reaction control system and altitude control system of a spacecraft. Hydrogen peroxide was one of the first monopropellants used in the thruster for the ACS of the Mercury project's manned spacecraft [1]. With the advent of better performing hydrazine, however, the use of hydrogen peroxide as a monopropellant has slowly faded. Strict environmental regulations and ever rising cost of handling hydrazine rekindled interest in hydrogen peroxide [2]. With improved stabilizer, hydrogen peroxide can be stored safely for longer. Hydrogen peroxide as a monopropellant has other advantages over hydrazine, such as lower vapor pressure, higher density and higher specific heat [3,4].

The catalyst of a monopropellant thruster decomposes the liquid monopropellant and releases a large amount of thermal energy which evaporates the decomposed species and heats them up to a high temperature. As a consequence, the catalyst bed of a monopropellant thruster is subjected to a harsh environment that is difficult to endure for typical catalyst material [5]. A good catalyst bed should maintain its specific surface area and resist breakup at high mass flow rate of the propellant to deliver the design thrust. A number of materials have been tested as catalyst supports: silver screen [6–8], monolith with alumina wash coated [9,10], and commercial alumina pellets [11–13]. Silver screens have been widely used for hydrogen peroxide decomposition ever since the dawn of space age and are still used in some spacecraft. The channeling effect that is typical in a silver screen however undermines the uniformity of the propellant flow [14]. As for monolith honeycomb, it has been widely used in automobile catalytic converters for its durable mechanical strength. Its specific surface area is low, but it could be increased with alumina wash coating. Separation of propellant flow in the channel of honeycomb structures poses additional problems in the monolith catalyst support [12]. Alumina pellets represent a superior catalyst support with a large specific surface area of 200 m^2/g. At elevated operating temperatures, however, the specific surface area of γ-alumina decreases sharply as the mesopores in alumina pellets get clogged. Additionally, γ-alumina pellets easily break apart due to poor mechanical strength and the rapid expansion of product gases from the liquid monopropellant's catalytic decomposition.

The present paper reports the doping of alumina pellets with lanthanum to enhance their thermal, and mechanical resistance at

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http://dx.doi.org/10.1016/j.ast.2015.07.003
1270-9638/

Abbreviations and acronyms

BET	Brunauer–Emmett–Teller	BCS	Bulk Crushing Strength
XRD	X-Ray Diffraction		

Table 1
Lanthanum doped alumina preparation condition.

Condition number	Mole ratio ($La:Al_2O_3$)	Heat treatment temperature (°C)	Condition number	Mole ratio ($La:Al_2O_3$)	Heat treatment temperature (°C)
1	1:2.4	900	4	1:5.5	900
2	1:2.4	1000	5	1:5.5	1000
3	1:2.4	1100	6	1:5.5	1100

higher operating temperature and propellant flow rate without significant decrease in specific surface area. Additives such as La, Li, K, and Ba were employed to improve catalyst properties particularly in a high temperature environment [15–17]. These additives, when doped on the alumina pellets, alter the micro-structure of alumina, which is normally sintered at high temperature. Lanthanum proved effective in high temperature applications and was selected for the present study.

Lanthanum was doped on alumina by wet impregnation method in controlled preparation conditions to determine the optimum process. Control parameters included lanthanum doping ratio and heat treatment temperature. The prepared lanthanum doped alumina (La/Al_2O_3) was analyzed by X-ray diffraction (XRD) to examine the crystal structure, Brunauer–Emmett–Teller (BET) to survey specific surface area and porosity, and bulk crushing strength (BCS) test to examine mechanical strength. A 50 N hydrogen peroxide monopropellant thruster was designed and built specifically for the performance evaluation of the prepared catalyst in actual operating conditions. Manganese oxide was then loaded on the prepared catalyst bed ($MnO_x/La/Al_2O_3$) and another catalyst, γ-alumina with manganese oxide ($MnO_x/\gamma\text{-}Al_2O_3$), was used as a control group for the endurance test in the 50 N thruster.

