Smart Functional Nanoenergetic Materials

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Energetic Material Design to Control High Pressure Dynamics Workshop
21 January 2015
UCLA IPAM Center
Why Nanoenergetic Materials

Important Components to Energetic Materials

• High Energy Density Fuel Components to Propellants, Fuels, and Explosives (High Concentrations)
• Burning Rate Modifiers (Low Concentrations)
• Gelling Agents for Hazards Reduction, MEMs systems, and others

Unique Properties

• Increased Specific Surface Area
• Increased Reactivity
• Increased Catalytic Activity
• Lower Melting Temperatures
• Lower Heats of Fusion, Increased Heats of Reaction

Implications to Propulsion

• Increased Burning Rates (> factor 5)
• Higher Efficiency (more efficient particle combustion, less two phase flow losses, for solids Isp ↑ 10s)
• Reduced Sensitivity
• Min/low smoke energetic materials
Motivation

- Condensed phase agglomerates can contribute to two-phase flow losses
- Two-phase flow losses can reduce motor performance by as much as 10%[a]
- Inclusion modified fuels or other composites can lead to smaller product particles, and potentially lower two-phase flow loss


Example of Burning Propellants

Combustion of μm Al far from surface

Combustion of nm Al close to surface

~1.8 ×’s increase in \( r_b \)

\[
\begin{align*}
\log (r_b) \quad [\text{cm/s}] \\
0 & 0.5 & 1 & 1.5 & 2 \\
0 & 0.5 & 1 & 1.5 & 2
\end{align*}
\]

9% nAl (ALEX) / 9% μAl

\[
r_b = 2.538P^{0.618}
\]

18% μAl

\[
r_b = 2.092P^{0.390}
\]


G. V. Ivanov, and F. Tepper, Challenges in Propellants and Combustion 100 Years after Nobel, pp.636-645, (Ed. K. K. Kuo et al., Begell House, 1997).
Example of Burning Propellants: the Surface

50 \mu m Al spherical agglomerate formed by inflammation of an aluminized aggregate

50-250 nm Al emerging from surface as aggregates (pre-agglomerate)

Al Burning Times

Experiment

Burning Time [ms]

Diameter [μm]

1173 K

1500 K

2000 K

Anticipated Times

d

d^2

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Issues and Motivation

Current Status: The full extent of the anticipated gains from nanoscale energetic materials has not been realized in large part due to: Low sintering temperatures, High surface area leading to large aggregates, Limited solids loading with nanoparticles, Oxide coatings lowering active metal content, Lack of fundamental understanding of burning process

Motivation: 3-D, hierarchical, ordered structures, controlled reactivity, addressable, improved processing
Approach and Organization

(a) Processing Nanoenergetic Materials
Aksay, Eichhorn, Zachariah

- Cluster Assembled Metal Mesoparticles
- Al₇[Si(NMe₃)₂]₂ Molecule
- Linked Tetrazines

Functionalized Graphene Sheet

(b) Multiscale Processing
Aksay, Eichhorn, Zachariah

- Energetic Bridging Molecules
- Tetrazine bridge

Pennsylvania State
Maryland

- Nanostructured Catalysts
- FGS

- Graphene Sponge

Princeton
Georgia Tech

- Metal NPs on FGS

(c) Modeling
Car, Selloni, Yang

- Temperature
- Heat release
- Propellants and FGS

- Molecular Dynamics
- Modeling at the Mesoscale

(d) Kinetics and Propulsion
Son, Thynell, Yetter

Combustion Wave Structure
Probing Reaction Dynamics

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Why Tetrazines and FGS?

- Substituted tetrazines are readily synthesized.
  - Can be tailored to application (energetics, fluorophores, coordination chemistry)
  - Covalent bonds formed via nucleophilic substitution of hydroxyls
- Tetrazine-based energetic materials are described by Los Alamos as a promising class of compounds materials for propellants and explosives.
  - High density, high nitrogen compounds with unusual combustion mechanisms due to high heats of formation
  - Ready addition of substituents for increased stability (more carbon) or increased energetics (more nitrogen)
- Functionalized graphene sheets (FGSs) are a reduced form of graphene oxide, containing high energy lattice defects and various oxygen functional groups distributed across a high surface area sheet.
  - FGSs are catalysts for monopropellant combustion through hydroxyls on defect sites
  - Defect sites and oxygen functionalities provide a variety of sites for chemical modification of the FGS
  - Graphene gels--3D high surface area porous matrices--can be used as containers for gases, liquids, and solids
- Tetrazines have been attached to FGSs via simple nucleophilic aromatic substitution and as covalent links between FGSs

