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Tailoring surface conditions for enhanced reactivity of aluminum powders with solid oxidizing agents



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ABSTRACT

The effect of processing liquids on particle surface hydration and subsequent reactivity of mixtures containing aluminum (Al) with different oxidizing agents was investigated. Recently, polar processing liquids were shown to significantly increase the surface hydration layer on Al particles and effect the reactivity of Al combined with polytetrafluoroethylene (PTFE). Processing mixtures of Al and PTFE using hexane (e.g., a non-polar liquid) limited surface hydration and produced significantly lower flame speeds than the same mixture processed in isopropanol (e.g., a polar liquid). Increased surface hydroxyl concentration was linked to higher exothermic behavior within a pre-ignition reaction (PIR) which may contribute to higher overall flame speed. This study extends the previous analysis toward assessing the influence of processing liquid on reactivity of aluminum with other oxidizing agents, specifically CuO, MoO₃ and I₂O₅. Results from DSC analysis show no PIR kinetics associated with Al and CuO or MoO₃, and Al+ CuO showed no difference in reactivity as a function of processing liquid. But, MoO₃ FTIR shows modified surface structures after treatment in a polar solvent. Correspondingly, Al + MoO₃ processed in polar solvent exhibited increased flame speed by 19% when compared to Al + MoO₃ processed in a non-polar liquid. For Al + I₂O₅, water in polar processing liquids produces various hydrated states of iodic acid (i.e., HIO₃ and HI₃O₈). Changing the hydration state of I₂O₅ significantly impacts reactivity. Results from this study confirm that carrier fluid used to process Al with metal oxides can also alter the surface structure of the metal oxide, thereby promoting greater reactivity with Al. A polar carrier fluid not only modifies the surface of Al but also hydration sensitive metal oxides such as MoO₃ and correspondingly promotes greater reactivity.

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1. Introduction

For reactive composites, combustion properties such as flame temperature, heat of combustion, and gas evolution can form the basis for evaluating reactant feasibility for an application [1]. Designing methods to enhance these properties enables a user to tailor reactivity toward applications that will lead to greater combustion efficiency and versatility. Simple processing conditions for preparing mixtures, such as the processing liquid used to combine and intermix reactants, can impact reactivity and thus be manipulated toward optimizing combustion. Most methods for intermixing solid fuels and oxidizers (e.g. multi-layer physical, chemical vapor deposition, extrusion, sonication, centrifugal) generally involve some sort of carrier fluid (or processing liquid) to

facilitate intermixing. In this way, understanding the mechanisms for reactivity that are influenced by the carrier fluid will impact strategies to optimize combustion.

Recently, the polarity of the processing liquid was found to significantly influence energy propagation of aluminum (Al) particles combined with poly(tetrafluoroethylene) (PTFE) [2]. Specifically, polar processing liquids were shown to increase the concentration and modify the surface structure of hydroxyl species on the aluminum oxide shell, which in turn facilitate a pre-ignition reaction (PIR) with the fluorocarbon. Infrared spectra showed evidence for a greater fraction of disordered, liquid-like hydrogen-bonded water molecules on the alumina layer of Al particles after processing in the polar liquids. The O–H vibrational features show processing liquid affects the structure of aluminum surface oxides and induces more exothermic PIR kinetics which in turn correlate with significant improvements in energy propagation [2]. However, this strategy for optimizing fuel particle reactivity by modification of the Al

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particle passivation shell using polar processing liquids may not be feasible for reactions that do not demonstrate a PIR.

The environment has also been shown to have an effect on altering the chemical composition of some oxidizing agents, specifically iodine pentoxide (I_2O_5) [3,4]. Iodine oxides are hygroscopic to the point of being deliquescent [5]. Selte et al. found that relative humidity (RH) has an effect on the hydration state of I_2O_5 when dissolved in a polar liquid and recrystallized in ambient air at varying RH [4]. Also, HIO_3 is a hydrated state of HI_3O_8 and I_2O_5 and in general, higher concentrations of HIO_3 will be seen with higher RH ambient air during recrystallization. Smith et al. [6] extended this analysis from RH in an air environment to water immiscibility (and polarity) of the carrier fluid used to intermix I_2O_5 with Al particles. They used differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to show that iodic acids are in greater concentration after processing I_2O_5 in polar liquids. Higher concentration of iodic acid produced significantly more gas upon reaction with Al that enhanced convective energy propagation and resulted in higher flame speeds.

