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Modeling the stability and growth of metalloid clusters for energetic materials

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Abstract. Metalloid clusters, defined as cluster systems with more metal/metal than metal/organic bonds, are currently under study as energetic materials that may retain the high energy density of bulk metals but offer substantially faster reaction kinetics. Considerable synthesis challenges remain, but these systems may in principle allow low-valence metals to oxidize within the reaction zone of a detonation. Here we present density functional theory and ab initio molecular dynamics simulations of ligated aluminum clusters, a prototypical metalloid system that can be reliably synthesized. Thermal decomposition and oxidation pathways are explored to gain a general understanding of how these unusual systems behave at elevated temperatures. The initial stages of cluster oxidation observed in molecular dynamics and metadynamics simulations are in good agreement with recent experimental gas-phase oxidation studies.

INTRODUCTION

Integration of combustible metals is a standard route for increasing the energy density of explosive and propellant formulations.[1, 2, 3] Bulk metals, however, have well-known limitations in terms of their combustion kinetics,[3] the native oxide layers that protect them,[4] and their tendency to agglomerate following ignition.[5] There has been considerable recent interest in developing metal/organic structures that address these issues and might allow for systems with fast reaction kinetics that still retain some of the high energy density of pure metals.[6, 7, 8, 9, 10, 11, 12] At the micron and nanoparticle scales, organic layers are being pursued as an alternative passivation to the native oxide layer,[6, 9] or as a means of assembling metal particles into structured energetic materials. In recent work we have considered low-valence metalloid clusters as materials that may allow metal oxidation on even faster timescales than coated nanoparticles.[7, 11, 12] Several experimental efforts have also begun on lab-scale synthesis of ligated metalloid clusters that could be tailored for energetics applications.[13]

In these proceedings we discuss simulations of the oxidation and unimolecular thermal decomposition of aluminum clusters ligated with cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands. These metalloid aluminum clusters are a prototypical system with high-energy density[7] that allows us to study basic stability and reaction processes in metalloid clusters with low-valence metals. Smaller clusters such as Al_4Cp_4 and $Al_4Cp_4^*$ can be reliably synthesized in larger quantities, while larger examples such as $Al_{50}Cp_{12}^*$ are challenging to produce in bulk. All these systems are synthesized from AlX (X=Cl, Br, or I) monovalent aluminum halide precursors formed in a specialized cocondensation apparatus.[14, 15, 16, 17, 18] This process, pioneered by Schnöckel and coworkers, has lead to the development of many striking group 13 metalloid systems including the large $Al_{77}[N(SiMe_3)]_{20}^{2-}$ and $Si@Al_{56}[N(2,6-iPr_2C_6H_3)SiMe_3]_{12}$. These clusters crystallize into low-symmetry molecular crystals that are very air-sensitive; in this report we focus on isolated clusters for comparison with recent gas-phase cluster studies in ultra-high vacuum. Reference [14] reviews the large body of work on synthesis of these compounds.

Our recent studies using ab initio molecular dynamics (MD) combined with a metadynamics (MTD) algorithm have suggested that the initial process in oxidation of Al_4Cp_4 and $Al_4Cp_4^*$ is a hindered crossing of the ligand's steric barrier by O_2. Following this step, the oxygen molecule splits as it interacts with the aluminum core, forming a temporarily stable oxidized system with Al-O bonds reminiscent of aluminum(III) oxides.[11, 12] Here we expand these simulations to understand the subsequent decomposition of the cluster, for comparison with preliminary thermally programmed reactivity (TPR) experiments by Bowen and coworkers on gas-phase $Al_4Cp_4^*$.[13] In this work, the pre-

viously observed dissociation of O_2 inside the Al_4 tetramer is followed by a complete detachment of a single $AlCp^*$ unit, a proton transfer, and removal of Cp^* ligand. These results are consistent with Bowen's recent experimental work, which showed oxygen primarily reacts with the metal core and that no oxidized ligand decomposition products are produced. Finally, we use nudged elastic band (NEB) and MTD methods as two ways to study the isolated unimolecular decomposition of the Al_4 tetramer metalloid clusters. The energy barrier for decomposition is larger than for the initial oxidation step, and proceeds via decomposition into four Al/ligand units. The calculated energies are in good agreement with tetramerization energies of $Al_4Cp_4^*$ from ^{27}Al NMR experiments.[14]

