

Article

Enhancing the Catalytic Performance of Platinum-Doped Lanthanum Hexaaluminate through Reduction Method Variation

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Abstract: The development of a catalyst for the ammonium dinitramide (ADN)-based monopropellant system has been of growing interest in space research. In this study, we investigated the development methodology for the platinum hexaaluminate (Pt-LHA) catalyst. The reduction of Platinum was performed in muffle and tubular furnaces by considering the different heating rates, with or without hydrogen gas flow conditions. The dispersion of Platinum on LHA was confirmed by using SEM analysis; the particle size of Platinum in Pt-LHA-1 and Pt-LHA-11 was 5.1–9.1 μm and <100 nm, respectively. Notably, agglomeration of Platinum was observed when the catalyst was calcinated in a muffle furnace without air or H_2 gas flow. Interestingly, the even dispersion of Platinum was revealed when the catalyst was calcinated in a tubular furnace at 4% H_2 in N_2 gas flow. As a result, Pt-LHA-7 to Pt-LHA-11 exhibited higher catalytic activity than Pt-LHA-1 to Pt-LHA-6 under H_2O_2 reactor conditions. The catalyst Pt-LHA-9 was further tested in a 1 N ADN thruster, demonstrating its capability to decompose the ADN-based monopropellant in an operation thruster.

Keywords: lanthanum hexaaluminate; platinum; LHA-based propellant; monopropellant; catalytic decomposition



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1. Introduction

Platinum-group elements play a vital role in various chemical reactions, both organic and inorganic, offering several important advantages to industrial and space applications [1–5]. Platinum impregnated on lanthanum hexaaluminate (LHA) [6], barium hexaaluminate (BHA) [7], monoliths [8], cerium oxide [9], $\text{Si-Al}_2\text{O}_3$ [10], $\gamma\text{-Al}_2\text{O}_3$ [2], etc. supports have been studied for high-temperature combustion reactions. Particularly, hexaaluminates have widely been used for high-temperature reaction conditions because their unique crystal structure grants them high thermal stability, with stable phase composition maintained even at temperatures up to 1600 °C [11]. Moreover, the impregnation method easily allows for the incorporation of Platinum or other active metals on the hexa-aluminate surface. It enhances the dispersion of the metals, resulting in improved textural properties and a higher number of redox centers. Additionally, these types of materials exhibit exceptional resistance to sintering and thermal shock, making them highly attractive for the decomposition of ADN-based monopropellants and other high-temperature applications [1,12–17]. R. Gugulothu, et al. [18] studied the catalytic decomposition of ADN using TGA–FTIR analysis and found N_2O , NO_2 , H_2O , and NH_3 prominent gaseous species upon combustion. Further, these gaseous species can react further with the catalyst and get decomposed into environment-friendly gaseous products such as N_2 and H_2O [17]. Our interest was to study the Platinum-doped hexaaluminate structure to decompose ADN-based monopropellants.

Maleix et al. [8,19] studied the Pt–Cu-based bimetallic catalyst doped on a monolith employed to decompose ADN-based propellant and found a lowering of the catalytic ignition temperature of 50 °C and 30 °C for FLP-106 and LMP-103S, respectively. The

decomposition temperature of LMP-103s was also lowered from 134 to 110 °C when only Platinum active metals were employed on monolithic support. Jeon et al. [20] also studied the Pt/Al₂O₃ and Cu/Al₂O₃ spherical beads for the decomposition of ADN-based propellant. The copper-based catalyst actively decomposed the propellant at a lower temperature than the Platinum-based catalyst. However, the formation was probable of Cu(NO₃)₂ during the combustion reaction [18]. Kang et al. [7] studied the combustion of HAN-based propellant on Platinum–Barium hexaaluminate catalyst in a thruster, and 71.9% combustion efficiency was achieved, showing the potential of the use of platinum catalyst in a real thruster. However, the different preparation conditions for Platinum catalysts and their catalytic activity for monopropellant decomposition have not been well understood. Hence, the research interest is to opt for the different calcination conditions to know the distribution of active metals on the LHA surface and measure their catalytic activity.

In this manuscript, we investigated the development methodology and catalytic performance of the Pt–LHA catalyst for the decomposition of ADN-based green monopropellants. The reduction of Platinum with or without H₂ gas was studied to find the reduction behavior of the Platinum group on the LHA surface. The dispersion of Platinum on LHA and its catalytic activity are discussed. Moreover, Pt–LHA catalyst performance was measured in a 1 N ADN thruster.

2. Experimental Section

2.1. Material and Methods

γ-Alumina pellet (1/8', Merck) was used as a source of support material for active metal. Lanthanum nitrate (La(NO₃)₃, Sigma Aldrich, Seoul, Republic of Korea) was used as a La source to prepare LHA. Chloroplatinic acid (H₂PtCl₆) was used as a source of Platinum impregnation on the surface of the LHA catalyst. Deionized water was used as a reaction medium to impregnate the metal on Al₂O₃. The phase composition of the catalyst was analyzed using an X-ray diffractometer RIGAKU SmartLab (manufactured in Tokyo, Japan). Sample data were acquired in the range of 10 to 90° (2θ) without making a catalyst powder with an incident K-alpha-1 optics monochromator. Scanning electron microscopy (SEM) was employed to scan the images of the catalyst using the Jeol JSM-IT800 (manufactured in Tokyo, Japan). A silver paste was used to prepare samples, and catalyst beads were scanned without the coating of conductive materials. The specific surface area of the catalyst was measured by N₂ adsorption and desorption measurements at 77 K using a Micromeritics Tristar II 3020 instrument (manufactured in Norcross, GA, USA), following the Brunauer, Emmett, and Teller (BET) method. X-ray photoelectron spectroscopy (XPS) spectra were measured using the Thermo VG Scientific, Sigma Probe (manufactured in Waltham, MA, USA). The Al Ka X-ray source of the dual anode was operated at 200 W. The analyzer was operated in the fixed analyzer transmission mode and set at a pass energy of 25 eV. All binding energies were calibrated relative to the Pt 4f_{5/2} peak at 71.2 eV. The density of the catalyst was measured using a Micromeritics AccuPyc II 1340 He gas pycnometer (manufactured in Norcross, GA, USA).