It is also noted that polar liquids are widely used to affect surface properties of materials for applications in fields like ceramics, pharmaceuticals and thin film processing. For example, evaporation and spray pyrolysis are simple methods to form a thin film on crystalline substrates such as glass or metal. A solution of a metal compound with a source in a polar solvent is pyrolyzed on a hot substrate in the spray pyrolysis technique for creating large area films [7]. Polarity of the solvent becomes particularly important when the surface morphology needs to be varied. Non-polar solvents are incapable of providing the diversity in morphology achieved by polar solvents [7]. In the pharmaceutical industry, polar solvents are utilized as reaction media, in separation and purification of synthesized products. Polar solvents need to be used in synthesis pathways for an active substance (i.e., excipient) because polar solvents aid in dissolution of disintegrants [8]. Also, supercritical fluids (SCF) are substances that cease to exist in distinct liquid or gas phase beyond their critical temperature and pressure values and need polar solvents of a certain pH strength to modify their solubility further. Solubility of a SCF is crucial for improved mobility such that a SCF can mimic a gas and also a liquid solvent. These beneficial properties of SCFs mean they can deliver higher mass transfer and better penetration efficiency into porous matrices [8]. Another illustration for use of polar solvents for enhancing effectiveness of materials for semiconductor applications is tetraethyl orthosilicate (TEOS) which is used as a crosslinking agent in silicone polymers. Silicone polymers are a precursor to silicon dioxide and source for zeolite synthesis. Silicon dioxide can often be polarized by replacing the ethoxy group by a hydroxyl group through a polar solvent during hydrolysis, therefore increasing its solubility in order to achieve greater supersaturation for initiating the nucleation process [9]. All of these studies indicate that the carrier fluid can chemically alter reactants and overall reactivity, even though the carrier fluid may be evaporated from the dry powder mixture prior to its use.

To the authors' knowledge, the impact of carrier fluid has not been analyzed for Al with metal oxides such as copper oxide (CuO) or molybdenum trioxide (MoO_3). The focus of this study is to isolate polarity of the processing liquid as a variable in processing a mixture of Al with CuO and Al with MoO_3 and assesses the influence of processing liquid on energy propagation. This study investigates the hypothesis that carrier fluid will have an impact on reactivity if: (1) PIR kinetics exist for the reaction (i.e., as in the case of Al+PTFE); or, (2) the carrier fluid chemically alters the reactants (i.e., as in the case of Al+ I_2O_5). Therefore, the objective is to examine the influence of processing liquid polarity on reactivity of Al+CuO and Al+ MoO_3 that do not exhibit a PIR nor bulk transform chemically upon immersion in a processing liquid. Two

Table 1

Composition of each formulation according to mass percent, equivalence ratio, and percent theoretical maximum density (TMD).

Formulation	Equivalence Ratio	Aluminum Wt.%	Oxidizer Wt.%	% TMD
Al + PTFE	1.5	40	PTFE–60%	16
Al + CuO	1.2	25	CuO–75%	17
Al + MoO_3	1	40	MoO_3 –60%	15
Al + I_2O_5	1.2	25	I_2O_5 –75%	18

processing liquids were investigated: a non-polar (hexane) and a polar (isopropanol) processing liquid.

2. Experimental

2.1. Reagents

The average particle diameters of Al (supplied by NovaCentrix; Austin, TX), CuO and MoO_3 (Sigma Aldrich; St. Louis, MO) are 80 nm, 50 nm, and 100 nm, respectively. Since Al is pyrophoric in nature, an alumina passivation layer (e.g., 3 nm thick) encapsulates the fuel core to facilitate safe handling of the material. Poly(tetrafluoroethylene) (PTFE) was supplied by DuPont Inc. as Zonyl™ MP 1100 with an average spherical particle diameter of 3 μ m. Diiodine pentoxide (I_2O_5) was supplied by Sigma Aldrich (St. Louis, MO) with an average particle size of 16 μ m.

