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A strategy for increasing the energy release rate of aluminum by replacing the alumina passivation shell with aluminum iodate hexahydrate (AIH)

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ABSTRACT

Aluminum iodate hexahydrate (AIH) is an oxidizing salt that can be synthesized on the surface of nanoaluminum (nAl) particles, replacing the inherent alumina (Al₂O₃) passivation shell. For nAl particles encapsulated by AIH, rates of reaction have been shown to be on a time scale relevant to a detonation. Yet, little is known about the reaction mechanism between AIH and Al or how the Al₂O₃ passivation shell encapsulating nAl particles affects the reaction mechanism. This study explores the reactive nature of AIH and nAl by examining ignition and energy transfer of two different AIH + nAl formulations. The first is AIH synthesized on the surface of nAl particles to a concentration ratio of 80 wt% AIH to 20 wt% nAl. This composite particle lacks the Al₂O₃ shell that inherently passivates nAl and replacing it with AIH, these particles will be referred to as Particle_{AIH+AI}. In comparison, a discrete mixture of 80 wt% AIH powder combined with 20 wt% nAl powder is also examined and the mixture is referred to as Mix_{AlH+Al}. Laser ignition studies show ignition and burn times are reduced for Particle_{AIH+AI} compared to Mix_{AIH+AI}, owing to the presence of the Al_2O_3 diffusion barrier that inhibits ignition in the Mix_{AIH+AI}. Also, flame speed measurements reveal that Particle_{AlH+Al} propagate at 3062 m/s while the Mix_{AlH+Al} at 1366 m/s. Further analysis using thermal equilibrium calculations show hydrogen gas generation may facilitate heat transfer and energy propagation. Equilibrium analysis using differential scanning calorimetry also show the decomposition energy of pure AIH is nearly the same as the ignition energy of Particle_{AIH+AI} but twice that energy is required to ignite Mix_{AIH+AI}. All of these results provide a stronger foundation for the impedance of the Al₂O₃ passivation shell on the rate of energy release for Al reaction under equilibrium and non-equilibrium conditions.

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1. Introduction

Recent work by Smith and co-workers [1–4] showed significant improvement in flame speeds for nano-aluminum (nAl) when aluminum iodate hexahydrate (AIH) is introduced into the particle composite [1–3]. In particular, a 30% increase was measured from laser induced air-shock from energetic materials (LASEM) estimated detonation velocities of AIH coated nAl combined with

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trinitrotoluene (TNT) [4]. In aluminum explosive mixtures, oxidation of nAl normally occurs after the reaction zone of detonating explosives has passed. The 30% increased estimated detonation velocity suggests that replacement of the Al_2O_3 passivation layer with AlH increases reaction rates to a point where nAl oxidation occurs in the detonation zone of the explosive. Because the efficiency of AlH alone as an oxidizer has not been studied, the increased estimated detonation velocities observed in AlH coated nAl particles may be a result of the effectiveness of AlH as an oxidizer, not the disruption and subsequent replacement of the Al_2O_3 shell with an oxidizing salt. Recently, a synthesis method has been developed to create pure AlH (i.e., not on the surface of nAl) so the efficiency of AlH as an oxidizer can be established.







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Multiple aluminum iodates, including AIH, were originally developed for their unique piezoelectric and optical properties [5–12]. These studies focused on growing large single crystals of different aluminum iodate species. In the synthesis methods described in previous studies [7,8,10,12], single crystal growth was a long process taking weeks and even months to complete. Recently, Smith et al. developed a rapid synthesis method that allows AIH to be synthesized in a powder form in a matter of hours. The rapid synthesis of AIH allows the effectiveness of AIH as an oxidizer to be studied independently.

The efficiency of AIH as an oxidizer will depend on its physicochemical properties. There are very few studies on the physicochemical properties of AIH; however, the thermal decomposition mechanism of AIH is briefly mentioned in Shklovskaya et al. [11] and Cradwick and De Endredy [7]. The decomposition mechanisms [7,11] are in general agreement with each other, except that Cradwick and De Endredy [7] differentiates between HIO₃ decomposition into H₂O and I₂O₅ while Shklovskaya et al. [11] includes the decomposition of HIO₃ into the dehydration of the water ring. The decomposition mechanism of AIH described in Cradwick and De Endredy [7] is shown in Eq. (1).

$$[\operatorname{Al}(\operatorname{H}_{2}\operatorname{O}_{6})](\operatorname{IO}_{3})_{3}(\operatorname{HIO}_{3})_{2} \xrightarrow{135^{\circ}C} \operatorname{Al}(\operatorname{IO}_{3})_{3}(\operatorname{HIO}_{3})_{2}$$
$$\xrightarrow{195^{\circ}C} \operatorname{Al}(\operatorname{IO}_{3})_{3}(\operatorname{I}_{2}\operatorname{O}_{5}) \xrightarrow{340^{\circ}C} \operatorname{Al}(\operatorname{IO}_{3})_{3} \xrightarrow{540^{\circ}C} \frac{1}{2} \operatorname{Al}_{2}\operatorname{O}_{3}$$
(1)

Cradwick and De Endredy [7] describes the powder diffraction patterns for the decomposition step at 340 °C as confirmation for the steps shown in Eq. (1). However, the diffraction patterns are not described or shown for any step in Shklovskaya et al. [11] or for the other mass loss steps in Cradwick and De Endredy [7]. We assume the steps shown in [7,11] are from measured mass loss at these steps and calculated mass loss from Eq. (1).

