PREPARATION AND CHARACTERIZATION OF LANTHANUM HEXAALUMINATE GRANULE FOR CATALYTIC APPLICATION IN AEROSPACE TECHNOLOGY

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1 Introduction

Monopropellant thruster using hydrazine as fuel has been a standard propulsion system for satellite attitude and altitude control. Liquid anhydrous hydrazine is decomposed into nitrogen, hydrogen and ammonia with large amount of heat upon the contact with the catalytic surface consisting of 30 wt% Ir on alumina support. Thus, the catalyst and reactor's temperature can be raised to 1273 K. *The state of art* catalyst technology provides a sufficient performance under high temperature and high pressure condition.[1]

However, hydrazine as carcinogen is very toxic, and is difficult to handle. It needs extensive safety system for fueling, resulting in high cost. Thus, R & D on small satellite in university and research institute suffered the problem of handling hydrazine in small scale without extensive safety system. [2]

Furthermore small and low cost satellites have very limited space, so propellant density is important. Therefore, it has been emphasized to develop the environmentally benign thruster system using other fuel and high density propellant than hydrazine. Hydroxylammonium nitrate (HAN), hydrazinium nitroformate (HNF), ammonium dinitramide (ADM) and ammonium nitrate (AN) blends have been considered as one of green propellants that can substitute hydrazine without sacrificing the thruster performance. However, the adiabatic combustion temperature of those blends is too high such as 1473 - 1673 K. Moreover, at higher pressures, 60 atm, a final flame temperature is raised to 2073 K.[3]

During high temperature combustion reaction, catalyst on alumina support is sintered and the alumina support undergoes phase transition to corundum, resulting in the degradation of catalytic activity.

Therefore, it is prerequisite to develop the high temperature catalyst support to maintain the catalytic reaction at 1473 - 1673 K. Hexaaluminate has been investigated extensively for the application of methane combustion in gas turbine.[4] The hexaaluminate has a high thermal stability associated with special layered crystal structure that is consisted of γ-Al_2O_3 spinel which is isolated by large ions, La, Ba, Sr, Ca etc.[4] Further it contains the relative low creep rate at temperatures higher than 1373K. These hexaaluminates can be prepared in powder form using either micro emulsion or alkoxide method. Therefore, the fabrication of the shaped body from the hexaaluminate powder is essential for the catalytic application in the propulsion system.

In this work, the lanthanum hexaaluminate-based catalyst was prepared as granule starting from the γ-Al_2O_3 alumina granule using simple impregnation.

2 Experimental

2.1 Preparation

Crystalline $Al(OH)_3$ (KC Chemical Corp.) was used as raw material for the preparation of the crystalline ρ-Al_2O_3 powder through fast thermal pyrolysis at 800 - 1000 K for 1-5 sec. The paste mixture was extruded from the 10-50 μm sized ρ-Al_2O_3 powder, with a micron sized filler such as wood flour and organic binder, both of which are destroyed during subsequent calcination of the extrudate, to introduce macro-mesopore structure.

The extrudate was placed in ambient condition for 12 h to increase pellet strength and was dried at 423K for 12 h.[5] The dried extrudate was subjected to a hardening process at 773 K for 6 h in air in order to remove the filler. These final extrudate was crushed and subsequently smoothed to a size of 14-30 mesh in a shaking bottle with water at a rate of ~ 3000 rpm for 6 h.

Then, the La precursor was added as impregnation and was dried at 333 K for 12 h. Subsequently, the La-doped alumina was calcined at 823 K for 6 h in air. Further calcinations were conducted at 1173 K, 1373K, 1473K, 1573K and 1673K for 2 h in air.

2.2 Characterization

The phase purity and the crystallinity of the alumina and the corresponding catalyst was determined using powder X-ray diffraction (XRD, D/MAX Ultima III,Rigaku, Japan) with Cu Kα radiation .

The BET N_2 adsorption-desorption isotherms were measured at 77 K with BELsorp – mini II (BEL, Japan).