The processing liquids were hexane (Fisher Scientific; Hampton, NH) and isopropanol (Macron Fine Chemicals; Center Valley, PA) that are reagent grade, or better, and were used without further purification. The water concentration of the processing liquids was determined by coulombic Karl Fischer volumetric titration (Mettler-Toledo model DL36; Columbus, OH). Hexane showed negligible water, isopropanol contained 0.1 vol.%.

Table 1 shows the mass percentage of each reactant as well as the mixture equivalence ratio. It is noted that I_2O_5 is highly reactive and easily oxidizes other compounds in the environment (i.e., carbon monoxide through Ditte's reaction and alcohols [3,6]) such that an equivalence ratio of 1.0 was used when mixing Al with I_2O_5 . While each of the compositions studied shown in Table 1 were not prepared at the same stoichiometry, the comparisons made for assessing reactivity are not a function of composition but instead a function of processing liquid used. In this way, each mixture was prepared in hexane or in isopropanol, then combustion behavior was compared for a given composition.

All mixtures were processed by adding a total of 500 mg of powder mixture to 60 ml of processing liquid. The powder-liquid mixture was processed using a sonic wand (Sonicator 3000, Mission; Farmingdale, NY) for 60 s, using a programmed cycle of 10 s on and off to aid intermixing of reactant powders. The solution was then poured onto a glass plate and the liquid evaporated in ambient air, with relative humidity varying between 30 and 70%. The mixed powder was then reclaimed, sieved to eliminate large agglomerations, and used for further experimentation.

2.2. Instrumentation

A flame tube apparatus [10] was used to measure flame speeds. The tube length is 10 cm with a 3 mm inside diameter. Powder is loaded into the tube to a constant bulk density for each composition and with negligible density gradients. For all mixtures, the powder was loaded into tubes to 15–18% of the theoretical maximum density (TMD).

Progress of the leading edge of the reaction was measured by a high-speed camera system aligned perpendicular to the direction of flame propagation. For repeatability, three tests were performed for each composition. The flame tube was positioned inside a

combustion chamber and a Phantom v 7.1 (Vision Research; Wayne, NJ USA) equipped with a Nikon AF Nikkor 52 mm 1:2.8 lens was used to record flame propagation. These reactions produce intense light emission that can saturate the sensor on the camera and provide erroneous measurements of flame speed. The amplitude of light is greatest in the reaction zone and the leading edge of the reaction zone is used to determine flame speeds. For this reason, neutral density filters and aperture reduction (f-stop) are required to reduce the amount of light that reaches the sensors. The amount of light that is blocked by neutral density filters and the f-stop is dependent on the amount of light that is produced for each reaction. A small portion (i.e., <20 mg) of each sample was tested prior to flame speed measurements to determine the f-stop setting and transmittance of neutral density filters. The Al + I₂O₅ reaction generates the highest light intensity and required neutral density filters to block 99% of the light followed by a 1/32 aperture size. For each composition the appropriate optics were coordinated to visually observe the leading edge of the reaction front during propagation and quantify a flame speed.

The reactions are initiated by a voltage pulse (15–18 V) into a wire in contact with the powder and flame front progression is measured from still-frame images (Vision Builder software, Vision Research). The frame rates used to record the reactions depend on the reaction speed. The frame rate was adjusted between 51,000 and 250,000 frames per second to allow a minimum of 10 frames to be captured at the highest resolution possible (e.g., 512 × 320). For the initial propagation distance (up to about 2 cm from the point of ignition), the reaction is unsteady and flame front progression is non-linear. This portion is considered an “entry region” and is not included in the calculation of steady state flame speed. Steady state propagation is attained beyond the first two centimeters of tube length from the point of ignition for all formulations examined here.

Thermal analysis was performed with a Netzsch Jupiter simultaneous thermal analyzer (STA) 449 differential scanning calorimeter (DSC). Samples were prepared by sonication of powder mixtures processed in each carrier fluid then allowed to dry in a similar manner as the flame speed samples. Samples were heated from 50 to 700 °C at 10 °C/min in an argon atmosphere. All samples were analyzed in an argon environment and experiments were performed in triplicate to ensure repeatability. It is noted that thermogravimetric (TG) analysis was performed on these samples also and no significant difference in mass throughout the temperature range analyzed was observed while comparing data for polar and non-polar processed mixtures.