Heat of formation:
- 1,2,4,5-tetrazine: $481 \text{ kJ/mol}$
- 3,6-dihydrazino-1,2,4,5-tetrazine: $536 \text{ kJ/mol}$
- 3,6-diazido-1,2,4,5-tetrazine: $1101 \text{ kJ/mol}$
Tetrazines Covalently Bind to FGS

- Aims for bridging sheets with bound tetrazines:
  - Porous matrix (graphene gel)
  - Energetic links to decompose and fragment matrix (increased nitrogen content)
  - Thermally and electrically conductive matrix

- Effect of binding tetrazines:
  - Are covalently bound tetrazines more stable?
  - What is the effect on the rate of tetrazine fragmentation?
  - Does this change the rate of energy release?
  - What are the reaction products?

<table>
<thead>
<tr>
<th></th>
<th>FGS₂</th>
<th>FGS-Tz2</th>
<th>FGS-Tz3</th>
<th>FGS-Tz4</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C</td>
<td>67.5</td>
<td>71.0</td>
<td>79.8</td>
<td>70.2</td>
</tr>
<tr>
<td>%N</td>
<td>0.0</td>
<td>12.1</td>
<td>5.8</td>
<td>18.0</td>
</tr>
<tr>
<td>%O</td>
<td>31.8</td>
<td>16.4</td>
<td>13.9</td>
<td>10.7</td>
</tr>
<tr>
<td>%Cl</td>
<td>0.28</td>
<td>0.50</td>
<td>0.37</td>
<td>1.08</td>
</tr>
</tbody>
</table>

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Covalent Bonds Stabilize Tetrazines to Achieve More Decomposition

- Confined rapid thermolysis (PSU): Rapid heating rate (2000 °/s) prevents vaporization of condensed phase
  - Reaction products past through infrared spectrometer for identification
- When heated to temperature high enough to initiate decomposition, bound tetrazines decompose into smaller molecular species
Covalently Bound Tetrazines Decompose at Higher Onset Temperature

- Only partial decomposition of Tz4
- Temperature rapidly increases with time (10^5 °/s)
- Fragments analyzed by mass spectroscopy
- Pure tetrazines start to decompose at lower T, but produce large mass fragments
- Tetrazines bound to FGS start to decompose at higher T, but with higher rate of decomposition to form smaller mass fragments
Bound Tetrazines Quickly Fragment into Smaller Molecules under Rapid Heating

- Fragmentation of compounds under extremely rapid heating ($10^5 {^\circ}/s$)
  - Pure tetrazines begin to decompose at lower temperature but generate large mass fragments, indicating incomplete decomposition
  - The decomposition of tetrazines bound to FGS begins at higher temperature with lower mass fragments, indicating more complete decomposition
Tz4 and Bound Tz4 Decompose through Different Mechanisms

- Molecular dynamic model: temperature raised instantaneously to 2700 K to ensure tetrazine decomposition
- Bound tetrazine rapidly and more completely decomposes; fragmentation proceeds on or near FGS
- Faster rate of reaction for tetrazine decomposition leads to higher rate of energy production
- Hypothesis: vibrational state of bound tetrazine very high → local temperature much higher than ambient…why?
Some liquid rocket motors use fuel in cooling passages ⇒ fuel film cooling produces coke ⇒ variability in heat transfer and clogging.

Additives may lower fuel decomposition temperature to enhance cooling without coking.

Graphene w and w/o catalyst may be used to accelerate decomposition kinetics.

Particle pinning to surface remains intact and therefore additive may subsequently be used to enhance gas-phase combustion.

Low concentrations may be suspended in liquid rocket fuels – more reactive catalyst desired.

Applications to ionic liquids should be considered.
Effects of Particles in Combustion Sprays

- Fuel propellant sprays are studied at low and elevated pressures (sub and supercritical) without and with combustion.
- The effects of the nanocomposite additives on the spray characteristics, ignition, and combustion are studied.

![Image showing comparison of spray characteristics at different Reynolds numbers (Re=1,400 and Re=3,500) and pressures (P=600 psi) with and without additives.](image)
Reaction Modeling of Graphene and Al Based Clusters/Composites in C/H/O/N Systems

Thermal decomposition modeling results of graphene with n-dodecane using ReaxFF consistent with experiments (with H. Sim and Adri van Duin, PSU)

- Dehydrogenation of n-dodecane:
  \[ C_{53}H_{20}O_2 \text{ (graphene)} + C_{12}H_{26} \rightarrow C_{53}H_{21}O_2 + C_{12}H_{25} \]
- C-C scission followed by the dehydrogenation to form smaller products:
  \[ C_{12}H_{25} \rightarrow C_4H_8 + C_8H_{17} \]