2.2. Catalyst Synthesis

The wet-impregnation method [11,21] was used to prepare a Pt–LHA catalyst (Figure 1). First, a 1/8' Al₂O₃ pellet was crushed by using a blender to get different mesh sizes such as 12–14, 14–16, 16–20, 20–25, and 25–30, and it was separated by using the sieving method. The desired mesh size (14–20) of γ-Al₂O₃ was polished in water by using an overhead magnetic stirrer at 300 rpm for 48 h. Next, γ-Al₂O₃ was cleaned using deionized water and dried in an oven at 100 °C for 24 h. The polished γ-Al₂O₃ was sieved again; a mesh size of 16–20 was used for further study.

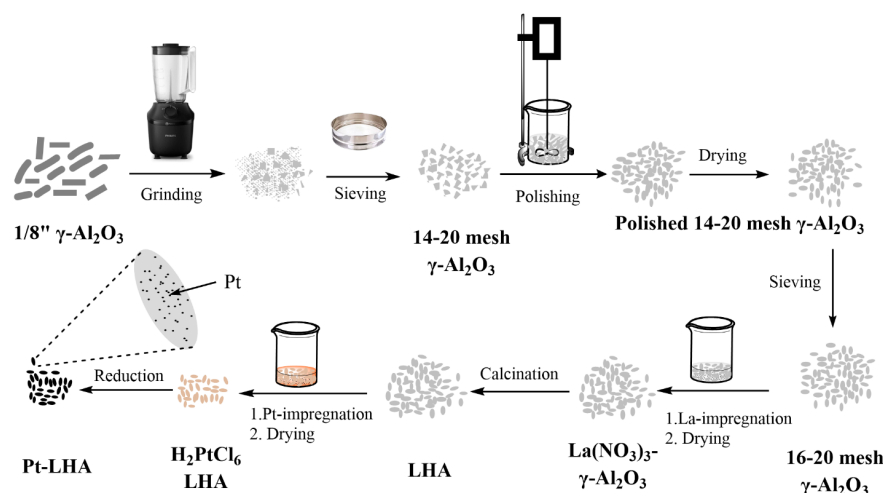


Figure 1. Schematic of synthesis Platinum-doped lanthanum hexaaluminate (Pt-LHA) catalyst.

2.2.1. Synthesis of Lanthanum Hexaaluminate (LHA)

The 1/5.5 equivalent ratio of La/ Al_2O_3 is required for the hexaaluminate phase formation. The required quantity of lanthanum nitrate was dissolved in water, and $\gamma\text{-Al}_2\text{O}_3$ (mesh size 16–20) was slowly added to the solution. The concentration of lanthanum nitrate in solution was 33 wt%. Further, the mixture was shaken for 5 min to ensure that there were no air bubbles in the solution. Consequently, it was dried in an oven at 60 °C for 12 h and 120 °C for 12 h. After drying, the material was calcinated at 900 °C (heating rate 2 °C/min and 2 h isothermal temperature), sintered for 4 h, heating rate 5 °C/min, and the isothermal temperature was 1400 °C in a muffle furnace. The furnace was closed, and heating was performed without the passing of any external gases during the process. However, there may be some air containing decomposed gases of lanthanum nitrate.

2.2.2. Pt Impregnation on LHA

A 20 wt% active metal, Platinum, was doped on the lanthanum hexaaluminate by the impregnation method. A 10 g of Chloroplatinic acid (CPA, a source of Platinum) was dissolved in water, and then 15 g of LHA was immersed in the solution. An effervescence was observed during the mixing of LHA. Further, the mixture was dried at 60 °C for 12 h, consequently, at 120 °C for 12 h. After drying, the catalyst was calcinated at 600 °C (at different heating rates and an isothermal temperature of 600 °C) for 4 h (Table 1). Catalysts Pt-LHA-1 to Pt-LHA-6 calcinated in a muffle furnace without gas flow under atmospheric conditions. However, the muffle furnace was closed; only a small vent (on the upper side of the furnace) was open. The catalysts Pt-LHA-7 to Pt-LHA-11 were calcinated in a tubular furnace with a 4% H_2 mixture and an N_2 gas flow of 0.2 L/min.

Table 1. Pt-LHA catalyst synthesis, mesh size 16–20.

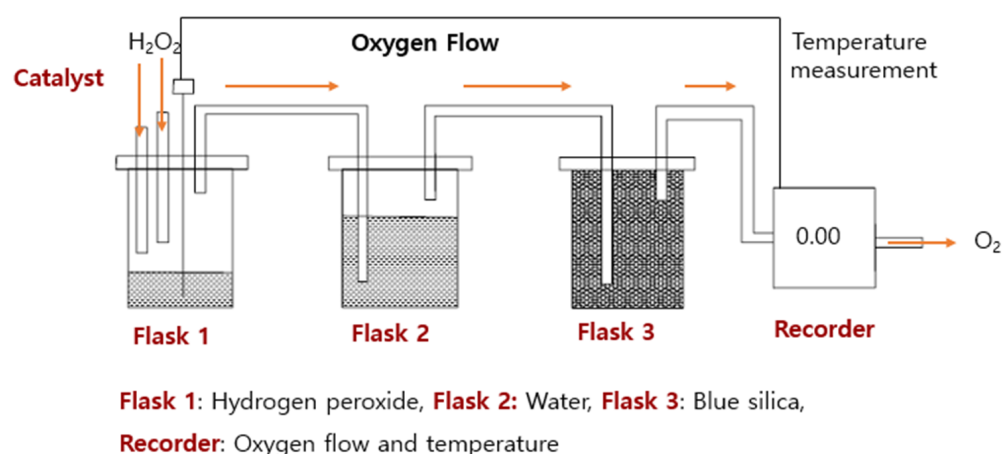
Catalyst	Weight before Calcination, g	Calcination Temperature, °C	Heating Rate, °C/min	Gas Flow, (0.2 L/min)	Weight after Calcination, g	Weight Loss (%)
Pt-LHA-1	3.02	600	5	-	2.53	16.05
Pt-LHA-2	3.10	600	4	-	2.61	15.84
Pt-LHA-3	3.21	600	3	-	2.71	45.39
Pt-LHA-4	3.28	600	2	-	2.79	15.06
Pt-LHA-5	3.64	600	1	-	3.11	14.55
Pt-LHA-6	3.15	600	0.5	-	2.76	13.84
Pt-LHA-7	2.29	600	5	4% H_2 + 96% N_2	1.93	15.74

Table 1. Cont.