The goal of this study is to characterize the reactivity of pure AIH particles mixed with nAl particles and compare to particles that replace the Al_2O_3 shell on nAl with AIH. To accomplish this goal, pure AIH was synthesized via a wet chemistry approach and AIH purity was confirmed using X-ray Diffraction (XRD). Then, the following series of experiments were performed: (1) a laser ignition study to examine the ignition time and energy, overall burn time and the intermediate and product species evolution; (2) an examination of flame speed of propagating powder in a channel; and (3) an equilibrium study to quantify exothermic and endothermic kinetics. All of these experiments provide a foundation for assessing the role of the Al_2O_3 oxide shell on the reactivity between Al and AIH.

2. Experimental

2.1. Material synthesis

The nAl powder was supplied by Novacentrix (Austin, TX) and has an average particle diameter of 80 nm with a 3-4 nm amorphous Al₂O₃ passivation shell, Fig. 1(A). This nAl powder was used for all samples examined in this study.

In the first sample, referred to as *Particle_{AIH+AI}*, nAl powder is chemically altered to disrupt the oxide layer and replace it with AIH. The synthesis process for AIH on the surface of nAl is thoroughly described in Smith et al. [1–3], but summarized here. Commercially available I_2O_5 powder, supplied by Sigma Aldrich (St. Louis, MO), is dissolved in distilled water to form an acidic iodate solution. Aluminum powder is added to the solution under continuous mixing until the nAl is dispersed in solution (i.e., < 60 s). The amount of nAl, I_2O_5 and water is set so the equivalence ratio (ER) is 1.1 and the water to Al ratio is 6:1 by weight. The slurry is poured into channels milled into an acrylic plate that is kept

in a fume hood while the solution evaporated (7 days). The recovered solid material is analyzed using powder X-ray diffraction (XRD) and is composed of multiple different compounds including AIH, Al, HI₃O₈, β -HIO₃. The samples tested here fall within the uncertainty of the sample shown in Smith et al. [3] with an ER of 1.1 (Table 2 and Fig. 7(a) in Smith et al. [3]). Figure 1(B) shows a TEM image of *Particle_{AIH+AI}* illustrative of the nodules and high roughness on the particle surface.

In the second sample, referred to as Mix_{AIH+AI}, nAl powder is combined with AIH powder in the same mixture proportions as Particle_{AIH+AI}. Because AIH powder is not commercially available, AIH had to be synthesized. The synthesis method for AIH is a modified version of the method described in Endredy [13] and described in detail in Smith et al. . In summary, I2O5 powder (same powder used in Particle_{AIH+A1} preparation) is dissolved in distilled water to form an aqueous iodate solution. Aluminum hydroxide (Al(OH)₃) powder, supplied by Sigma Aldrich (St. Louis, MO), is mixed with the iodate solution to a molar ratio of 5:1 (IO_3^- :Al). The solution is heated to 130 °C under reflux conditions until the Al(OH)₃ is dissolved (between 30 min and 24 h depending on particle size) and the solution is clear. When Al(OH)₃ is completely dissolved, the solution is cooled to room temperature and acetonitrile (ACN) is added at a volume ratio of 1:1. The ACN causes the solution to become bi-phasic. When the two phases are mixed for approximately 2 h, AIH particles grow large enough to be filtered from solution and washed with cold water. The powder recovered is pure AIH, determined by powder X-ray diffraction (XRD). Figure 1(C) shows a scanning electron microscopy (SEM) image of AIH particles. Particle size analysis indicates that the AIH particles have a measured specific surface area of 0.14 m²/g evaluated in an API Aerosizer particle size analyzer (TSI Incorporated). The pure AIH particles are mixed with nAl in an 80 wt% AIH to 20 wt% Al ratio via sonication using a non-polar carrier fluid to ensure adequate dispersion of the two discretely separate powders, Fig. 1(D). The sonication process is programmed for 2 min in 10 s on/off cycles to avoid heating. The slurry is poured into a $\mathsf{Pyrex}^\mathsf{TM}$ dish and the powder mixture is reclaimed for further experimentation after the carrier fluid evaporates in a fume hood (about 24 h). It is noted that this mixture (\textit{Mix}_{AIH+AI}) inherently includes an AI_2O_3 passivation shell surrounding the nAl particles that is not included in Particle_{AIH+Al}. The presence of Al₂O₃ in the total mixture is 4% by mass. An objective of this study is to understand the impedance of the Al₂O₃ passivation shell in the overall ignition and energy transfer of nAl with AIH.