Fourier Transform Infrared Spectroscopy (FTIR) was performed on Al + CuO and Al + MoO₃ formulations. Spectroscopy was performed using a Tensor 27 (Bruker Optics) operating with a deuterated, L-alaninedoped triglycine sulfate (DLATGS) detector, at an average of 128 interferograms. The potassium bromide beamsplitter and a mid infra-red source was used. Samples were prepared by sonication of powder mixtures processed in each carrier fluid then allowed to dry in a similar manner as the flame speed samples. The sample was loaded on an attenuated total reflectance (ATR) accessory with a 1.8 mm round ZnSe crystal (Pike Technologies as MIRacle ATR). About 5–10 mg of powder was placed on the crystal and scans were made at a resolution of 4 cm⁻¹, apodized with Blackman-Harris 3-Term.

2.3. Simulations

Heat of combustion, adiabatic flame temperature and gas generation were calculated for each reaction using thermal equilibrium software, REAL code, based on the formation enthalpy and mass fraction of the reactants [11]. These simulations were performed assuming a constant volume of 0.01 m³/kg, temperature of 2000 °C,

and internal energy equal to zero. For each simulation, the stoichiometric mixture used experimentally was assumed. This calculation also assumes complete combustion (i.e., all Al is converted to Al₂O₃). Heat of formation for each composition was determined assuming the elemental forms of the constituents form the products (i.e., I₂ + 2.5O₂ → I₂O₅).

3. Results and discussion

Fig. 1 shows the effect of processing liquid on flame speed for Al + PTFE [2]; Al + I₂O₅ [6]; Al + CuO; and, Al + MoO₃. Note that the absolute values of flame speed should not be compared across different mixtures, but instead comparison is made for a single mixture as a function of the carrier fluid. Multiple formulations are presented for reference regarding the distinction each mixture has between carrier fluids. Overall, there is a very large difference in flame speed as a function of carrier fluid for Al + PTFE and Al + I₂O₅ (Fig. 1a and b, respectively); a slight difference for Al + MoO₃ (Fig. 1d); and, no difference for Al + CuO (Fig. 1c) as a function of carrier fluid.

Convection forms the prevailing mode of energy transfer during flame front progression due to the low bulk density and abundance of air voids within the tube loosely filled with powder mixture. The loose powder fill and gas generation during reaction in the confined space of the tube promotes advection. Table 2 shows results from the thermal equilibrium simulations that indicate combustion properties for each composition shown in Fig. 1. Overall, mixtures with high gas generation generally produce faster flame speeds. The correlation to gas generation in Table 1 and flame speed in Fig. 1 is not direct. Gas generation rate may be more indicative of convective behavior and is not calculated in the simulations shown in Table 2. But, generally overall gas generation is one indicator of the potential for a reaction to be strongly convective during energy propagation. Each composition studied produces at least 17 wt.% of the products in the gas phase as shown in Table 2 and flame speeds of at least 100 m/s (Fig. 1). It is also noted that Al + I₂O₅ was prepared at a lower bulk density (i.e., 18 vs 30 wt.% TMD) such that the very high flame speed measured for Al + I₂O₅ may partially be an artifact of its lower bulk density. Further discussion of results shown in Fig. 1 will focus on each composition individually as a function of processing liquid used in powder mixture preparation, rather than a comparison between different compositions.

For Fig. 1a the only variable introduced into the experiment is the processing liquid which does not affect mixture homogeneity of the reactants, as observed using SEM analysis shown in Padhye et al. [2] for Al + PTFE, and in Supplementary information for other mixtures examined in this study. Also, the flame speeds reported in Fig. 1a show good repeatability (i.e., small error bars indicating small deviation in measurement between different experiments) and is another indication of consistent reaction behavior resulting from good reactant mixture homogeneity. Because physical mixing properties are similar for each carrier fluid, kinetic variations may contribute to enhanced flame speeds.