Catalyst	Weight before Calcination, g	Calcination Temperature, °C	Heating Rate, °C/min	Gas Flow, (0.2 L/min)	Weight after Calcination, g	Weight Loss (%)
Pt-LHA-8	2.29	600	4	4% H ₂ + 96% N ₂	1.94	15.31
Pt-LHA-9	2.94	600	3	4% H ₂ + 96% N ₂	2.49	15.10
Pt-LHA-10	2.69	600	2	4% H ₂ + 96% N ₂	2.27	15.51
Pt-LHA-11	2.40	600	1	4% H ₂ + 96% N ₂	2.034	15.34

2.3. Catalytic Activity Test Using an H₂O₂ Reactor

Platinum is an active metal with H₂O₂ and easily decomposes H₂O₂ into H₂O and O₂. Hence, the catalytic activity of Platinum with H₂O₂ can be measured using an H₂O₂ reactor (Figure 2). Further, the H₂O₂ reactor was employed to measure the catalytic activity of Pt-LHA. It consists of 250 mL of borosilicate glass reaction flask (Flask 1), 100 mL of borosilicate glass water flask (Flask 2), and 500 mL of blue polyethylene silica flask (Flask 3). They were connected using Teflon tubing. The upper part of the flasks were closed by a sealing lid. A blank test was performed without a catalyst to confirm the reactivity of 70% H₂O₂ with reaction flasks, ensuring the safety of the flask for further catalyst tests.

Figure 2. Schematic of the H₂O₂ reactor.

A known mass of ~70 (69.42) wt% H₂O₂ was poured into reaction flask 1. Further, a given quantity of catalyst was added, and we immediately closed the flask for 10 min. The catalytic decomposition of H₂O₂ generates a hot gas mixture at nearly atmospheric pressure, which may comprise molecular oxygen, steam, and a small quantity of gaseous H₂O₂. These gases enter flask 2, which contains water, where their temperature is lowered and water vapor condenses. Further, gases may contain oxygen that was passed into flask 3 and purified using silica gel. The dry oxygen was measured using a gas flow meter. The temperature of flask 1 and the gas flow meter were connected to the portable data acquisition system to record data.

3. Results and Discussion

The synthesis of LHA from a pellet by the wet impregnation method is simpler than the so-gel and coprecipitation methods [11]. Hence, the wet impregnation method was employed to develop LHA support. When lanthanum nitrate was impregnated on γ -Al₂O₃ and calcinated at 900 °C, only the lanthanum oxide (La₂O₃) and gamma γ -Al₂O₃ phases were observed in the XRD graph (Figure 3).

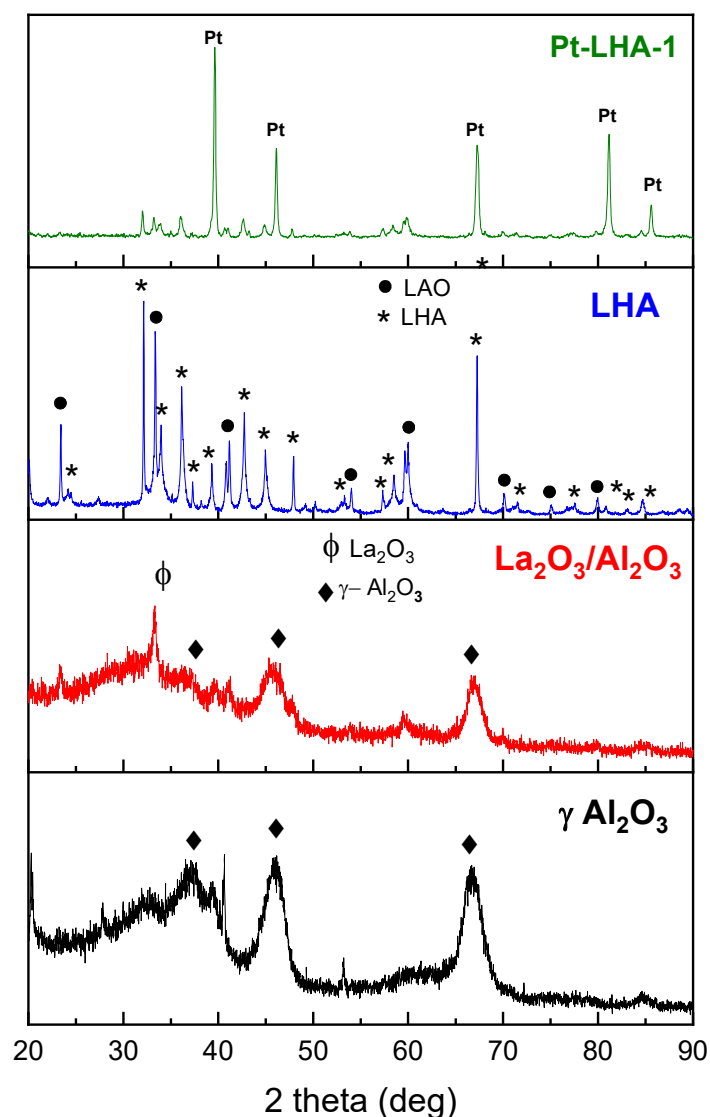


Figure 3. XRD graph of pure gamma Al_2O_3 , lanthanum doping in Al_2O_3 ($\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$), LHA, and Pt-LHA-1.