2.2. Laser ignition and spectroscopic experiments

Figure 2 schematically illustrates the laser ignition and spectroscopic measurement experiments. Approximately 5 mg of loose powder of either Particle_{AIH+Al} or Mix_{AIH+Al} is placed on top of a graphite block sample holder (see Fig. 2). A diode laser (Apollo Instruments F50-976-1, Xantrex XTR 6-110 power supply, Lauda Proline RP 845 chiller) is focused to an approximately 1.3 mm diameter beam at the powder sample. The 974.8 nm wavelength beam has a spatial mode of TEM₀₁ and a total power of 2.5 W. All experiments use a laser pulse of 100 ms such that ignition energy can be measured. The ignition energy from the laser experiments is spatially averaged across the beam and assumes an absorptivity equal to the absorption efficiency of a 80 nm Al particle calculated from Mie theory [14] and is approximately 0.04. Although the mixtures also contain AIH, the optical properties of AIH are not known. Approximating the absorptivity of the mixture with properties of Al may not provide an exact ignition energy, but the relative ignition energy between the two samples is an indication of the differences in reaction from a mechanistic perspective.





А





С

WD10.4mm 6.0kV x1.2k 25µm



D



Fig. 1. (A) TEM image of as received 80 nm nAl ×200k magnification and imaged with a Hitachi H-9500 transmission electron microscope (TEM). (B) TEM image of *Particle*_{AIH+AI} at ×200k magnification. TEM samples were prepared using acetonitrile to suspend nanoparticles on a lacy carbon grid and imaged with a Hitachi H-8100 scanning transmission electron microscope (STEM) operated at 200 keV. (C) SEM image of pure AIH at an accelerating voltage of 6 kV showing hexagonal pyramidal geometries. (D) SEM image of Mix_{AIH+AI} and (E) EDS overlay of (D) at an accelerating voltage of 6 kV demonstrating uniform dispersion of nAI on pure AIH (blue – AI, other – AIH). Note (C)-(E) images were taken with a Hitachi S-4300 high resolution field emission SEM.



Fig. 2. Schematic of the laser ignition and spectroscopic experimental setup. The light source is not present for emission measurements. The powder sample is not shown but is placed on the sample holder. Also, a computer is included in schematic and illustrated above the spectrometer/camera.

Both emission and absorption spectroscopic measurements start simultaneously with the laser firing. Emission measurements provide insight on ignition delay time and overall burn time. Absorption measurements provide insight on species evolution during reaction. A 220 mm focal length, f/3.9 spectrometer (SPEX model 1681A) with a 600 g/mm grating and 100 μ m slit is coupled to a Photron Mini AX-200 detector. This setup provides an average spectral resolution of 1.1 nm in the 440–580 nm band. This spectral band is chosen since the B² Σ^+ – X² Σ^+ AlO [15] and B³ $\Pi^0_{u^+}$ – X¹ Σ_g +l₂ [16] bands are both present and anticipated during reaction. Spectral calibration is conducted using Hg and Kr lamps.

The absorption experiments used a LED source with a 6200 K color temperature (Ventas LED Constellation 120E15). A Roscolux #359 medium violet filter is placed in front of the spectrometer slit to equalize the dynamic range over the spectral range. The filter also blocks most (>90%) of the emission from the combustion event. No filter is used in the emission experiments. The camera is set to 1000 f/s with an exposure of 1 ms. The camera and laser are synchronized using a delay generator (Stanford Research Systems, DG535). A schematic of the setup is illustrated in Fig. 2.

Data is processed using an in-house MATLABTM script. Spectral features are identified, first light defines ignition delay time, and overall burn time are measured. Emission measurements are used for first light and burn time analysis whereas the absorption experiments identify the first appearance of AlO and I_2 species. The ignition time for emission experiments is the first data point where the signal intensity is 10x the standard deviation of the noise, and the final data point for burn time is the last data point that matched this criterion.

Because of the increase of optical depth from the particles, it is challenging to rely on monitoring the signal for a given wavelength, especially for the I_2 feature for the absorption experiments. The earliest time when the AlO signal (any of the bands) is above the noise level is noted manually. A similar process is also used with I_2 although the inflection point (near 550 nm) is where the v''=0 and v''=1 I_2 bands start to overlap [16]. The vibrational structure does not appear until later times where presumably more I_2 is recombining from elemental iodine (I). Both samples are tested at least 3 times to ensure repeatability.

