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Final Report

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**SUPERATOMS AND METAL-SEMICONDUCTOR MOTIFS
FOR CLUSTER MATERIALS**

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The study of catalysis grows ever more important as economic, environmental, and social concerns regarding energy and fuels become more pressing. It holds the keys to unlocking the promise of a more sustainable future through development of alternative fuels, lowering energetic requirements for chemical reactions, and decreasing pollutant and waste yield from unwanted reaction side products. However, a comprehensive understanding of catalysis from a molecular point-of-view still evades us. Such a perspective is necessary to approach the design of new catalysts with these characteristics.

Many current surface chemistry techniques have greatly advanced our understanding of catalysis, however such methods often involve bulk materials, which due to their nature sometimes do not provide the atomic-level control. As a complementary technique, gas-phase clusters are well suited to catalytic studies where a precise, controlled environment of a few atoms or molecules is essential. For this reason gas-phase clusters are ideal models for surface active sites, where bulk methods may struggle due to such things as surface defects and inhomogeneities. Furthermore, some sub-nanometer sized clusters have been shown to be responsible for catalytic behavior on surfaces, even in the presence of larger nanoparticles, demonstrating potential for direct applications in catalyst development beyond surface active site modeling.

Before cluster-derived catalysis can be developed on any useful scale, the fundamental physical and chemical behavior of such systems needs to be explored in greater detail. Clusters can be generated reliably and reproducibly and manipulated easily, allowing for systematic investigations on the effects of cluster size, stoichiometry, oxidation and ionic charge state, elemental composition, and geometry on electronic structure and chemical reactivity.

Our cluster investigations were conducted with two experimental systems. The first, a guided-ion beam mass spectrometer (GIB-MS) allows us to gather chemical reactivity data via a quadrupole-octopole-quadrupole (QOQ) arrangement. Charged clusters are first generated via laser ablation of a target metal rod and subsequent supersonic expansion of the ablated atoms and a backing gas consisting of methane, O₂, or other gas in helium or argon. We can select a specific mass of interest via the first quadrupole. The mass-selected ion then mixes with a reactant gas in the octopole collision cell, and any reaction products are detected with the final quadrupole.

The second experimental system combines a time-of-flight mass spectrometer (TOF-MS) with a colliding pulse mode-locked (CPM) dye laser at 624 nm for ultrafast ionization of neutral clusters. This induces coulomb explosion, breaking the cluster apart into high charge state fragments. Examining ionization mechanisms in such a way yields electronic information about the molecules, which in turn gives insight into their chemical reactivity.

We extended reactivity studies of anionic transition metal oxide clusters with CO to studies of clusters involving Fe, Co, Ni, and Cu. We also performed ionization and coulomb explosion studies on silane, a precursor to silicon thin film-based solar cells and transistors, as well as catalytically-interesting transition metal (Ti, V, Cr, Nb, Ta) oxides and carbides.

Further GIB-MS experiments and density functional theory calculations indicate that differences in the CO binding energy to the transition metal site and the overall change in energy and spin multiplicity from reactants to products underlie the variation in relative reactivity observed for the oxidation of CO by anionic transition metal oxide clusters. Experimental reactivity studies of MO₂⁻ and M₂O₃⁻ (M = Fe, Co, Ni, and Cu) reveal that anionic oxide clusters with the same number of atoms and stoichiometry, but different elemental compositions were

observed to exhibit specific trends in relative oxidation reactivity with CO. The anionic MO_2^- and M_2O_3^- clusters are found to be most reactive for $\text{M} = \text{Fe}$ and Cu and relatively less reactive for $\text{M} = \text{Co}$ and Ni (see Fig. 1). Theoretical electronic structure studies within the density functional theory framework indicate that the most reactive clusters either have relatively large initial binding energies of CO to the cluster which provide sufficient energy to overcome any subsequent barriers to oxidation, or that the reaction preserves the same overall spin multiplicity from reactants to products (Fig. 2). Out of all the clusters we examined, CoO_2^- shows the lowest reactivity with CO. As shown in the reaction profile (Fig. 2B), the reaction requires a spin inversion in order to be overall exothermic, illustrating that spin effects can play a prominent role in cluster reactivity.

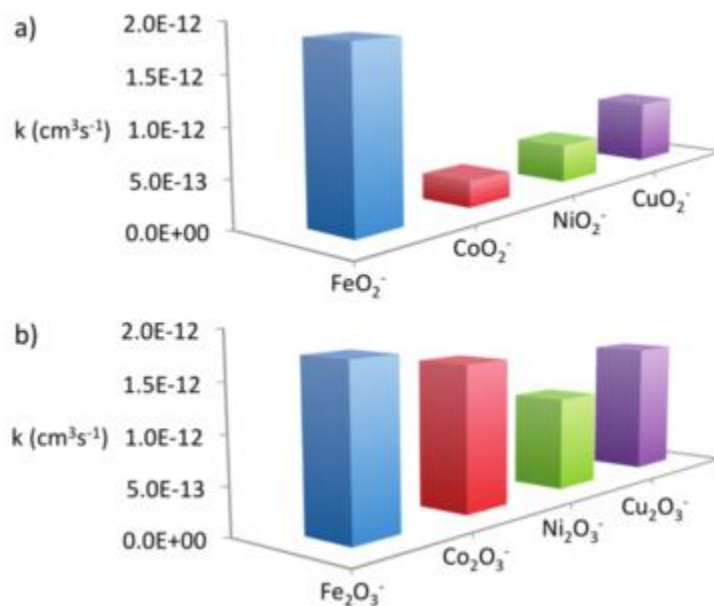


Figure 1. Rate constants for the oxidation of CO by MO_2^- (a) and M_2O_3^- (b), where $\text{M} = \text{Fe}$, Co , Ni , and Cu .

