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13. SUPPLEMENTARY NOTES

14. ABSTRACT The key objective of our work has been to study the interaction of aluminum and aluminum based clusters with organic templates, with oxygen and water, and develop protocols that would enable the synthesis of cluster assembled materials based on reactive and non-reactive motifs. Our studies on the reactivity of aluminum clusters with propene showed that the reactivity was related to the location of the unoccupied molecular orbital and that clusters like Al_{12}^-, Al_{15}^-, Al_{18}^-, and Al_{21}^- can readily bind to propene and hence may be suitable building blocks to generate such materials. For Al_{13}, a superhalogen superatom discovered by us, our studies showed that an ionic assembly composed of Al_{13} and super-alkali K_3O is stable and ideal to generate an ionic solid. Through synergistic efforts combining theoretical studies in my group and experiments in A. W. Castleman's (AWC) group at PSU, we identified $Al_4H_7^-$ as a very stable species that is resistant to oxygen and ideal building blocks for cluster materials. We also showed that the reactive aluminum clusters can be made less reactive by adding H atoms as it changes the spin state of the system. We also established general protocols for using the findings on free clusters to generate cluster assembled materials and in collaboration with experimental groups, synthesized a cluster solid of As_7K_3 species through a directed chemical synthesis. Recently, in a synergistic efforts combining experiments in AWC group at PSU, we have discovered an unusual size dependent reactivity of aluminum cluster anions with water, in that Al_{16}^-, Al_{17}^-, and Al_{18}^- are found to produce hydrogen through processes linked to their geometries. The studies provide a new Approach to synthesize hydrogen from water, on demand, and have just been published in SCIENCE. We believe that these developments are important towards cluster based materials for propulsion and nanoenergetic applications

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Final Report

Aluminum Cluster-Based Materials for Propulsion and Other Applications

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Contract No. FA9550-05-1-0186

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ABSTRACT

We have just examined the role of spin accommodation on the reactivity of aluminum and aluminum-hydrogen anion clusters with oxygen. Experimental reactivity studies on small aluminum and aluminum hydrogen clusters had revealed that unlike small pure Al_n^- clusters where Al_{13}^- is the smallest non-reactive species, $Al_4H_n^-$ ($1 \leq n \leq 13$) clusters with an odd number of hydrogen atoms are all stable against etching by oxygen. Preliminary theoretical investigations reveal that the reactivity of the species could be related to the energy required to excite the cluster from the singlet to the triplet state, displaying a unique relation between spin and reactivity. The present finding may provide novel ways to modify the reactivity of non-reactive species and to induce the reactivity in non-reactive species. The combination of aluminum clusters with transition metal atoms to modify the spin state can lead to spin dependent catalyses.

The supplement requests support to carry out a systematic examine of the effect of spin excitation We plan to carry out investigations on a wide range of $Al_nH_m^-$ clusters containing different number of aluminum atoms. While clusters with 3-5 Al atoms may be useful as hydrogen storage materials, those with a few dozen aluminum atoms may find use in fuels. In addition, we plan to dope small aluminum clusters with transition metal atoms (Nb and V) to examine if the spin effects can be used to design novel catalysts.

The theoretical investigations will be carried out in close collaboration with the experimental effort by Castleman and co-workers at Pennsylvania State University. It is hoped that this synergistic effort will lead to a new classes of materials with potential applications in propulsion fuels, hydrogen storage and catalysts.

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I. INTRODUCTION

This is a request for supplemental funds in the proposal on "Aluminum Cluster-Based Materials for Propulsion and Other Applications" Grant #: FA9550-05-1-0186 currently funded by the AFOSR. The current proposal relates to the formation of cluster assembled materials based on Al_{13}^- clusters combined with super-alkali and other atoms. The choice of Al_{13}^- was driven by the considerable body of experimental and theoretical work that indicated that while aluminum particles are generally susceptible to etching by oxygen, the Al_{13}^- cluster is resistant to etching by oxygen[1-2]. Since aluminum particles are often the ingredients in modern solid fuel propellants, higher burning rates could be attained by using smaller particles with preponderance of surface atoms. However, efforts in this direction are limited by the fact that ultra-small aluminum particles generally agglomerate and oxidize. As Al_{13}^- is resistant to etching, the cluster materials based on this motif will not oxidize under ordinary conditions and could offer a new class of fuels. The inert behavior of Al_{13}^- can be attributed to special features in its electronic structure. A simple model that can describe some of the qualitative features of the electronic states in clusters corresponds to a nearly free electron gas, confined to a spherical region. Within such a simplified model, the electronic states group into electronic shells 1s, 1p, 1d, 2s, 1f, 2p, ---. Clusters where the valence electrons lead to filled shells can exhibit enhanced stability and chemical inertness. Assuming that each Al atom contributes three valence electrons, an Al_{13}^- cluster has 40 valence electrons and corresponds to filled 1s, 1p, 1d, 2s, 1f, and 2p shells.[1]