In preparation to model the oxidation of Al clusters and composite particles, thermal oxidation of Al nanoparticles was performed using ReaxFF (with S. Hong and Adri van Duin, PSU)

- ReaxFF reactive force has been developed for Al/C/H/O systems.
- Hot spots were observed at outer surface of 2.8 nm (864 atom) particle during oxide formation for NVT simulations at 300, 500, and 900 K.
- Hot spots generated voids, which accelerated transport and reaction by reducing reaction barrier for diffusion from 36 kcal/mol to 2.9 kcal/mol

Number of n-dodecane w or w/o oxidized graphene \((C_{53}H_{20}O_2)\) at 1800 K (density = 0.12 and 0.31 g/cc)

Dehydrogenation of n-dodecane:

\[ C_{53}H_{20}O_2 \text{ (graphene)} + C_{12}H_{26} \rightarrow C_{53}H_{21}O_2 + C_{12}H_{25} \]

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Modeling and Simulation of Heat Transport and Combustion of Nanoenergetic Materials

- **Atomistic Scale Modeling of Heat Transport in Nano-Particle Laden Fluids**
  - study heat transport in nano-particle laden fluids using MD simulations and calculate transport properties
  - results serve as inputs to macro-scale combustion models

- **Macro-Scale Modeling of Combustion of Metal-Based Heterogeneous Reactive Materials**
  - investigate mechanisms that control burning rate of mixtures
  - explored the effects of particle entrainment and agglomeration on burning properties of nano-aluminum and water mixtures
    - nano-aluminum and water mixtures
    - aluminum, water, and hydrogen peroxide mixtures
    - nickel-clad aluminum pellets
Effect of Particle Entrainment and Agglomeration on Combustion of Nano-Al/Water Mixtures

- Does nano-Al agglomerate during combustion?
- Does particle motion affect burning behaviors?
- Aluminum particles can be entrained by the flow water vapor generated by water vaporization
- Particle velocity: \( u_p = r_b \left( \frac{\rho_i}{\rho_g} \right)^n \), \( 0 \leq n \leq 1 \)
  - \( n = 0 \): no entrainment; \( n = 1 \): complete entrainment
- Burning rate: \( r_b = a p^m \)
  - Diffusion regime: \( 0 < m < 0.5 \)
  - Kinetics: \( 0.5 < m < 1 \)
- Pressure dependence of burning rate due to
  - combustion mechanism (burn time: \( t_b \sim p^{-q} \))
  - particle entrainment
- **Entrainment lowers burning rate** by increasing flame thickness and decreasing heat flux
- Particles cluster and agglomerate (d~3-5 \( \mu \)m) due to inter- & intra-particle attractive forces
  - Favorable agreement with experimental data only when entrainment & agglomeration are considered
Heat Transport in Metal-Based Energetic Materials

- How does particle size affect thermal conductivities of particle & particle-laden fluid?
- Can macro-scale models be directly applied for systems with nano-particles?
- Equilibrium MD (EMD)
  \[ \lambda = \frac{1}{k_B V T^2} \int_0^\infty \left\langle J(t) \cdot J(0) \right\rangle \, dt \]
- Non-equilibrium MD (NEMD)
  \[ \lambda = \frac{-q}{dT / dx} \]
- Models validated for bulk solid argon
- For aluminum, potential function exerts significant effect on predictions
- Predicted thermal conductivities orders of magnitude lower than bulk value (230 W/m-k)

Classical MD treats only phonon mode

<table>
<thead>
<tr>
<th>Potential</th>
<th>Aluminum Thermal Conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EMD</td>
</tr>
<tr>
<td>Lenard-Jones</td>
<td>35 – 262</td>
</tr>
<tr>
<td>Sutton-Chen</td>
<td>0.017-0.041</td>
</tr>
<tr>
<td>Cleri-Rosato</td>
<td>0.025-0.035</td>
</tr>
<tr>
<td>Glue</td>
<td>0.47-1.3</td>
</tr>
<tr>
<td>Mishin</td>
<td>0.75-1.75</td>
</tr>
</tbody>
</table>
• Mike Zachariah (Metallic Clusters and Mesoscopic Aggregates)
• Steve Son (Integration of Nanoenergetic Composite Ingredients/Mixtures and their Reactive Characterization)
• Stef Thynell (Experimental and QM Investigation of Decomposition and Early Chemical Kinetics of Ammonia Borane)
• Extras
Research Approach

Combustion Characteristics, Propulsive Behaviors, Burning Properties

Meso-Scale Models

100s Atoms (Periodic Systems)

Inter-Atomic Potential Functions

Molecular Dynamics

Quantum Mechanics

Models

Thermodynamic and Transport Properties, Ignition Characteristics, Reaction Mechanisms