Scanning electron micrographs were obtained using HITACHI S-4700 (Hitachi, Japan) operating at 25 kV. Elemental analysis was performed using an energy dispersive X-ray microanalyzer (Oxford, England) attached to the SEM.

The mercury intrusion and extrusion were obtained using AutoPore IV 9500(Mercury Porosimetry, Micromeritics instrument corporation, USA)

Granule strength was measured by a FG-5020 (Force gauge, Lutron electronic enterprise, Taiwan)

3 Result and Discussion

3.1 The fabrication of granule

In propulsion applications, the state of the art catalyst like Shell-405 on a priority carrier was necessary for propellants decomposition. When gibbsite, $Al(OH)_3$, calcined at 773K ~ 873K for 5 sec, gibbsite was changed into ρ-Al_2O_3. The paste mixture was extruded from the obtained ρ-Al_2O_3 powder, with a micron sized filler such as wood flour and organic binder.

The cross section of the extruded granule exhibited many macropores as shown Fig. 1. The severe attrition and high pressure extrusion more than 120 kg/cm^2 resulted in more uniform macropore alumina pellet. The crushing strength of the extruded granules ranged from 10 to 15N for the 14~18 mesh granule.[1]

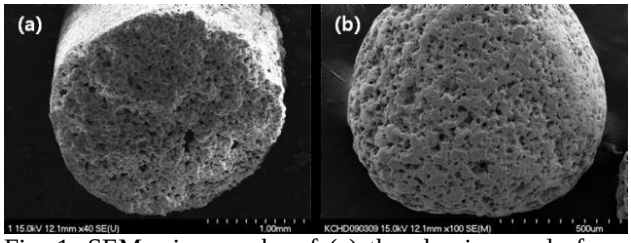

Fig. 1. SEM micrographs of (a) the alumina made from $Al(OH)_3$ and (b) the spherical alumina granule after the attrition.

The macroporous nature of the alumina was observed from the mercury intrusion and extrusion measurements. The macro-pore sizes peaked at 20 ㎛ and 1 ㎛. The meso-pore size was also around 3-4 nm as shown in Fig. 2. A continuous distribution of pore sizes existed between these two characteristic pore sizes, connecting the pores that facilitated the diffusion and adsorption of the reactants and products. Therefore, the permeability and tortuosity were 216 mD (millidarcies) and 21.5, respectively, while the threshold pressure was only 10.1 psi because of the unusual pore architecture.

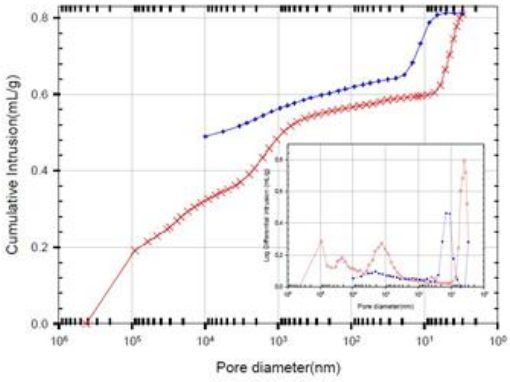

Fig. 2. The cumulative pore volume and its corresponding pore size distribution (inset) that were obtained from the mercury intrusion and extrusion measurements. The red and blue lines indicate the intrusion and extrusion, respectively.

In this work, the lanthanum hexaaluminate-based catalyst was prepared as granule starting from the γ-Al_2O_3 alumina granule such as shown Fig. 1-(b). using simple impregnation.