Our recent work in collaboration with the experimental group of A. W. Castleman, Jr. at Pennsylvania State University, has brought out some exciting findings that may provide a more generalized and systematic approach towards making a new class of aluminum based clusters that are inert towards oxidation.[3] To illustrate the new findings, we briefly recall the previous work on pure aluminum clusters. A beam containing pure aluminum

clusters anions of all sizes containing up to 50 atoms was reacted with oxygen under ambient conditions. The resulting mass spectra of the reacted species showed that all the clusters except Al_{13}^-, Al_{23}^-, and Al_{37}^- were reacted away by the oxygen. In the current work, hydrogen atoms were added to aluminum clusters to generate $Al_nH_m^-$ clusters with a view to examining the electronic behavior of the system one electron at a time.[3] The results were truly surprising and we use the $Al_4H_n^-$ series ($1 \leq n \leq 13$) to illustrate the unexpected findings. When the clusters were reacted with oxygen, all the clusters with an even number of hydrogen atoms (and odd number of valence electrons) reacted with oxygen (see Fig. 1) whereas the clusters with an odd number of hydrogen atoms (and an even number of electrons) did not react.

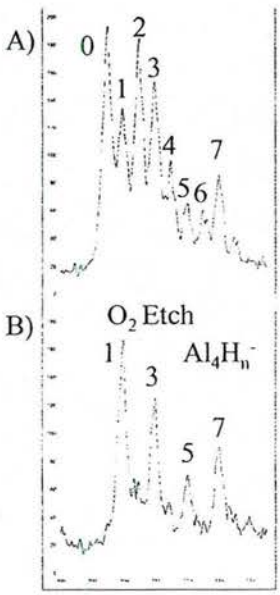

Fig. 1. A) Mass Spectrum of $Al_4H_x^-$ Clusters. B) Mass Spectrum of A) after exposure to molecular oxygen.

No such even/odd effect is observed in pure Al_n^- clusters as oxygen etches all the sizes up until Al_{13}^-. Further, since pure Al_4^- is etched away by oxygen, it was surprising that the addition of a single H atom made it so unreactive. An $Al_4H_3^-$ has the same number of electrons as in Al_5^- and they both contain even number of electrons. Why is then only Al_5^- reactive while $Al_4H_3^-$ does not react? Theoretical studies were needed to unravel the microscopic mechanism.

II. PRELIMINARY RESULTS:

We have recently completed preliminary theoretical investigations[4] on the reactivity of pure Al_n^- and $Al_4H_m^-$ clusters. The studies that indicate that reactivity depends on the spin excitations of the cluster. Molecular oxygen is spin triplet in its ground state. The most likely reaction product with small aluminum clusters is AlO_2^-, which has a spin singlet ground state. Furthermore, reactivity requires the filling of the minority LUMO's in $^3O_2$. The filling of these orbitals may be thought of as a spin multiplicity $3 \rightarrow 1$ excitation of the oxygen half of the complex and the reaction has to conserve the overall spin of the system.[5] For clusters with odd number of electrons, the spin of the extra electron could align opposite to the majority spin electrons of the $^3O_2$ molecule and the spin conservation does not require any spin excitation of the metal counterpart. The situation is different for clusters with even number of electrons, since the decrease in the spin multiplicity of the oxygen half of the reacting cluster has to follow the spin excitation of the remaining portion to conserve the total spin. Consequently, the ability of the cluster to become spin excited to accommodate the triplet spin of oxygen plays a critical role in reactivity. This is seen in Fig. 2 that shows the spin density on an $Al_5O_2^-$ and on a $Al_4H_3O_2^-$ clusters.

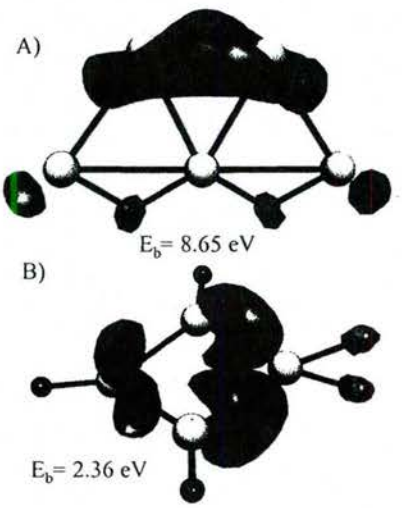

Figure 2. A) Spin Density plot of Al_5^- interacting with O_2 after relaxation. E_b indicates binding energy. B) Spin Density plot of $Al_4H_3^-$ interacting with O_2 after relaxation.