The LHA phase was confirmed when the material was sintered at $1400\text{ }^\circ\text{C}$. Interestingly, two different phases, such as lanthanum mono-aluminate (LAO) (Perovskite, JCPDS: 01-073-3684) and lanthanum hexaaluminate (LHA, JCPDS: 01-077-0311), were observed. The LHA phase can be formed when LAO reacts with $\gamma\text{-Al}_2\text{O}_3$. However, the LAO and LHA phases can be observed simultaneously when $\text{La}_2\text{O}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ is heated above $1150\text{ }^\circ\text{C}$ [12]. The complete LHA phase was not formed even though the catalyst was sintered at $1400\text{ }^\circ\text{C}$ and the surface area was $5.95\text{ m}^2/\text{g}$. A 20 wt% of Platinum was doped on the LHA surface by the impregnation method by employing different experimental conditions. The XRD peaks of Platinum (Pt-LHA-1) were matched with JCPDS (03-065-2868) and confirmed the Pt impregnation. In addition, the average density of Pt-LHA-1 was also measured, and it was 4.8 g/cm^3 .

The surface morphology of LHA and Pt-LHA-1 was revealed by SEM analysis. Generally, $\gamma\text{-Al}_2\text{O}_3$ has a porous structure in its original phase. However, the porous structure can be changed when it is treated with the doping element. Figure 4 presents the bright spots of Platinum (average size $3\text{--}6\text{ }\mu\text{m}$) on the LHA surface and confirms the impregnation of Platinum.

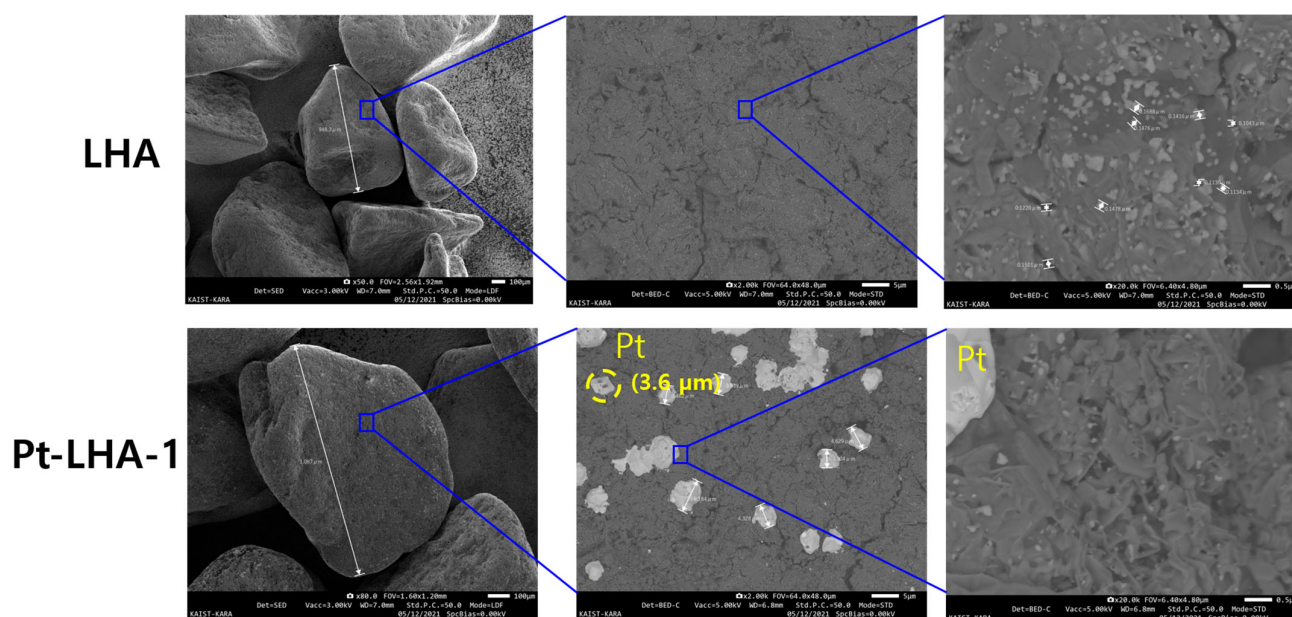


Figure 4. SEM images of LHA and Pt-LHA-1.

The EDS technique is useful for analyzing the surface composition of the specimen. LHA and Pt-LHA-1 contain Pt, Al, La, and O elements, which were detected using EDS (Figure 5).

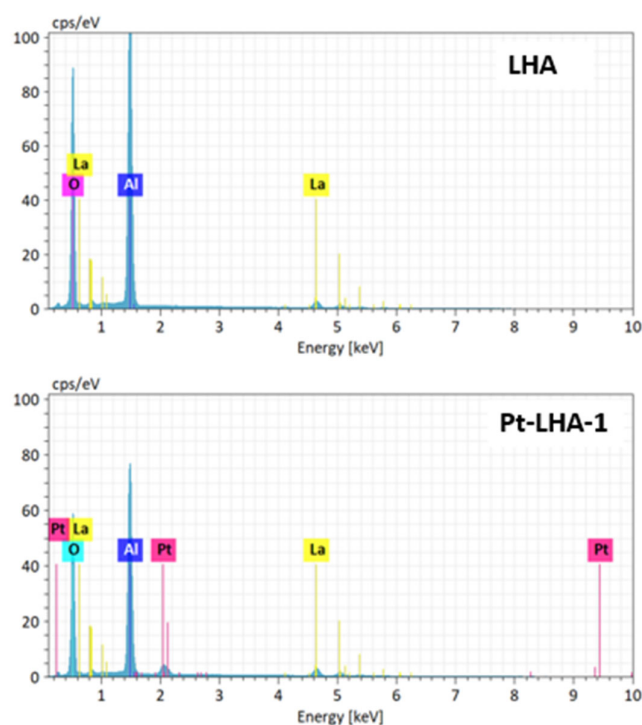


Figure 5. EDS spectra of LHA and Pt-LHA.

3.1. Effect of Calcination Temperature Heating Rate

The catalytic activity also depends on the distribution of active metals on the surface of the supporting material. We studied the effect of calcination temperature heating rate, which may significantly affect the Platinum dispersion on the LHA surface. Hence, the catalyst was reduced without pre-calcination in muffle and tubular furnaces at different heating rates. In general, the catalyst can be pre-calcinated in air and then reduced in H_2

gas flow for better dispersion [2]. However, our study was focused on the distribution of Platinum without pre-calcination. The SEM analysis technique was employed to reveal the dispersion of Platinum on the LHA surface. Before calcination, the catalyst was dried in an oven at 60 °C for 12 h and 120 °C for 12 h.