The kinetics for Al and PTFE were observed by Osborne and Pantoya [12] using differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis and they noted a prominent exotherm prior to the main Al oxidation reaction. The exotherm is attributed to a pre-ignition (PIR) reaction between fluorine species in the fluoropolymer and the alumina passivation shell surrounding the Al particles. This PIR promotes subsequent decomposition of the fluoropolymer and bulk Al oxidation. Higher concentrations of hydroxyl groups on the aluminum oxide surface have been shown to increase the magnitude of the PIR and overall reactivity of aluminum and fluoropolymer mixtures [2,13,14]. The processing liquid affects aluminum surface crystal structure. The strong hydrogen bonding

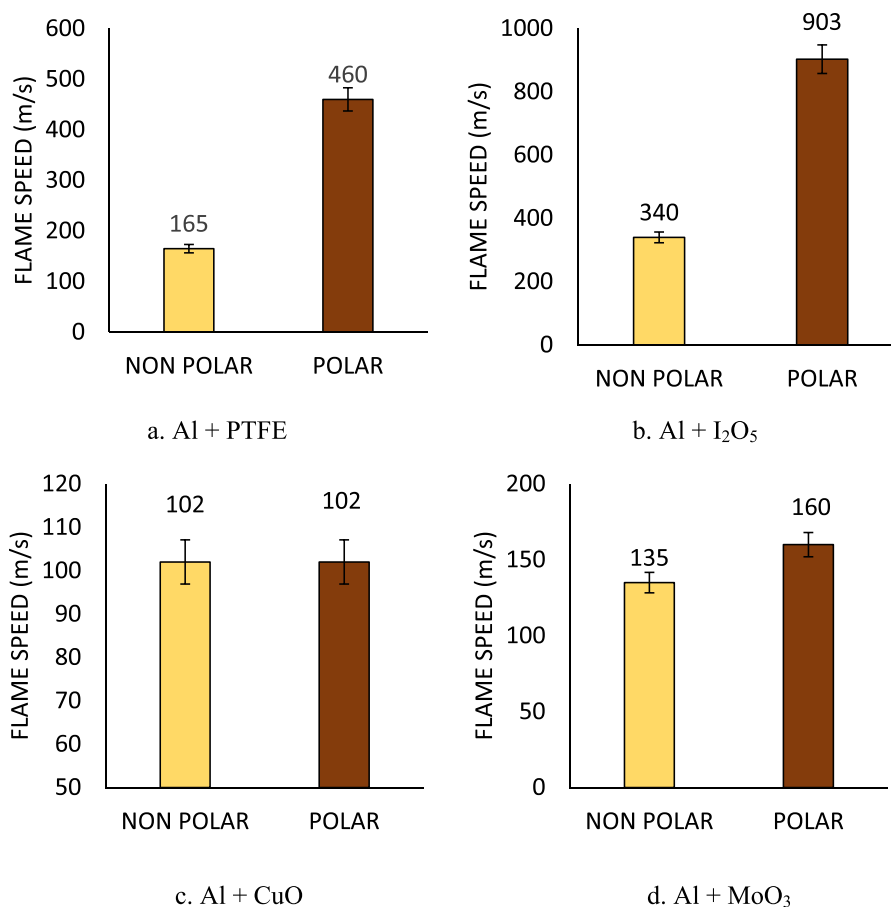


Fig. 1. Flame speed results as a function of processing liquid with hexane (i.e., nonpolar) and isopropanol (i.e., polar) liquids indicated in each figure for a. Al + PTFE; b. Al + I₂O₅; c. Al + CuO; and, d. Al + MoO₃. The error bars give the 95% confidence limits based on three tests and the average flame speed is reported above each bar in m/s.

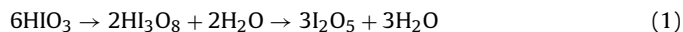
Table 2
REAL code thermal equilibrium simulations for all formulations.

Formulation	Adiabatic Flame Temperature (K)	Heat of Combustion (kJ/kg)	Total Gas Generation (wt.%)
Al + PTFE	2759	7424	88
Al + CuO	2785	3786	26
Al + MoO ₃	2896	3879	17
Al + I ₂ O ₅	3875	5812	70

forces in isopropanol influence the structure of hydroxyl bonds on alumina that in turn affect the exothermic surface reaction between fluorine from PTFE and hydroxyl bonds on alumina [2]. From DFT calculations the effect of liquid polarity and the subsequent hydrogen bonding forces on structural modification of aluminum showed bond distances and atomic charges increase whereas frequencies decrease due to the influence of added water on the alumina surface [15]. These structural modifications result in weakened OH bonding and could contribute to the observed enhanced PIR [15]. The PIR that is enhanced by alteration of the hydroxyl layer on the aluminum oxide surface may then contribute to the higher flame speeds shown in Fig. 1a for Al + PTFE processed using isopropanol.