3.2. Thermal stability of alumina support

The theoretical adiabatic flame temperatures of HAN-based monopropellant blends, such as AF-M315SE and LGP 1846, were reported between 2083K and 2469 K. The adiabatic flame temperature of hydrogen peroxide, water and ethanol blend was between 1716 and 2000 K.[6] The adiabatic temperature of ammonium dinitramide (ADM) for complete combustion was 1998 K, but hydrazine possess adiabatic flame temperatures of only 1173 and 1223 K.[3,7]

Several authors reported that the sequence and the approximate temperatures for phase transition were : from boehmite to γ-Al_2O_3(573 K), : from γ-Al_2O_3 to δ-Al_2O_3(1123 K) : form δ-Al_2O_3 to θ-Al_2O_3 (1327 K) and from θ-Al_2O_3 to α-Al_2O_3 (≥1473 K). [8-10]

In order to investigate the effect of heating temperature on the structure of alumina support, the X-ray diffraction patterns at different temperatures are shown in Fig. 3,4 and 5. The prepared alumina support was converted progressively at over 1173 K, finally to α-Al_2O_3 at over 1473 K as shown in Fig. 3.

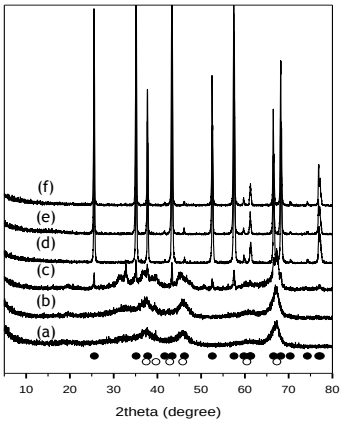

Fig. 3. XRD of γ-Al_2O_3 (a) calcined at 773 K, (b) calcined at 1173 K, (c) calcined at 1373 K, (d) calcined at 1473 K, (e) calcined at 1573 K and (f) calcined at 1673 K ; (●) corundum syn (PDF#10-0173) and (○) Aluminum oxide (PDF#04-0880)

The $LaMn_1Al_{11}O_{19}$ hexaaluminate was reported to be appeared, when the sample is calcined at 1323K. [4] The general process based on a microemulsion-assisted sol-gel technique for making lanthanum hexaaluminate powder was complex and further it needs granulation process. Our method using simple impregnation to obtain lanthanum doped γ-Al_2O_3 pellet was relatively simple. Fig. 4. and 5. showed that lanthanum doped γ-Al_2O_3 wasn't completely convert to α-Al_2O_3 at over 1473 K, the lanthanum hexaaluminate crystal peaks appeared [JCPDS 34-0467].

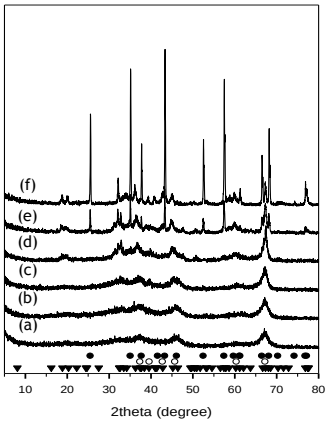

Fig. 4. XRD of La/Al_2O_3 (La/Al = 1/24) (a) calcined at 773 K, (b) calcined at 1173 K, (c) calcined at 1373 K, (d) calcined at 1473 K, (e) calcined at 1573 K and (f) calcined at 1673 K ; (●) corundum syn (PDF#10-0173), (○) Aluminum oxide (PDF#04-0880) and (▼) lanthanum hexaaluminate(PDF#34-0467)

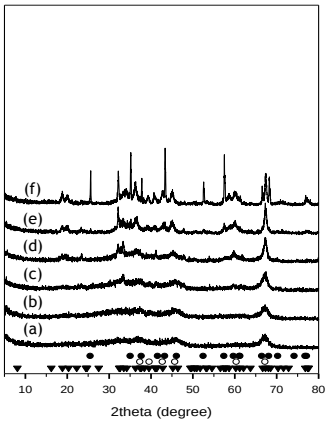

Fig. 5. XRD of La/Al_2O_3 (La/Al = 2/24) (a) calcined at 773 K, (b) calcined at 1173 K, (c) calcined at 1373 K, (d) calcined at 1473 K, (e) calcined at 1573 K and (f) calcined at 1673 K ; (●) corundum syn (PDF#10-0173), (○) Aluminum oxide (PDF#04-0880), (▼) lanthanum hexaaluminate(PDF#34-0467)

Fig. 6. showed that the surface area of γ-Al_2O_3 was decreased drastically from about 200 to 5~7 m^2g^{-1}, after the calcination at 1573 K. But the surface area of lanthanum doped γ-Al_2O_3 was decreased to 18~20 m^2g^{-1}. This suggests that lanthanum retarded the

sintering at high temperature, resulting in the high surface area for catalytic application.