3.1.1. Calcination of Catalyst without Hydrogen Flow

The study aimed to find the dispersion of Platinum by considering the calcination of the catalyst without pre-calcination in a muffle furnace, without the flow of air or H₂ gas. The catalysts such as Pt-LHA-1, Pt-LHA-2, Pt-LHA-3, Pt-LHA-4, Pt-LHA-5, and Pt-LHA-6 were calcinated at different heating rates of 5, 4, 3, 2, 1, and 0.5 °C/min, respectively, in a muffle furnace without air or H₂ gas flow; the isothermal temperature was 600 °C for 4 h (Table 1). In general, the thermal decomposition of chloroplatinic acid above 510 °C can generate metallic Pt [22], and XRD results confirmed the calcination temperature of 600 °C was sufficient to reduce the Pt(IV) into the metallic form Pt(0) (Supplementary Materials—Figure S38). The catalyst fabricated at a low heating rate temperature exhibited a darker color than at a high heating rate temperature (Figure 6). However, the intensity of these black spots was different from the catalyst calcination temperature. Hence, our interest was to know the surface morphology of the catalyst to see Platinum dispersion by using the SEM technique.

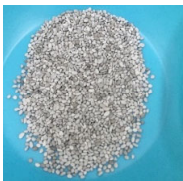
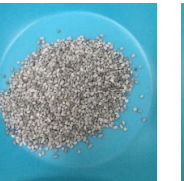
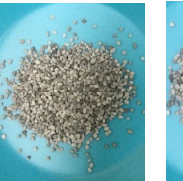
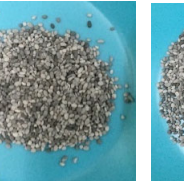
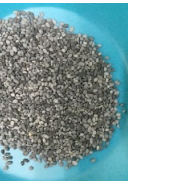
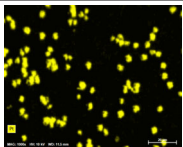
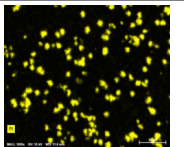
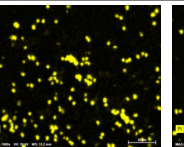
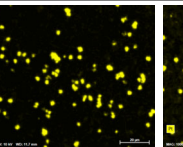
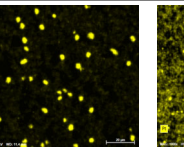
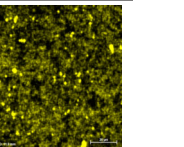
Catalyst	Pt-LHA-1	Pt-LHA-2	Pt-LHA-3	Pt-LHA-4	Pt-LHA-5	Pt-LHA-6
Images						
SEM mapping Images (20 µm) MAG: 1000x, HV: 10 kV, WD: ~11 mm						
PtAverage size (µm)	5.2–9.1	2.8–5.3	1.4–6.6	1.7–4.3	<3.4	<3.0
BET Surface area (m ² /g)	8.34	9.93	9.78	9.25	9.67	9.93

Figure 6. Images of catalysts from Pt-LHA-1 to Pt-LHA-6 calcinated without H₂ gas condition.

The SEM images of Pt-LHA-1 to Pt-LHA-6 were recorded, and the average Platinum size was measured (Supplementary Materials—Section S1). Notably, the surface area of Pt-LHA (8.34 to 9.93 m²/g) was improved over LHA (5.95 m²/g). The deposition of Platinum in an agglomerated form was seen on the surface of LHA. A catalyst calcinated at a high heating rate exhibited a larger size of Platinum agglomeration than the low heating rate condition (Figure 6). The Pt agglomeration size of Pt-LHA-1 (Supplementary Materials—Figure S1) was 5.2 to 9.1 µm, which was higher than Pt-LHA-7 (Supplementary Materials—Figure S7). Barbier et al. [23] describe the agglomeration of Platinum as due to the capillary condensation of water. The decomposition of chloroplatinic acid generates hydrochloric acid and water, which can desorb from the catalyst surface at a temperature above 300 °C. However, due to the capillary condensation phenomenon, the dissolution of PtCl₄ can occur, which can be dislodged from its site and then crystallize in large aggregates when complete water evaporates. In the case of Pt-LHA-1, a high heating rate reaction may generate high steam pressure, and capillary condensation occurs in larger pores as a result, lowering the dispersion of Platinum and aggregates into larger particle sizes. However, at a low heating rate, Pt-LHA-6 may generate partial steam pressure, and only small pores may

be involved in capillary condensation of water, which, as a result, increases the dispersion of Platinum and lowers Platinum agglomeration. Hence, considering this phenomenon, it was revealed that the agglomeration of particles increased with an increase in the heating rate of the catalyst. Furthermore, mapping images along with EDS spectra of Pt–LHA-1 to Pt–LHA-6 clearly distinguish the distribution of Pt, La, Al, and O on the catalyst surface (Supplementary Materials—Section S2).

3.1.2. Reduction of Catalyst with Hydrogen Flow

The catalyst reduction process was performed in a tubular furnace. A 4% H₂ in N₂ gas was used during the process at a flow rate of 0.2 L/min. The catalysts, viz., Pt–LHA-7, Pt–LHA-8, Pt–LHA-9, Pt–LHA-10, and Pt–LHA-11 were reduced at different heating rates of 5, 4, 3, 2, and 1 °C/min, respectively. The isothermal temperature was 600 °C for 4 h.