2.3. Flame speed experiments

About 750–800 mg of powder mixture (Mix_{AIH+AI}) is loaded into acrylic channels that are 7 cm long by 0.5 cm wide and milled from an acrylic block that is 2.54 cm wide and 8 cm in length. Also, a 2.54 cm wide 8 cm length acrylic block is adhered to the top of

the milled acrylic block. The enclosed channel is now filled with a sample to direct energy propagation axially along the channel. This setup is the same apparatus described by Smith et al. [3] to measure flame speeds of *Particle*_{AIH+AI} with data that is included here for completeness. It is noted that there is a difference in bulk density between the two samples. For *Mix*_{AIH+AI} the bulk density is < 30% of the theoretical maximum density (TMD) while for *Particle*_{AIH+AI} the bulk density is > 90% TMD.

For all samples the loaded channels are placed in a blast chamber with viewing ports and a high-speed camera is positioned perpendicular to the direction of flame propagation. Each sample is ignited at one end with nichrome wire attached to a voltage generator. The Mix_{AIH+AI} reactions are recorded with a Phantom v710 high speed camera at 240,000 f/s and 768 \times 112 pixels, with an exposure time of $3\,\mu s$. The Particle_{AIH+Al} reactions are recorded with a Phantom v1611 high-speed camera at 381,818 f/s and 384×64 pixels. In both samples, the intensity of light created by the reaction is greatest at the leading edge of the reaction, and to view this location, the f-stop on the lens (i.e., f/32) and neutral density filters are coupled to block out > 99% of the light emitted. Image analysis is performed with the Phantom camera control program to track flame propagation and measure flame speed. The time and distance measurements are exported into a spreadsheet and plotted along with a linear curve fit. All data reported produced an R² value greater than 0.99. Each experiment is performed in triplicate to establish repeatability.

2.4. Differential scanning calorimetry equilibrium experiments

Equilibrium calorimetric studies are conducted with a differential scanning calorimeter (DSC) (Model Q20, TA instruments, New Castle, DE) at 10 °C/min in an argon environment. Indium is used for calibration of the DSC. The melting point of indium obtained from the DSC measurement is within 0.1 °C of published values. Platinum pans sealed with a lid are used for running samples. The lid contains a micron-scale hole for releasing gas generated in the reaction. Due to the high reactivity of *Particle*_{AIH+AI} that is documented in Gottfried et al. [4] during similar equilibrium testing, Mix_{AIH+AI} sample size is kept less than 1.5 mg in all experiments. For pure AIH powder, a 5 mg sample is used. All DSC data are processed with TA Universal Analysis V4.5A software for determining onset temperatures and heat of reaction. Experiments are performed in triplicate to ensure repeatability.

2.5. Powder X-ray diffraction

The data was collected on a Rigaku Ultima III powder diffractometer operated in continuous $\theta - 2\theta$ mode from 15° to 60° 2 θ with parallel beam geometry. The step size was 0.02° with a collection time of 2°/min. The MDI Jade V9.1.1 software provides both qualitative and quantitative data analysis used to identify crystalline species for samples heated to varying temperatures.

3. Results

3.1. Laser ignition

Each experiment consisted of a bright flash once the sample ignited with a simultaneous crackling sound as the material burned. A purple cloud, likely from recombining iodine, would form after the crackling sound and towards the end of the test. No qualitative differences are observed during the event, however, more residue remained on the graphite plate after the test for the physical mixtures (*Mix*_{AIH+AI}). The residue was not further analyzed, however there may be unburned material due to an incomplete reaction or solid products from the reaction. It is also noted that *Mix*_{AIH+AI}

Table 1

Summary of laser ignition and flame speed results for *Particle*_{AIH+AI} and *Mix*_{AIH+AI} samples. Average values are reported first with the standard deviation in parentheses. Note: * is from [1].

	Ignition time (ms)	Estimated ignition energy (mJ)	First AlO (ms)	First I_2 (ms)	Burn time (ms)	Flame speed (m/s)
Particle _{AIH+Al}	54.9 (4.9)	5.49 (0.49)	52.8(4.6)	57.5(9.1)	27.5(2.1)	3062(314)*
Mix _{AIH+Al}	81.0 (15.4)	8.1 (1.54)	70.0 (2.0)	75.3(2.1)	44.4(23.5)	1366(233)



Fig. 3. Time resolved series of absorption spectra from *Particle*_{AIH+AI}. All times are listed from the start of the laser irradiance. Both AlO and I_2 features appear nearly simultaneously with respect to the time resolution and the statistical variation between tests. As such, it is difficult to determine additional kinetic details.

samples did not burn as fast as $Particle_{AIH+AI}$ samples such that residue may remain from the less powerful nature of the reaction.