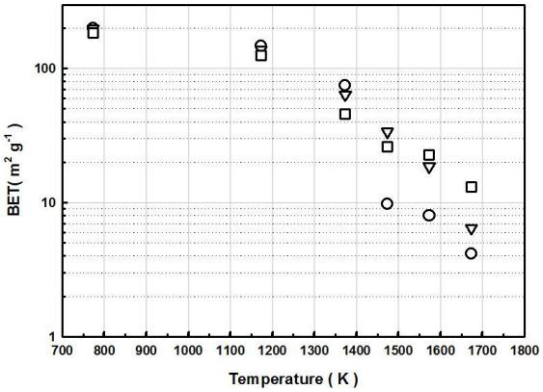

Fig. 6. Surface area as a function of heating temperature : (○) parent alumina, (▽) La-doped alumina (La/Al = 1/24) and (□) La-doped alumina (La/Al = 2/24).

SEM micrograph as shown in Fig. 7. showed the similar pore shape of macro-mesopore structure after the calcination at over 1473 K. The macro-mesopore was one of the important factors for catalysts in propulsion system, due to facilitated penetration of propellant into the interior porous structure of the support. [1]

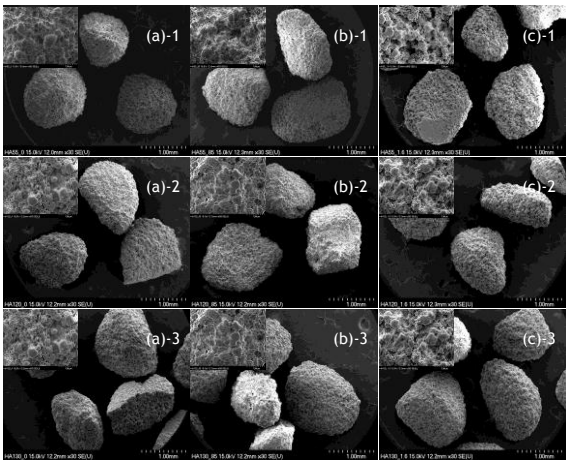

Fig. 7. SEM micrographs of (a) γ-Al_2O_3 , (b) La/Al_2O_3 (La/Al=1/24) and (c) La/Al_2O_3 (La/Al=2/24) : 1;calcined at 823K, 2; calcined at 1473K and 3; calcined at 1573K

Granule strength was measured by a force gauge, as shown in Table 1. The size of each granule was 14-18 mesh and data was modified from average of 15 measurements. Irrespective of the heating temperatures, the overall strength was about 10-14 N.

Sample	Crushing Strength (N)					
	823 K	1173 K	1373 K	1473 K	1573 K	1673 K
Al_2O_3	8	12	14	14	14	14
La/Al_2O_3 (La/Al=2/24)	13	11	12	14	16	17
La/Al_2O_3 (La/Al=4/24)	10	7	11	10	12	11

Table. 1. Granule strength as a function of heating temperature. The standard deviation was ±4 (N).

4. Conclusion

Fabrication of the shaped body of high thermal stability was possible employing γ-Al_2O_3 alumina granule and simple impregnation. The crushing strength of the alumina support was also maintained the same after the high temperature heating.

In this work, it was possible to prepare the alkali or alkaline earth doped γ-Al_2O_3 alumina granule using simple impregnation, which is suitable for catalytic application at high temperature.

This work can be applied to develop thermally stable catalysts for high performance green propellant in the propulsion system without incorporation of complicated granulation procedure.

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