The PIR is not limited to fluorocarbons, but is present when other halogenated compounds serve as the oxidizing agent [16,17]. In this way, the processing liquid may affect alumina surface reactions and the reactivity of oxidizers such as I₂O₅. Fig. 1b confirms that flame speed is significantly impacted by carrier fluid for Al + I₂O₅. Interestingly, however, the PIR remains relatively unchanged for Al + I₂O₅ mixtures processed in either a polar or a non-polar processing liquid, as seen in the shaded region of Fig. 2a. Smith et al. [6] show polar processing liquids transform I₂O₅ into iodic acids (i.e.,

HIO₃, HI₃O₈). Dehydration occurs in accordance with the following steps that show HIO₃ dehydrates to form HI₃O₈ (an intermediate [HIO₃][I₂O₅] complex) which can undergo full dehydration to I₂O₅ [4].



The DSC traces in Fig. 2b confirm isopropanol processed powders are comprised of HIO₃ and HI₃O₈, which dehydrate at 110 °C and 210 °C, respectively, while the hexane processed powders primarily contain the lower hydration HI₃O₈ species. In Fig. 2b the DSC results clearly demonstrate the mixture processed in the polar liquid retains a greater amount of water, which is known to condition the aluminum oxide passivation layer. Similar to the PIR reaction for Al + PTFE mixtures [2], at PIR temperatures the conditioned oxide shell is primed to undergo reaction with traces of iodine liberated by the thermal decomposition of iodine oxides. The PIR then activates Al particles toward rapid oxidation in the bulk Al combustion phase.

In both steps of the reaction in Rxn. (1), 5 wt.% of the products are gas in the form of water vapor. Thermal equilibrium simulations show that when the dehydration reaction happens at 2000 K,

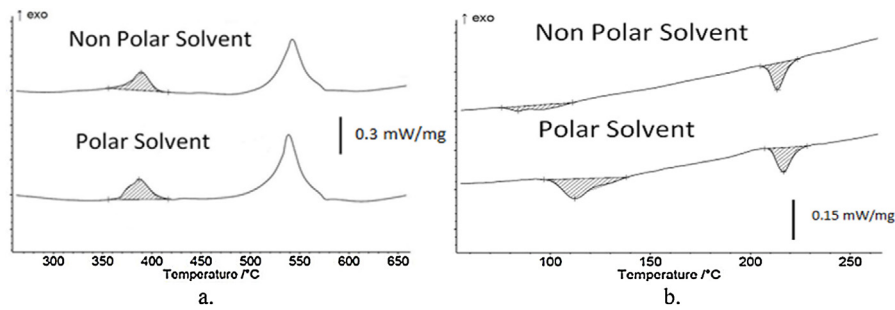


Fig. 2. a. Heat flow curves from DSC data of Al + I₂O₅ in the PIR temperature zone (shaded) and the main reaction temperature zone. Analysis performed in argon at 10° per minute heating rate. b. Heat flow curves from DSC data of Al + I₂O₅ in the HIO₃ and H₃O₃ dehydration temperature range. Analysis performed in argon at 10° per minute heating rate.

25 wt.% of the products are gas in the form of water, iodine, and oxygen [5]. The increased gas production in these dehydration steps makes the reaction more convectively driven than the hexane processed mixture and may contribute to the dramatic difference in flame speed shown in Fig. 1b.

In Fig. 1c, the variation in flame speed with carrier fluid used in processing Al + CuO is insignificant. A thermal equilibrium analysis of Al + CuO (and Al + MoO₃) using DSC is shown in Fig. 3a (and b). No pre-ignition reaction (PIR) is observed in the DSC data for Al + CuO (or Al + MoO₃) processed in either the hexane or isopropanol; i.e., there is no indication of exothermic behavior prior to the main Al oxidation reaction. For Al + CuO, Figs. 1c and 3a imply that in the absence of the PIR, processing liquid polarity does not significantly affect reactivity.