2. Catalyst support and catalyst preparation

2.1. Catalyst support preparation

The lanthanum doped alumina catalyst support was prepared by wet-impregnation method. Commercial γ-alumina ($\gamma\text{-}Al_2O_3$, Alfa-Aesar) pellets were purchased, crushed and screened with a 10 to 16 mesh size (1.18–2.0 mm). Lanthanum nitrate ($La(NO_3)_3$, Sigma-Aldrich, 99.99% purity) was dissolved in deionized water. The amount of dissolved lanthanum nitrate was determined by mole ratio of lanthanum atom to alumina. In this paper, two mole ratios were tested: 1.2.4, and 1:5.5. The mole ratios were checked by Energy Dispersive x-ray Spectroscopy, with Magellan 400. The γ-alumina pellets were immersed into 0.75 M lanthanum nitrate aqueous solution, and dried at 105 °C. Heat treatment procedure then followed and three different heat treatment temperatures were tested: 900 °C, 1000 °C, and 1100 °C. The different catalyst support preparation conditions are summarized in Table 1.

2.2. Catalyst preparation

The active material, manganese oxide (MnO_2), was also introduced by wet-impregnation method. The preparation procedure was referred to the procedure from An et al. The 50 g of prepared catalyst supports were immersed into the 122.4 g of sodium permanganate solution ($NaMnO_4$ 40 wt.% aqueous solution, Sigma-Aldrich) to load 60 wt.% on the catalyst. They were then dried at 120 °C in a convection oven for 24 hours, and calcinated at 500 °C for 5 hours. The supports were washed by water and dried to remove impurities [18]. Fig. 1 shows the prepared $MnO_x/La/Al_2O_3$ catalyst. For our control group, manganese oxide was loaded on γ-alumina pellets by using the same preparation procedure. MnO_xLa/Al_2O_3 and $MnO_x/\gamma\text{-}Al_2O_3$ was 67.2 wt.%, and 62.6 wt.%, respectively.

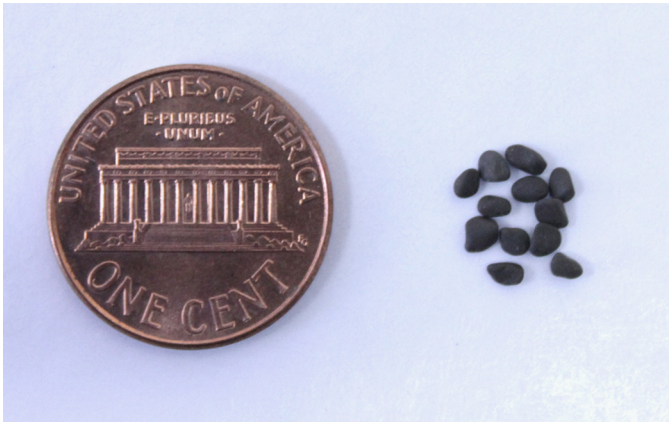

Fig. 1. The prepared $MnO_x/La/Al_2O_3$ catalyst.

3. Catalyst support characterization

3.1. XRD analysis

XRD analysis was conducted to examine the crystal structure on a RIGAKU D/MAX-2500 XRD machine with conditions of 40 kV, and 300 mA. Fig. 2 shows XRD analysis results, and they reveal that lanthanum aluminate was formed for all preparation conditions. ICDD number of $LaAlO_3$ was 031-0022. At conditions 1 and 4, structure of alumina was γ-alumina, and ICDD number was 056-0458. At conditions 2 and 5, δ-alumina was detected and ICDD number was 004-0877. At conditions 3 and 6, alumina structure were also δ-alumina, and its ICDD number was 00-046-1131.

3.2. BET analysis

BET analyses were conducted to survey the micro-structure of the prepared lanthanum doped alumina catalyst supports, and more specifically the surface area, and pore size and volume. BET analyses were conducted with nitrogen absorption isotherms at 77.3 K. Micromeritics' Tristar II 3020 system was used. Tables 2 and 3 show the analysis results, for the two different preparation mole ratios respectively.

The porosity affects the resistance to thermal rupture, which directly impacts durability. More porous material experienced more