COMPUTATIONAL METHODOLOGY

The decomposition of the Al_4Cp_4 cluster was studied using the climbing−image nudge elastic band (CI-NEB) approach [19, 20] implemented in the Quantum Espresso package.[21] Norm-conserving pseudopotentials were used to model the ion-electron interactions with a 30 Ry kinetic energy cutoff for the planewaves. Electronic exchange and correlation effects were treated within the PBE parameterization.[22] The Brillouin zone was sampled at the gamma point for the isolated Al_4Cp_4 cluster. The path threshold (norm of the force orthogonal to the path) was set to 0.02 eV/Å and all images were allowed to relax. Molecular dynamics calculations were performed using a Car-Parrinello method as implemented in the CPMD code [23], again using the PBE parameterization. Interactions between the nuclei and electrons are described with Vanderbilt ultra-soft pseudopotentials and a planewave basis set with a 25 Ry cut-off energy. Simulations were performed in the NVT ensemble with Nose-Hoover thermostats and a thermostat frequency of 2600 cm^{-1}. A small time step of 4 a.u. (0.097 fs) was used for the integration of equations of motion with a 400 amu fictitious electronic mass. Non-periodic boundary conditions were used. The dynamics of the $Al_4Cp_4^*$ oxidation are accelerated by the high simulation temperature (2000 K). We chose the coordination number of one Al atom with respect to all other aluminum as a collective variable for MTD simulations. Metadynamics simulations were performed at 300 K, relying on the artificial bias rather than elevated temperature to accelerate the chemical reactions. Further details on the MTD method as applied to these clusters can be found in Ref. [12].

RESULTS AND DISCUSSION

Oxidation of $Al_4Cp_4^*$

We extended our previous MTD work on the oxidation of $Al_4Cp_4^*$ cluster, beginning new simulations from the point at which the O_2 was driven inside the cluster by the artificial metadynamics bias. This starting geometry is shown in Figure 1a and is used as the basis for extended ab initio molecular dynamics runs.
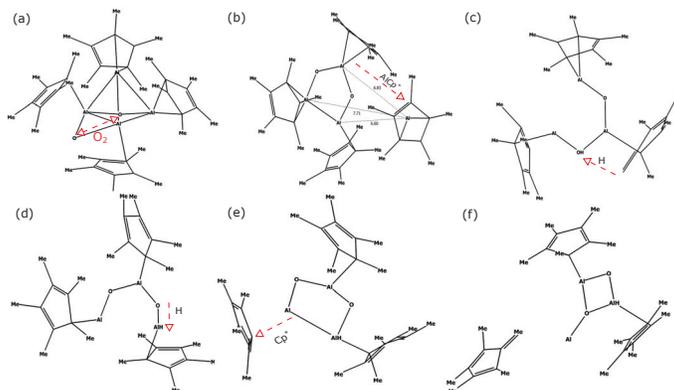

FIGURE 1. Dissociation pathway and intermediate products of O_2 interactions with Al core atoms in the $Al_4Cp_4^*$ cluster.

The oxygen interaction with the core leads to an immediate instability in which one $AlCp^*$ unit is eliminated from the cluster (Figure 1b). This is followed 15 ps later by a proton transfer from a Me on the ligand to an O (Figure 1c). The H moves to a nearby Al atom soon after (Figure 1d). After an additional 27 ps a Cp^* unit is detached from the core

(Figure 1e). The remaining cluster structure (Al(H) $Al_2O_2Cp_2^*$) has a planar core (Figure 1f) and is stable for more than 40 ps of simulation time at 2000 K. Preliminary TPR studies by Bowen have shown that the decomposition products of O_2 and $Al_4Cp_4^*$ are primarily ligand, Al/ligand units, and a small quantity of Al_2OCp^*. No oxidized products from the ligand were observed. Our simulations here are so far entirely consistent with these final products, though within the current simulation time we have not yet reached the anticipated Al_2OCp^*. Further work is ongoing to continue to evolve the cluster towards this ultimate product.