An absorption spectrum series is shown in Fig. 3 as a representation of how the data was obtained. Comparative results between samples are shown in Table 1. Several band heads from the AlO $B^2\Sigma^+ - X^2\Sigma^+$ transition are observed as well as the I₂ transition. Aluminum monoxide (AlO) is observed very early in the event, but is not as prevalent at later times, likely due to the prompt aluminum oxidation reaction. The quasi-continuum portion of the iodine feature partially overlaps with the AlO transition which complicates the determination of how long AlO is present. Little vibrational structure is observed from I₂ early on (e.g., 52 ms spectrum) whereas I2 becomes more evident later in the event (i.e., 70 and 150 ms in Fig. 3). This observation is likely due to I_2 recombining from atomic I during cooling as shown for the spectrum at 150 ms. Nevertheless, I₂ features are observed by the inflection point near 550 nm where the v''=0 and v''=1 bands overlap [16]. Tests with pure AIH and pure Al (each in a separate experiment) were also conducted to observe if the laser heating caused gasification that could appear in the other spectra. The laser conditions did not provide enough energy to gasify pure AIH or nAl powder, such that all spectral features are likely from the reaction.

Times of overall first light (emission) corresponding to ignition time, first AlO and I₂ (absorption), and overall burn time (emission) are summarized in Table 1 for both samples. In short, *Particle*_{AIH+AI} samples react quicker and burn faster than *Mix*_{AIH+AI} samples. The ignition delay, whether thermal emission, or AlO or I₂ absorption, is at least 30% longer for *Mix*_{AIH+AI} samples compared to *Particle*_{AIH+AI} samples. The difference in ignition time compared to appearance of AlO or I₂ is within the scatter of the data and therefore it is difficult to determine if one event precedes the other (within the time resolution). Similarly, the burn time is 61% longer for the Mix_{AIH+AI} samples which also had more scatter. The overall ignition energy is estimated by assuming the samples have an absorptivity equal to that of an 80 nm Al particle since the optical properties of AIH are unknown and at these particle sizes the interaction of light is within the whole particle volume and not a surface phenomenon. The overall ignition energy is lower for *Particle*_{AIH+AI} samples but on the order of mJ for both samples (i.e., based on the estimated absorptivity).

3.2. Flame speeds

Flame speeds are measured for Mix_{AIH+AI} and compared to previously reported values for $Particle_{AIH+AI}$ [3]. Table 1 shows the highest flame speeds are for $Particle_{AIH+AI}$ and are about three times faster than Mix_{AIH+AI} . We suspect the presence of the oxide shell contributes to the reduced flame speed for the Mix_{AIH+AI} ; however, other factors including density and contact between fuel and oxidizer can also have an effect on flame speed and measurement standard deviation, especially for burn time measurements.

3.3. Equilibrium analysis

Figure 4 shows DSC thermograms of pure AIH and Mix_{AIH+AI} . Pure AIH does not exhibit any exothermic peaks, but instead four endothermic peaks at temperatures up to 700 °C. These four endothermic peaks are detailed in Table 2 with a total calculated AIH decomposition energy of 4.18 mJ. The four endothermic peaks are similar to the peaks shown in Shklovskaya et al. [11]; however, the mechanism presented in Shklovskaya et al. was not confirmed with XRD. The XRD patterns are shown in Fig. 4b when AIH is heated past each endotherm. When AIH is heated to 150 °C (first step), AIH becomes amorphous; however, TGA mass loss agrees with Cradwick and De Endredy [6] that this step is the dehydration of the water ring surrounding the Al. When AIH is heated to 250 °C (second step), the XRD indicated the sample was 67% anhydrous aluminum iodate and 33% I₂O₅. When AIH is heated to 450 °C (third step), the XRD indicates the sample is pure anhydrous aluminum iodate. The final step of AIH decomposition is anhydrous aluminum iodate decomposing into Al₂O₃.

When AIH is mixed with nAl (i.e., Mix_{AIH+Al}), two major exothermic peaks are observed at 274 °C and 549 °C and detailed in Table 3. The first exothermic peak is attributed to pre-ignition reaction (PIR); i.e., an interface reaction between nAl particle surface (which is Al₂O₃) and the surrounding oxidizer (AIH). The possible surface reactions between Al₂O₃ with iodates that are released upon AIH decomposition are known to be exothermic and detailed using simulations in [17]. The second exothermic peak represents nAl core oxidation with oxidizers available in the AIH structure to form alumina, iodine gas, aluminum oxides, and aluminum iodates (consistent with data shown in Fig. 3). A DSC thermogram of a sample similar to $\textit{Particle}_{AIH+AI}$ used in this experiment is presented in Gottfried et al. [4] and included in Fig. 4(a) to show an endotherm at 140 °C followed immediately by a runaway exotherm at 150 °C that damaged the thermocouple and DSC. For this reason, *Particle*_{AIH+Al} samples were not further analyzed here.

Decomposition Endotherm	Onset (°C)	Peak (°C)	Endothermic Enthalpy J/g
First	118.7	133.8	248.00
Second	192.8	203.4	38.52
Third	339.4	389.4	187.80
Fourth	501.9	534.8	361.10
Total			835.4
4.18 mJ for 5 mg of sample			

Table 2

Table 3

Exothermic properties of Mix_{AIH+AI}.

Decomposition energy of AIH.