It is further noted that the flame speeds observed for Al + CuO in Fig. 1c are lower than reported in past studies (i.e., 102 m/s compared with 600 m/s) [1]. The reason for this could be the higher packing density for these samples (i.e., approximately 18% TMD compared to 7% TMD in [1]). This decrease in flame speed as a function of bulk density is consistent with that observed for Al + MoO₃ in [18]. Compacting powders tends to limit convective influences that facilitate propagation.

Fig. 1d shows that the processing liquid has an effect on the flame speed for Al + MoO₃ even though no PIR is detected (Fig. 3b). In Fig. 1d for polar liquid processing, the flame speed is 19% higher than the same mixture processed in the non-polar liquid. The increase in flame speed likely results from the tendency of MoO₃ to form hydrates under ambient conditions, resulting in Mo-O compounds that can undergo complex changes in structure and composition [19]. To further examine surface modification of MoO₃ compared with CuO as a function of carrier fluid, FTIR analyses were performed.

Fig. 4 shows FTIR absorbance spectra for CuO and MoO₃ as a function of processing liquid polarity. The spectra for CuO in both the non-polar and polar processing liquids looks similar; in fact,

the spectra almost perfectly overlap, indicating little effect from the carrier fluid. However, MoO₃ spectra is distinctly different in the two liquids; and, for the polar processed MoO₃, the spectrum shows a stronger intensity of light absorbed by species present on the surface of these particles.

Both CuO and MoO₃ are capable of hydration under processing conditions that contain water. For hydration, CuO needs one water molecule while MoO₃ bonds with two water molecules. Water from the polar liquid hydrates MoO₃ forming hydrogen bonds with hydroxyls on the surface of the particle. During hydration, these two water molecules coordinate differently in the oxide structure by: (1) altering the hydroxyl coordinations on the surface; (2) increasing the concentration of the hydroxyl layer; and, (3) increasing hydrogen bonding forces between layers that bind water molecules [20]. The FTIR spectra from Fig. 4b. confirm improved hydration of MoO₃ surface, which is evident from the increase in absorbance intensity overall and in particular in the 3300–3800 cm⁻¹ wavenumber region corresponding to hydrated species. In contrast, the surface structure of CuO is less sensitive to hydration. Hydrated CuO is less polar compared to hydrated MoO₃, therefore CuO is less affected by the polarity of the surrounding processing liquid [21,22]. It is also noted that if sufficient moisture is present in the environment at elevated temperatures, it is possible to maintain an extensively hydrated surface up to 230 °C [23–25]. In summary, polar liquids hydrate both Al and MoO₃ particles such that the overall concentration of water is greater than with Al and CuO particles. Also, during hydration, the hydrogen bonding forces may also weaken particular hydroxyl coordinations or may re-structure the surface with hydroxyl coordinations that more favorably promote surface reactions. The precise mechanism for surface alteration that affects reactivity is not yet understood, but the distinct chemical influence associated with surface treatment is now confirmed and the correlation to overall reactivity is also observed in Fig. 1d for Al + MoO₃.

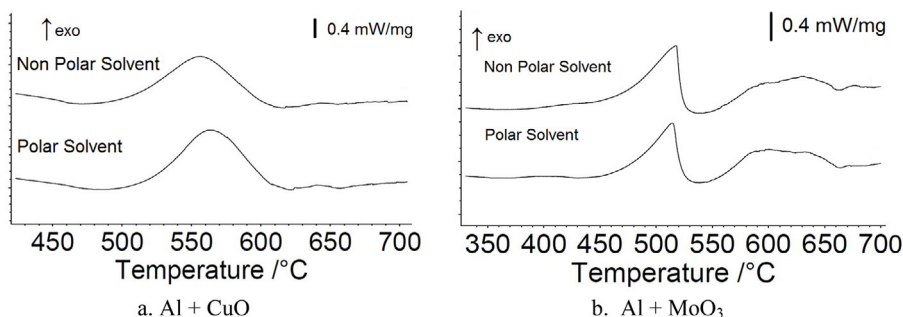


Fig. 3. Heat flow curves from DSC data for a. Al + CuO and b. Al + MoO₃. Analysis performed in argon at 10° C per minute heating rate. Note the Al oxidation reaction at 550° C for Al + CuO and 500° C for Al + MoO₃.