SEM images of catalysts Pt–LHA-7 to Pt–LHA-11 clearly show the distribution of Platinum particles on the LHA surface (Supplementary Materials—Figures S7–S11). However, the distribution of Platinum was not similar to that of the catalysts Pt–LHA-1 to Pt–LHA-6. Only Pt–LHA-7 shows small Pt agglomeration on the LHA surface; however, it is not similar to Pt–LHA-1 (Supplementary Materials—Figures S1 and S7). This may be due to the high-temperature heating rate, resulting in capillary condensation [23]. Catalyst Pt–LHA-8 to Pt–LHA-11 shows an even distribution without agglomeration of Platinum with an average size of ≤ 100 nm (Figure 7). As the Pt particle size was very small, powder XRD was used to understand the dispersion of the metal. The low-intensity broad peak of Pt–LHA-7 to Pt–LHA-11 was observed in the XRD graph (Supplementary Materials—Figure S39), revealing the dispersion of Pt on LHA with an average particle size of 60–80 nm. The effective dispersion of Pt may be due to the lowering effect of capillary condensation in a hydrogen gas environment. The passing of blowing gas (hydrogen gas) may help to dislodge the HCl and water steam immediately during the calcination process and lower the effect of capillary condensation on Platinum reduction. Moreover, the PtCl₄ intermediate may also be immediately reduced to Pt(0) without polymerization [23]. The heating rate was also not affected significantly by Platinum dispersion. This may be due to lowering the reduction temperature of Platinum in hydrogen gas flow conditions; the maximum hydrogen gas uptake has been reported at 375 °C [2,23,24]. The mapping images show the distribution of elements, such as La, Al, O, and Pt, on the catalyst surface (Supplementary Materials—Section S2). The particle size of Platinum is very small; hence, the TEM analysis technique is necessary for further investigation.

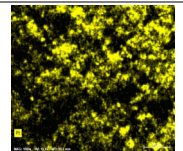
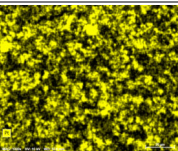
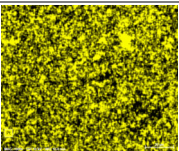
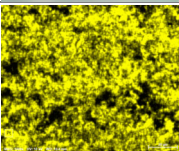
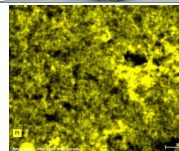
Catalyst	Pt–LHA-7	Pt–LHA-8	Pt–LHA-9	Pt–LHA-10	Pt–LHA-11
Images					
SEM Mapping Images MAG: 1000x, HV: 10 kV, WD: ~11 mm					
Pt _{average} size (nm)	≤ 100	≤ 100	≤ 100	≤ 100	≤ 100
BET Surface area (m ² /g)	8.40	8.11	8.45	8.59	8.45

Figure 7. Images of catalyst Pt–LHA-7 to Pt–LHA-11 calcinated in 4% H₂.

3.2. Catalyst Activity Using an H_2O_2 Reactor

The rate of decomposition of monopropellants depends on the catalyst activity. Hence, it is significant to know the catalyst activity before conducting the thruster test. However, the use of safe analytical tools known as the “batch reactor”, is necessary for studying the catalyst activity with ADN-based solutions. As we did not have the necessary equipment, we utilized a simple H_2O_2 reactor to test the catalyst activity. In addition, Platinum is reactive with H_2O_2 at room temperature. Hence, considering the advantages, Pt catalyst reactivity was measured using a simple H_2O_2 reactor. The H_2O_2 reactor test was a representative method for the initial screening of catalysts for ADN thrusters based on their catalytic activity. The catalyst activity of different catalysts, such as Pt-LHA-1 to Pt-LHA-6 and Pt-LHA-7 to Pt-LHA-11, was measured with 69.42 wt% H_2O_2 . The catalyst activity was compared based on the oxygen flow rate results, and furthermore, a suitable catalyst was selected for the 1N ADN-based monopropellant thruster. The catalyst amount and quantity of H_2O_2 were ~0.0200 g and ~50 g, respectively (Table 2), and the reaction time was 10 min for each test.

Table 2. Experimental parameters for the catalyst activity test.

Catalyst	Catalyst Weight Taken (g)	Weight of 69.42 wt% H_2O_2 (g)	Concentration of H_2O_2 after Reaction (wt%)
Pt-LHA-1	0.0201	50.6	68.46
Pt-LHA-2	0.0200	50.7	68.21
Pt-LHA-3	0.0200	50.3	67.98
Pt-LHA-4	0.0201	50.6	67.96
Pt-LHA-5	0.0202	50.6	67.72
Pt-LHA-6	0.0199	50.3	66.33
Pt-LHA-7	0.0200	50.13	65.15
Pt-LHA-8	0.0201	50.16	65.53
Pt-LHA-9	0.0199	50.42	65.40
Pt-LHA-10	0.0200	50.09	64.20
Pt-LHA-11	0.0199	50.65	63.67

Pt-LHA can decompose H_2O_2 into water and oxygen, and oxygen can then be measured using a mass flow meter. In this experiment, the graph of oxygen gas flow (L/min) was recorded concerning time; the average oxygen flow rate of the selective curve section was considered for comparison of catalyst activity (Supplementary Materials—Figures S36 and S37). In addition, the concentration of H_2O_2 remaining in the reaction flask was measured using a refractometer (Table 2). The catalyst, Pt-LHA-11 exhibited the highest oxygen flow rate and proportionally low concentration of H_2O_2 (63.67 wt%) compared to the other catalysts. The oxygen flow rate results of catalysts Pt-LHA-7 to Pt-LHA-11, were higher than those of catalysts Pt-LHA-1 to Pt-LHA-6 (Figure 8). It may be concluded that the catalyst calcinated in a muffle furnace has lower catalytic activity than the catalyst calcinated in a tubular furnace. The distribution of Platinum on LHA was improved from Pt-LHA-1 to P-LHA-6; similarly, catalytic activity was also improved. SEM images revealed that Pt-LHA-6 has a smaller size ($\leq 3.0 \mu\text{m}$) of metallic Platinum than Pt-LHA-1 ($\geq 5.2 \mu\text{m}$), hence there may be more active sites on LHA for H_2O_2 decomposition. The only difference in catalyst development was their heating rate. The low heating rate catalyst synthesis process revealed a smaller Platinum particle size than the high heating rate catalyst synthesis conditions; hence, Pt-LHA-6 shows improved activity for H_2O_2 decomposition.