Sample	Pre-ignition reaction			Reaction of Al core		
	Onset (°C)	Peak (°C)	Exothermic Enthalpy (J/g)	Onset (°C)	Peak (°C)	Exothermic Enthalpy (J/g)
Mix _{AIH+A1}	274.3	299.3	100.7	548.9	576.7	893.8

Table 4

Summary of CEA simulation results.

Sample	Flame temperature (°C)	Molecular weight (g/mol)	H and H_2 gas (mol%)
Particle _{AIH+AI}	3197	59	25.95
MixAIH+AI	2994	62	15.62



Fig. 4. (A) Heat flow as a function of temperature for a heating rate of 10 °C/min and in an argon environment for pure AIH, *Mix*_{AIH+AI}, and *Particle*_{AIH+AI} from [4] exhibiting thermal runaway. (B) PXRD diffraction patterns of AIH samples heated to temperatures of endothermic reactions shown in (A).

An equilibrium simulation using NASA CEA [18] was performed for both samples with constant pressure (101.3 kPa) and results are shown in Table 4. There is no available data on the thermodynamic properties of AIH. Therefore, the heat of formation of AIH was estimated by summation of the heats of formation for its components (i.e., Al, H₂O, HIO₃, IO₃) [19]. The estimated value is -2831.79 kJ/mol. Although the actual heat of formation will likely differ, this value is used in all calculations such that any trend should be indicated accurately in relative terms. It is noted that Al₂O₃ was added into the calculation for the *Mix*_{AIH+AI} sample to account for the oxide layer.

As expected, the adiabatic flame temperature for the *Particle*_{AIH+AI} (i.e., without Al₂O₃) was slightly higher with an equilibrium temperature of 3470 K (3197 °C) compared to 3267 K (2994 °C) for the *Mix*_{AIH+AI}. Similarly, the mixture-averaged product molecular weights were similar (59 and 62 g/mol for *Particle*_{AIH+AI} and *Mix*_{AIH+AI}, respectively) with aluminum oxide, atomic iodine, and water being the most prevalent species. Interestingly, the combined mole fraction of atomic and molecular hydrogen

was approximately 0.25 for the $Particle_{AIH+AI}$ versus 0.15 for the Mix_{AIH+AI} .

4. Discussion

Significant differences in ignition delay, ignition energy, burn time, and flame speed are observed between *Particle*_{AIH+AI} and *Mix*_{AIH+AI}. In the laser ignition analysis, *Mix*_{AIH+AI} lags in ignition time by 32% (81 ms compared with 54 ms, Table 1). Upon reaction, absorption spectra from AlO and I₂ (Fig. 3) lag by about 25% for *Mix*_{AIH+AI}. Overall burn time is 38% longer for *Mix*_{AIH+AI}. Table 1 shows measured flame speeds for *Particle*_{AIH+AI} are nearly triple that of *Mix*_{AIH+AI}. All of these results reveal differences between the two samples. The main difference between the *Particle*_{AIH+AI} and *Mix*_{AIH+AI} is that the Al₂O₃ shell has been converted into AIH in the *Particle*_{AIH+AI} sample. The shorter ignition time, reduced ignition energy, and reduced burn time (shown in Table 1), and significantly increased flame speeds for *Particle*_{AIH+AI} compared to *Mix*_{AIH+AI} suggests that conversion of the Al₂O₃ shell

into AIH is a determining parameter in the observed differences. The mechanisms causing the differences are explored below.

The differences between non-equilibrium and equilibrium results for Mix_{AIH+A1} and Particle_{AIH+A1} suggest a different reaction mechanism between the two samples. For laser ignition studies, heating of the sample should be approximately equal for both samples as heat transfer properties should be similar due to similar composition. The Al₂O₃ accounts for only 4% of the total mixture mass and thus should not appreciably contribute to the heating time of the sample. In Table 2 (i.e., equilibrium data), the total decomposition energy for pure AIH is 4.18 mJ. In Table 1 (i.e., nonequilibrium data), the ignition energy for Particle_{AIH+Al} is 5.2 mJ. The good correspondence suggests that the first step in ignition for Particle_{AIH+AI} is decomposition of AIH. In Mix_{AIH+AI}, the ignition energy (8.1 mJ) is almost double the decomposition energy for pure AIH. It should be noted that absorptivity of particles outside the Rayleigh limit [20] (i.e., on the order of or larger than the wavelength of light) is typically greater than the absorptivity for particles within the Rayleigh limit (i.e., smaller than the wavelength of light). Similar effects have been observed in previous works on the optical properties of metal oxide particles [21,22] and suggests that the laser energy absorbed for the microscale pure AIH particles in the Mix_{AIH+AI} sample should be greater than the Particle_{AIH+AI} samples. In other words, the ignition energy is likely even greater for the Mix_{AIH+AI} such that the difference in ignition energy may be an underestimate. The significant difference in the energy between decomposition and ignition suggests a difference in reaction mechanism. Under equilibrium conditions, Mix_{AIH+A1} shows two distinct exothermic peaks starting at 274 °C (PIR) and 549 °C (Al⁰ core reaction) (Table 3). For Mix_{AIH+AI}, Al core reaction onset is at higher temperature (549 °C) normally observed in nAl composites near the Al melting point (660 °C) (Table 3) [23]. The increase in onset temperature in Table 3 compared with the ignition energy in Table 1 indicates that in the Mix_{AIH+AI} sample additional energy is required to initiate the reaction and that the additional energy is most likely melting of the Al core to promote mass diffusion through the shell and initiate the main reaction. The correspondence between the decomposition energy for pure AIH and ignition energy for Particle_{AIH+AI} indicates that Al⁰ in the core of the nAl particle is reacting before the melting point of nAl is reached. An ignition temperature lower than Al melting for Particle_{AIH+AI} is consistent with results reported in Gottfried et al. [4] for AIH coated nAl particles.