In case of $Al_5O_2^-$, the O-O bond breaks and the O_2 molecule is bound to Al_5^- by a large energy of 8.65 eV. On the other hand, for $Al_4H_3^-$, the binding energy of O_2 to $Al_4H_3^-$ is much less, namely 2.36 eV. The differences in binding energy are consistent with experimental observations that while $Al_5O_2^-$ is etched by oxygen, $Al_4H_3^-$ is not etched. A more detailed analysis indicated that the differences in O_2 binding could be related to the ability of the clusters to accommodate spin excitation. Cases where the energy required to excite the cluster from its singlet ground state to the triplet state is high, the O_2 bind weakly and the clusters are resistant to etching by oxygen while cases where the excitation energy is small, O_2 bind strongly and the clusters are easily etched.[3] This relationship is further shown in Fig. 3 where

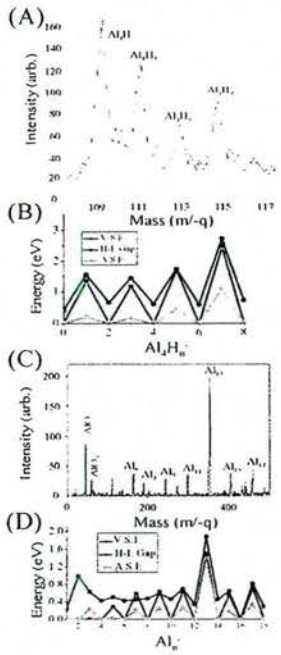

Fig. 3. A) Mass Spectrum of $Al_4H_x^-$ Clusters after exposure to Oxygen. B) The HOMO-LUMO Gap, vertical spin excitation energy, and adiabatic spin excitation energy of $Al_4H_x^-$. C) Mass Spectrum of Al_n^- clusters after exposure to molecular oxygen. D) The HOMO-LUMO Gap and vertical and adiabatic spin excitation energies in Al_n^-

panels (A) and (C) show the experimental mass spectra of the etched $Al_4H_n^-$ and pure Al_n^- clusters, respectively and the black lines in panels (B) and (D) indicate the spin excitation energy

for the $Al_4H_n^-$ and pure Al_n^- clusters and one can note a direct correlation between the calculated line and the mass spectra of the etched species.

III. PROPOSED WORK:

To our knowledge, we are the first group to identify the role of spin and in particular, spin excitation, on the reactivity of pure and compound aluminum clusters. Our investigations can have far reaching implications since the reactivity of metal clusters with oxygen can have dual implications. Firstly, oxygen is a strong etchant and consequently, clusters that are stable and inert can be ideal building blocks for cluster assembled materials. Secondly, oxidation is also important in the elimination of pollutants, and the study of oxidation reactions helps us identify potential catalysts e.g. for conversion of CO to CO_2.[6-8] As to the first aspect, our studies show that by controlling the amount of hydrogen, the non-reactive clusters can be made reactive while the reactive species can be made non-reactive. Since the phenomenon is general, it may be possible to make the cluster assembled materials from aluminum clusters of virtually all sizes by adding controlled amount of hydrogen to increase the spin excitation and making them unreactive. A different approach is required for catalysis applications. Here, one can tune the spin excitation energy, to design more efficient catalysts. This can be accomplished, e.g. by doping clusters with selected transition metal atoms to reduce the spin transition energy or changing the multiplicity of the reactant.

We plan to carry out investigations on a wide range of $Al_nH_m^-$ clusters containing different number of aluminum atoms to further ascertain the new findings. In addition, we plan to dope small aluminum clusters with transition metal atoms (Nb and V) to examine if the spin effects can be used to design novel catalysts.

I am requesting an extra amount of $ 20,000 to hire a post doctoral associate for six months to investigate some of these exciting possibilities. If our findings confirm our expectations, this may provide a novel direction to accomplish efficient fuels, hydrogen storage, and novel catalysts.

IV. EXPECTED OUTCOME:

The current studies would have implications in three different areas. First, the possibility of passivating larger aluminum clusters by adding small amount of hydrogen may allow development of fuels through assembly of non-reactive species. Secondly, studies based on smaller aluminum clusters coated with large amount of hydrogen may have implications for hydrogen storage. Finally, combining aluminum clusters with transition metal atoms may allow development of novel catalysts through tuning of electronic structure. If these expectations are proven, it should be possible to go beyond aluminum and extend to other metals.

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