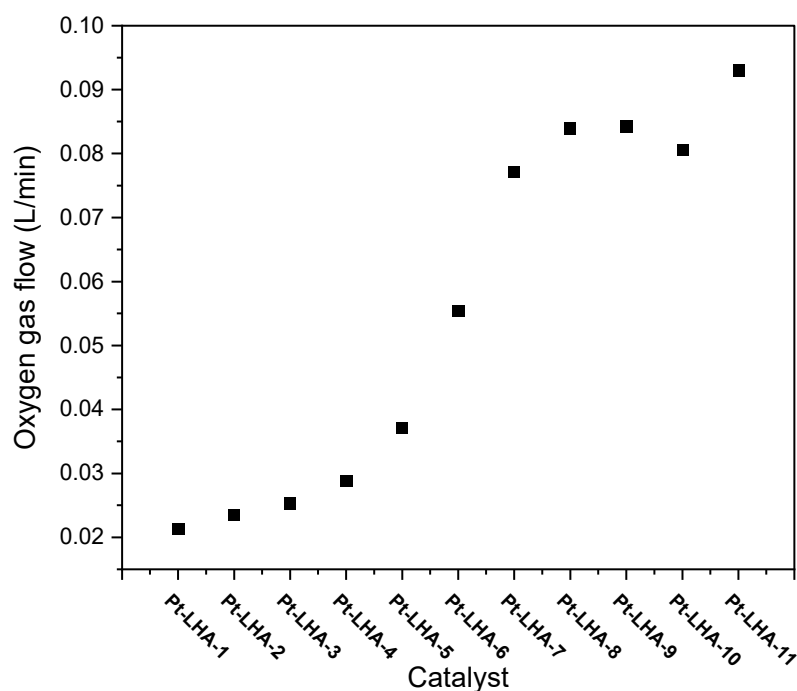


Figure 8. Oxygen flow rate measurement of different Pt-LHA catalysts using an H_2O_2 reactor.

Furthermore, the catalyst Pt-LHA-7 to Pt-LHA-10 effectively decomposed the H_2O_2 and delivered oxygen flow in the range of 0.077 to 0.084 L/min. Interestingly, Pt-LHA-11 delivers more efficient decomposition capability (oxygen flow, 0.093 L/min) than the other catalysts mentioned (Figure 8). This may be due to the small size of Platinum on the LHA surface, which gives it better catalytic activity. The small size of Platinum may provide more active sites that can be available for the decomposition of propellants. It means that the catalysts Pt-LHA-7 to Pt-LHA-11 may be selective catalysts for ADN-based propellant thrusters. Furthermore, the temperature of Flask 1 containing H_2O_2 in each experiment was measured. According to the catalytic activity of each catalyst, the temperature was changed (Supplementary Materials—Figures S36 and S37).

3.3. Hot Fire Test

Our research goal was to find a suitable catalyst for the decomposition of ADN-based propellant for a 1 N monopropellant thruster. In the H_2O_2 activity test experiment, it was found that the catalyst Pt-LHA-1 to Pt-LHA-6 was less active than the catalyst Pt-LHA-7 to Pt-LHA-11. Hence, the catalyst Pt-LHA-9 was used in this study. With the addition of a thermal bed, the total quantity of catalyst in the catalyst bed was 1.5 g. The total propellant combusted on the catalyst was 182 g in 365 s. Figure 9 shows the schematic of the reactor and one representative result of the hot fire test. It was found that the reactor achieved the desired chamber pressure (10 bar) with a maximum temperature of 1332 °C at T2. Hence, it can be concluded that the development process of a platinum-based catalyst may be suitable; further catalysts can be used for the decomposition of an ADN-based monopropellant propulsion system. Figure 10 shows the catalyst condition after the thruster test; the bright spots of Platinum particles were found on the uneven surface of LHA. Furthermore, the surface area of the catalyst was lowered from 8.45 to 4.1 m^2/g . It can be confirmed that the physical condition of the catalyst changed after the firing test.

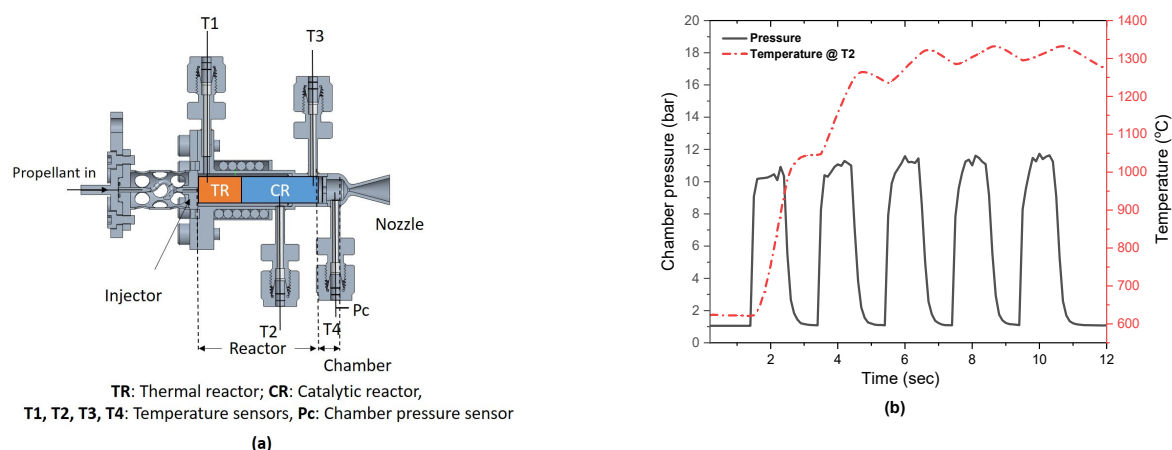


Figure 9. (a) Pictorial view of a monopropellant engine and (b) representative test data of a hot fire test, temperature, and pressure curves.