In Gottfried et al. [4], Particle_{AIH+AI} has a runaway reaction after an endotherm starting at 140 °C. The endotherm at 140 °C was thought to be dehydration of the water ring in AIH based off limited dehydration studies of AIH in Shklovskaya et al. [11] and Cradwick and De Endredy [7]. Figure 4 confirms the dehydration mechanism in Shklovskaya et al. [11] and Cradwick and De Endredy [7] and confirms that the runaway reaction observed in Gottfried et al. [4] is a result of the dehydration of the water ring in AIH. Since a runaway reaction is observed after the dehydration of AIH in Particle_{AIH+A1} but not in Mix_{AIH+A1}, it can be assumed that the increase in reactivity is a direct result of water being released from dehydration of AIH in the shell of the nAl particle. Since less energy is needed to ignite Particle_{AIH+AI} (Table 1) and a runaway reaction is observed in $Particle_{AIH+AI}$ (Fig. 4) when dehydration of AIH occurs, we propose water released from AIH is oxidizing Al⁰ (aluminum in the core of nAl) to initiate the reaction. The Al⁰/water reaction is similar to the mechanism of the nAl/water reaction in ALICE (i.e., Al and ice) rocket propulsion [24,25]. Therefore, CEA simulations are used to further examine the effects of water (and hydrogen) on nAl reactions.

The CEA simulations give an estimate of the adiabatic flame temperatures, molecular weight of the combustion products and also show a difference in hydrogen vapor production between the two samples (Table 4). The most significant result of the CEA simulation between the two samples is the hydrogen gas production, with mole fractions of 0.25 for the *Particle*_{AIH+AI} versus 0.15 for the *Mix*_{AIH+AI}. This simulation does not take into account the structural differences between samples and the main difference between the two samples is the presence of the Al₂O₃ shell. The Al₂O₃ shell reduces the amount of active Al (i.e., Al⁰ or nAl core) in the *Mix*_{AIH+AI} sample (i.e., *Mix*_{AIH+AI} has only 16% active aluminum whereas the *Particle*_{AIH+AI} has 20% active aluminum). The increased H and H₂ mole fractions from *Particle*_{AIH+AI} compared to *Mix*_{AIH+AI} suggests that more Al⁰ (in the nAl core) is being oxidized by water in *Particle*_{AIH+AI}. One of the proposed chemical reactions for oxidation of Al by water in Ingenito and Bruno [25] is shown in Eqs. (2a) and (2b).

$$Al(s) + H_2O \rightarrow AlOH(s) + \frac{1}{2}H_2$$
 (2a)

$$2\text{AlOH} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_3 \tag{2b}$$

In both reactions in Eq. (2), hydrogen gas is produced showing that when Al^0 is oxidized by water, hydrogen gas is produced. Therefore, higher concentrations of hydrogen gas from the CEA simulation is most likely a result of higher Al° content of the *Particle*_{AIH+AI} compared to *Mix*_{AIH+AI} sample. It is also noted that the heat of reaction of both Reactions (2a) and (2b) is exothermic (-962.32 kJ/mol) [25]. Since these reactions are exothermic, and a runaway reaction is observed (Gottfried et al. [4]) in the *Particle*_{AIH+AI} samples when dehydration of the AIH is observed, the runaway exothermic reaction may be oxidation of Al^0 by water.

When the CEA results are compared with heat flow plots from Fig. 4, the effects of the diffusion barrier can be observed. In Fig. 4(a), an exothermic reaction is not observed for Mix_{AIH+AI} until 250 °C (i.e., after all of the water in AIH has left as vapor). Since no exothermic reaction is observed in Mix_{AIH+AI} until after all of the water has vaporized, the Al₂O₃ shell most likely inhibits water from reacting with Al⁰ and replacement of the Al₂O₃ shell with AIH is necessary to initiate the reaction between water and Al⁰. Because a runaway reaction is observed in the Particle_{AIH+Al} sample during the dehydration of AIH formed from the Al₂O₃ surface and a runaway reaction is not observed in the Mix_{AIH+AI} sample with the Al₂O₃ shell intact, the intimate contact between the water in AIH and the Al⁰ in the nAl core may be a determining factor of the increased reactivity of the Particle_{AIH+Al} composites. It is noted that the CEA simulations do not take geometry of the system into account so the effects of the Al₂O₃ shell diffusion barrier are not accounted for using this method and also only contains six iodinated species, but are likely the dominant reacting species.