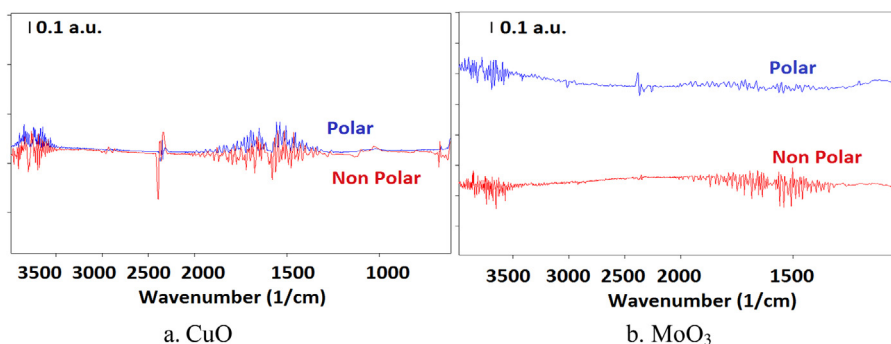


Fig. 4. FTIR spectra for samples suspended in non-polar and polar solvents for a. CuO b. MoO₃.

Using REAL code simulations, an analysis on combustion properties was performed to elucidate further the influence of added water concentration to the binary mixture. The percentage of water present in the polar liquid (i.e., 0.1 vol.% for isopropanol) was added as an oxidizer percentage in the simulation calculations, as an upper limit for water concentration in the mixture. For hexane the water percentage was assumed to be zero, while for isopropanol the mass proportion of MoO₃ became 0.599 and water is 0.001. Therefore, the total mass proportion of the oxidizer remained at 0.6 as per the equivalence ratio. Results show that the heat of combustion increases from 3879 kJ/kg without water to 3948 kJ/kg when the mass proportion of water from the processing liquid was accounted for as an oxidizer in the calculations. The increased heat of combustion is slight but strengthens the argument that small increases in water concentration (i.e., from greater hydration layer thickness) lead to higher heat of combustion that may also contribute to the slight increase in flame speed (Fig. 1c).

It is understood that modified surface crystal structure for the various solids in contact with polar or non-polar liquids suggested above requires additional experimental validation, including experiments with other metal oxides, further spectroscopic analysis, variations with particle sizes and investigation of kinetic mechanisms. As follows from above, carrier fluid influences energy propagation via chemical alterations of particle surfaces as observed with MoO₃. Both Al and MoO₃ surfaces are exposed to hydrogen bonding forces within polar liquids that then influence the overall energy propagation within a mixture. The variations in flame speed are a consequence of chemical affects as shown here. Physical mixture homogeneity is not a factor because experimental flame speed measurements show good repeatability and SEM and EDS indicate uniform mixing as a function of carrier fluid (see Supplementary information section for more on this). These results present an effective tool (i.e., selection of carrier fluid) for controlling the propagation characteristics of high energy density composites.

4. Conclusion

The effect of carrier fluid on particle hydration of aluminum (Al) fueled energetic mixtures and the resulting influence on reactivity was studied for different metal oxides (i.e., MoO₃ and CuO) and compared with other oxidizing agents, including fluoropolymers (PTFE) and halogenated oxides (I₂O₅). For fluorocarbon containing mixtures; processing liquid polarity plays a major role in enhancing the Al flame speeds via surface reactions (i.e., pre-ignition reaction, PIR) between the alumina passivation shell and fluorine species. For another halogen containing species, such as I₂O₅, the PIR was not altered by processing liquid. Instead, water in polar processing liquids reacts with I₂O₅, to form various iodine acidic species. These acids generate gas upon combustion and contribute to enhanced

convection and increased flame speed. As an extension, the processing liquid impact was investigated for metal oxides. Results show that for Al + CuO processing liquid polarity produces no change in reactivity. But, Al + MoO₃ in contrast, shows an increase (i.e., 19%) in flame speed when processed in a polar liquid. This increase was attributed to hydration of MoO₃ that is not as significant with CuO. The added hydroxyl concentration and modified surface hydroxyl structures on MoO₃ shown with FTIR may contribute to the increased flame speed. These are important findings for optimizing combustion through selection of processing agents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2017.01.016>.

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