Nudged Elastic Band and Metadynamics Calculations of Cluster Decomposition

We next consider thermal decomposition of an isolated Al_4Cp_4 cluster using NEB calculations. Two possible pathways, based on high temperature MD simulations, were tested for this purpose. In the first, the Al_4Cp_4 cluster decomposes simultaneously into four basic monomer units, and in the second scheme a single AlCp monomer detaches, followed by instantaneous decomposition of the intermediate structure Al_3Cp_3 which is known from previous calculations to be unstable. The decomposition energy profile of both cases is shown in Figure 2.
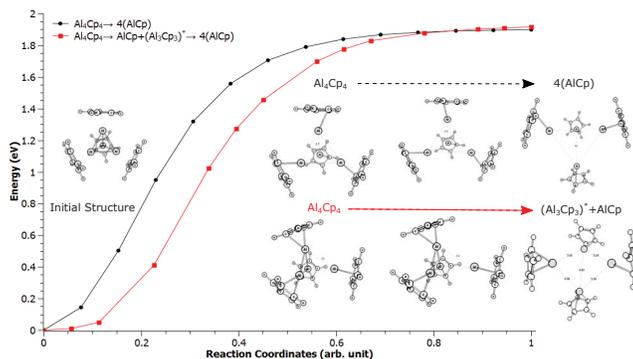

FIGURE 2. Decomposition of the Al_4Cp_4 cluster along the reaction coordinate using climbing-image nudged elastic band.

The overall dissociation barrier in both cases is identical at 177 kJ/mol, with a steeper energy barrier early in the dissociation for the first pathway. Metadynamics simulations were performed to further explore the free energy landscape without specifying an exact NEB pathway. We choose the coordination number (CN) of a reference Al atom (Al_{ref}) with respect to other Al atoms as a collective variable for this purpose. The free energy profile with respect to the CN of this atom is shown in Figure 3, along with snapshots from the trajectory.
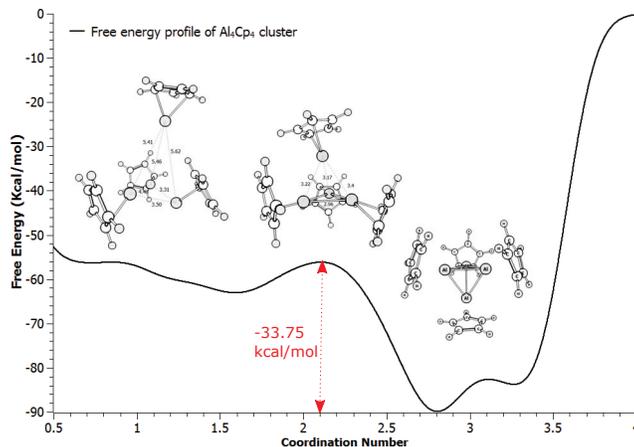

FIGURE 3. 1-D free energy profile of the decomposition of Al_4Cp_4 cluster along the reaction coordinates.

A deep minima is observed around a coordination number of 2.8, as expected for the ground state configuration of the tetramer. As the coordination number drops due to the artificial MTD bias, the cluster begins distorting

until the $Al_{ref}Cp$ unit detaches. A transition state of 142 kJ/mol is observed moving out of the initial minimum. The $Al_{ref}Cp$ unit continues to evolve on a flat energy surface while the remaining Al_3Cp_3 complex starts to break down as the coordination number decreases towards zero. The temperature and the associated cluster dynamics results in a somewhat altered transition state for this process as compared to the nudged elastic band, but the energies derived from both methods are in good agreement with the experimental tetramerization energies of $Al_4Cp_4^*$ from ^{27}Al NMR experiments (approximately 150 kJ/mol).[14]

Conclusions

We find that O_2 has a preference for interacting with the low-valence metal core in small aluminum metalloid clusters, moving through the steric barrier of the ligand rather than oxidizing the ligand directly. This is in very good agreement with preliminary experimental gas-phase oxidation studies by Bowen, Eichhorn and coworkers.[13] Extended ab initio molecular dynamics simulations (>70 ps) were performed to study the cluster decomposition following oxidation, and while the products have not yet evolved to their final state the intermediate steps are also consistent with experiment. Simulations of the isolated thermal decomposition of ligated Al_4 tetramers show that detachment of a single monomer or simultaneous detachment of all four monomers have identical energy barriers, and lead to the same final products. Current work is ongoing to study ligand variations in small Al metalloid clusters, in hopes of improving the barriers for thermal decomposition and oxidation while keeping the mass fraction of aluminum as high as possible.

Acknowledgments

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