The relative percent changes between ignition and flame speed between the samples cannot be explained by equilibrium alone. There are two additional considerations important to note that may contribute to the measurements: (1) inherent bulk density variations in the flame speed measurements between the two samples; and, (2) kinetics or transport may be controlling mechanisms for reaction because of the significant concentration of hydrogen gas produced in the reaction (Table 4).

In confined flame speed experiments, Sanders et al. [26] and Pantoya et al. [27] found that flame speed decreases with increasing density for nanocomposite powders. The density of *Particle*_{AIH+AI} (i.e., > 90% TMD) is greater than *Mix*_{AIH+AI} (i.e., < 30% TMD) yet the flame speed of *Particle*_{AIH+AI} (i.e., 3062 m/s) is greater than *Mix*_{AIH+AI} (i.e., 1366 m/s) (Table 1). Therefore, the mechanism promoting flame speed may be more kinetically limited in *Particle*_{AIH+AI} than diffusion limited. Further studies are required to determine the effects of density on nAl and AIH reactions.

Transport may also increase flame speed through additional hydrogen gas produced from the *Particle*_{AIH+AI} samples. Hydrogen premixed flames have a propagation speed on the order of 1 m/s [28]. Although the air within the void space and hydrogen produced are likely not perfectly premixed, this propagation speed provides a reference point. This speed is much slower than the speeds measured and reported in Table 1 for both samples. It is hypothesized that the presence of hydrogen mixed with the surrounding air and heat from the reaction acts as an ignition aid as hydrogen diffuses quickly due to its low molecular weight.

The additional hydrogen produced from the *Particle*_{AIH+AI} sample could significantly increase reaction rates because of the convective heat and mass transfer of the hydrogen vapor. The Knudsen diffusion can be calculated to estimate the transport of hydrogen. However, since the Knudsen diffusion is proportional to most probable velocity from kinetic theory, and the other values in the comparison are velocities, we feel it is appropriate to calculate the most probable velocity. Consider the mean speed of a molecule as calculated from kinetic theory [29] shown in Eq. (3).

$$V = \sqrt{\frac{8k_bT}{\pi m}}$$
(3)

In Eq. (3), *V* is the most probable velocity from the Boltzmann distribution, k_b is Boltzmann's constant, *T* is the temperature, and *m* is the mass of the atom/molecule. The mean speed of a hydrogen molecule at even 1000 K (substantially lower than flame temperature predicted through equilibrium) is over 3.2 km/s using Eq. (3). Any hydrogen atoms that do not react prior to diffusing will be even faster. Transport on the order of several km/s will potentially keep up or move faster than the flame speed. As such, hydrogen has the potential to aid in the energy propagation and may contribute to the larger relative increase in flame speed compared to the decrease in ignition time for the *Particle*_{AIH+AI} sample.

5. Conclusion

Equilibrium and non-equilibrium reactivity of aluminum iodate hexahydrate (AIH) combined with nano-aluminum (nAl) powder is experimentally examined. One sample consisted of a mixture of nAl combined with AIH; the other sample consisted of nAl with native Al₂O₃ passivation shell replaced with AIH. The two samples had the same concentration of AIH but Mix_{AIH+Al} includes the Al₂O₃ shell that constitutes 4 wt% of the total mixture mass. Results can be described in terms of ignition and reaction behaviors. In the laser ignition analysis, Mix_{AIH+Al} lags in ignition time by 32%. While Mix_{AIH+Al} exhibited slightly longer ignition time and higher ignition energy, the values were on the same order of magnitude. In flame speed studies, ParticleAIH+AI speed is three time greater than Mix_{AIH+AI}. By comparing thermal equilibrium analysis and laser ignition studies, we propose that decreased reaction time and increased flame speed are a result of oxidation of Al⁰ by water from dehydration of AIH and that intimate contact between AIH and Al in the core of the nAl particles (with no diffusion barrier from Al₂O₃) facilitate the increased reaction rates. Regarding energy release rates, thermal chemical equilibrium simulations suggest that there is significantly more hydrogen gas generation in Particle_{AIH+AI} than in Mix_{AIH+AI} and may promote energy propagation through accelerated thermal transport. Inherent density differences between Particle_{AIH+AI} and Mix_{AIH+AI} may also affect the discrepancy between flame speeds compared with ignition time and energy differences. The results suggest when the Al₂O₃ shell is removed and replaced with AIH, energy release rates are exceptionally fast owing to oxidation of Al by water from AIH decomposition and not limited by diffusion of oxygen through an Al₂O₃ barrier.

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