Time Scales

1 fs

1 ns

1 μs

Length Scales

1 Å

10 nm

1 μm
Significant Accomplishments

- Explored the **effects of particle entrainment and agglomeration on burning properties** of nano-aluminum and water mixtures
- Studied the **effects of hydrogen peroxide on combustion of aluminum and water mixtures**
- Investigated the **effect of packing density on burning properties** of metal-based energetic materials
- Developed equilibrium and non-equilibrium MD simulation frameworks to study **heat transport in metal-based nano-energetic materials**
Combustion of Aluminum/Water/Hydrogen Peroxide Mixtures

- What is the effect of hydrogen peroxide on burning properties of Al/water mixtures?
- Model is employed to investigate burning behaviors of Al/water/H$_2$O$_2$ system
  - Pressure: 1-20 MPa; Particle size: 3-70 μm
  - O/F: 1.00-1.67; H$_2$O$_2$ conc.: 0-90 %
  - Particle entrainment phenomenon is considered
- Results compared with experimental data of Son’s group (Purdue)
- For large particles, pressure dependence of burning rate is attributed to particle entrainment effect (and not reaction kinetics)
- Transition from diffusion to kinetically-controlled conditions causes the exponent to increase from 0.35 at 70 μm to 1.04 at 3 μm
- Burning rate nearly doubled when the concentration of hydrogen peroxide increases from 0 to 90 %

![Graph showing burning rate vs. pressure for different concentrations of H$_2$O$_2$.](https://example.com/graph1.png)

![Graph showing pressure exponent vs. particle diameter.](https://example.com/graph2.png)
Effect of Packing Density on Burning Properties of Nickel-Clad Aluminum Pellets

- How does packing density affect burning rates of metal-based energetic materials?
- Flame propagation of nickel-coated aluminum particles in argon environment studied
- Particle size is 79 µm and pressure is 1 atm
- Energy conservation for the pellet:
  \[ \rho_mC_p,m \frac{\partial T}{\partial t} = \lambda_m \frac{\partial^2 T}{\partial x^2} + \dot{Q}_{\text{gen}} - \dot{Q}_{\text{conv}} - \dot{Q}_{\text{rad}} \]
- Conduction & radiation heat losses to ambiance
- MD diffusion coefficients inputs to the model
- Five different models of thermal conductivity employed to identify the most accurate model
- Maxwell-Eucken-Bruggeman thermal conductivity model offers best predictions
  - treats both random (Bruggeman) and dispersed (Maxwell) particle distributions
- Burning rate increases sharply at a packing density of 60 %.
Publications

Increased Rate and Extent of Fragmentation for Bound Tetrazines

Pure Tz4

FGS-Tz4

- Nanocalorimetry (UMd/NIST): Endotherms from sample fragmenting on sample pad during extremely rapid heating ($10^5 \degree/s$); only bond breaking observed
  - Products of fragmentation leave sample pad, ported to mass spectrometer for analysis
- Onset of fragmentation delayed to higher T → tetrazine more stable with respect to higher temperature when bound to FGS
- Larger amount of energy absorbed upon fragmentation, indicating a larger extent of fragmentation in tetrazines bound to FGS
More Complete Fragmentation a General Mechanism for Bound Tetrazines

Effect of binding tetrazines to FGS is similar regardless of tetrazine used:
- Bound tetrazines are stable to higher temperature, but
- When fragmentation begins, it is rapid and more complete.
- This results in a faster rate of reaction leading to higher rates of energy release.
Summary and Targets

• bis-Tetrazines covalently bind to FGSs
  - Tz4 effective and rigid bridging agent
  - Covalent bond confirmed by CV, XPX, FTIR, thermal analysis, and modeling
• Tetrazines covalently bound to FGS decompose at higher temperature and more completely
  - Models indicate a directed decomposition pathway
  - Higher rate of energy release shown in experiment and model

• Targets:
  - Define the mechanism for bound tetrazine decomposition
  - Develop new hybrid materials with higher nitrogen content
  - Combine hybrid materials with liquid and solid propellants
    - Ignition and combustion
    - Hypergolic fuels
    - 3-dimensional graphene gels
  - Incorporate hybrids into printable, conductive inks
    - Energetic devices: addressable igniters
Research Area Overview

- Solid and liquid propellants with energetic additives
- Characterization of combustion behavior of composite additives and propellants containing additives

Advanced Diagnostics Multiscale Modeling

- Reaction analysis and model development of propellants with composite particles
- Analysis of transport properties
- Reaction analysis of interstitial ingredients
- Analysis of entrainment, sintering, and agglomeration
- Strand

Solid Propellant

Liquid Propellant