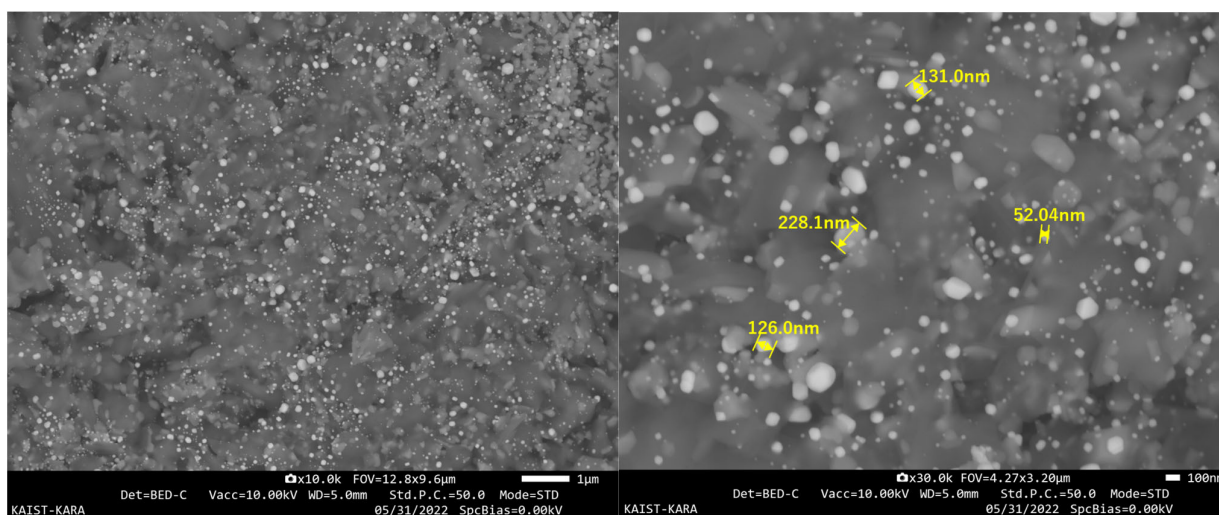


Figure 10. SEM image of the catalyst after the hot fire test.

3.4. XPS Analysis

The surface chemistry of Pt-LHA-9 was investigated using X-ray photoelectron spectroscopy (XPS). This technique helps to investigate the active phase of Platinum that can be responsible for the decomposition of ADN-based propellant. Platinum can be reduced into different chemical forms, such as Platinum metal, PtO, and PtO₂. The outermost *f* orbitals (4*f*_{5/2} and 4*f*_{7/2}) and *d* orbitals (Pt4*d*_{3/2} and 4*d*_{5/2}) of Platinum-ejected electron binding energy can be measured using XPS (Figure 11a). The peaks from the XPS spectra provide a relative number of electrons with a specific binding energy. The asymmetric peaks of the 4*f* orbital were observed at different binding energies; the peak was located at 73.2 (Pt4*f*_{5/2}) and 69.9 (Pt4*f*_{7/2}), indicating the presence of Pt(0) [25,26]. Similarly, the binding energy of the *d* orbital was also measured; the peak of Pt4*d*_{3/2} and Pt4*d*_{5/2} was exhibited at 330.3 and 313.5, respectively, confirming Pt(0) (Figure 11b). Furthermore, XPS spectra of Pt-LHA-9 after the combustion test were also measured to confirm the chemical or electronic change of Platinum metal. Interestingly, a similar asymmetric spectrum of 4*f* and 4*d* orbitals was found (Figure 11), except for the intensity of electron counts. It does indicate that Platinum does not undergo any chemical change even after being exposed to very high adiabatic temperatures in acidic conditions.

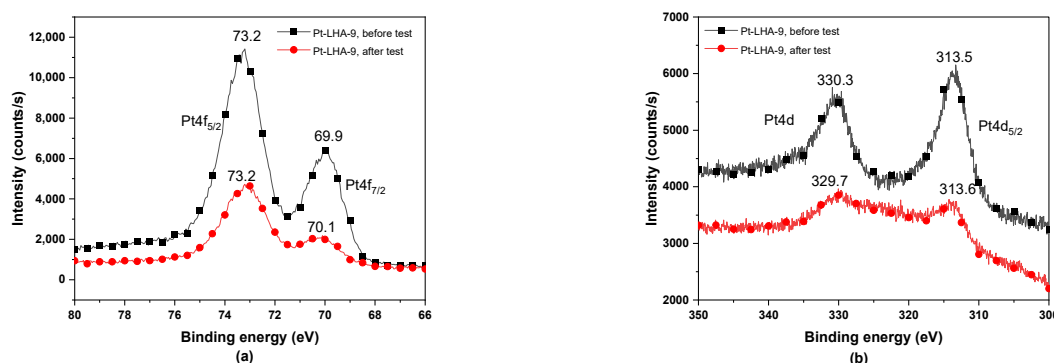


Figure 11. XPS spectra of Pt-LHA-9 before and after test (a) f orbital and (b) d orbital.

4. Conclusions

In summary, the study was focused on the dispersion of Platinum on the LHA surface using various calcination conditions. The results showed that the Platinum was agglomerated on the LHA surface when it was calcinated in the muffle furnace. More Platinum agglomeration was observed at a high-temperature heating rate, which may be due to the capillary condensation of water. For example, Pt-LHA-1 has Platinum size of 9.1 μm and Pt-LHA-5 has a size of 2 μm . Interestingly, when the catalyst was calcinated in hydrogen gas conditions in a tubular furnace, it resulted in smaller, non-agglomerated Platinum particles. SEM analysis supported the confirmation of the distribution of Platinum on the LHA surface. However, the small size of Platinum particles required to be confirmed by using the TEM analysis technique. Pt-LHA-6 to Pt-LHA-10 displayed higher activity compared to Pt-LHA 1 to Pt-LHA-5 when tested in the H_2O_2 reactor. Furthermore, Pt-LHA-9 demonstrated effective performance in a 1 N ADN monopropellant thruster, achieving a chamber pressure of 10 bar and a decomposition temperature exceeding 1300 $^\circ\text{C}$. The oxidation state of Pt(0) was the active and responsible phase for the ADN decomposition and was revealed by XPS analysis. However, the Pt-LHA-9 catalyst condition was changed after the firing test and was confirmed by using SEM and BET analysis. To conclude, the study highlights that the reduction of the Pt-LHA catalyst in an H_2 atmosphere leads to favorable dispersion and activity for ADN-based monopropellant applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13111413/s1>, Figures S1 to S11: Catalyst SEM images; Figures S12 to S35: Catalyst mapping images and EDS spectrum; Figures S36 and S37: Catalyst activity test; Figures S38 and S39: XRD graphs.

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Conflicts of Interest: The authors declare no conflict of interest.

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