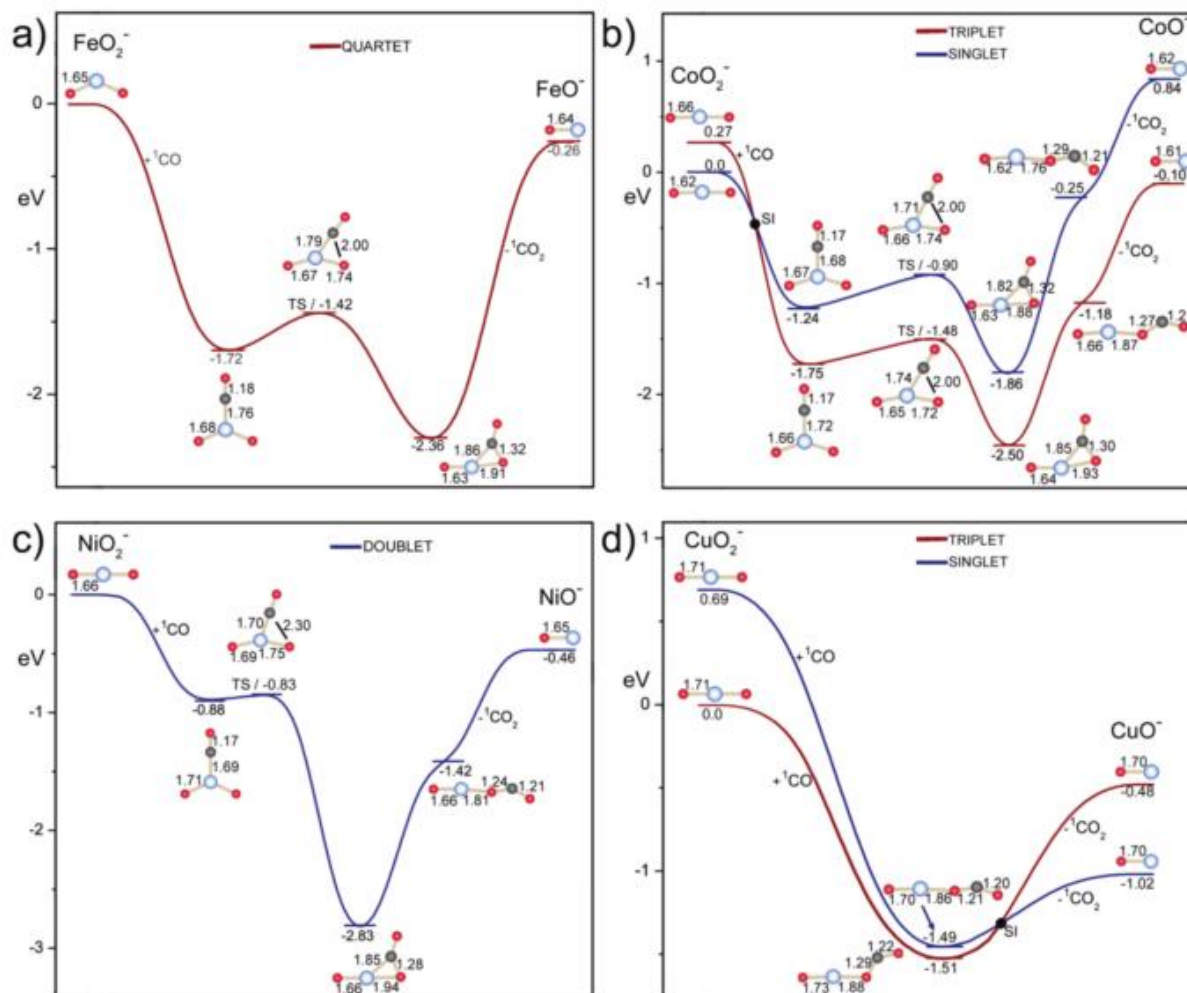


Figure 2. Calculated reaction profiles of a) FeO_2^- b) CoO_2^- c) NiO_2^- d) CuO_2^- with CO. A spin inversion point is present in the reaction with CoO_2^- and CuO_2^- .

In other related work, we chose to investigate reactions of silane using the TOF-MS and CPM dye laser instrument to probe energetics of SiH^{3+} formation for possible applications in creating amorphous hydrogenated silicon (a-Si:H) thin films, which are used in solar cells and thin-film transistors. We examined the ionization and fragmentation of molecular silane with laser intensities ranging between 7×10^{12} and 1×10^{15} W/cm² at 624 nm. The ionization potential of silane determined using both multiphoton ionization (MPI) and tunneling ionization (TI) models agrees with the vertical ionization potential of the molecule. In addition, we applied the tunneling ionization model to the generated fragments of silane to determine their appearance

potentials. MPI values for SiH^{3+} , SiH^{2+} , SiH^+ , Si^+ , as well as H^{2+} and H^+ are consistent with vertical potentials, whereas the TI measurements are found to be in accord with adiabatic potentials. The tunneling appearance potentials observed for the fragments H^{2+} and H^+ are lower than reported for other techniques. In fact, the appearance potential measurements for these species resulting from silane are lower than their ionization potentials. The fragmentation rate of silane is determined to be nearly 20 times larger than the ionization rate. The main precursor for producing a-Si:H thin films, SiH^{3+} is the dominant fragmentation product making up roughly a third of the total ion yield, a substantial increase from other techniques.

We applied similar techniques to investigate changes in maximum ionization states as the result of femtosecond pulse ionization of small early transition metal oxide (MxOy) clusters, where $\text{M}=\text{Ti}$, V , Cr , Nb , or Ta . Maximum charge states for each cluster distribution are reported as observed under various ionization conditions. Regardless of metal composition, it is observed that every cluster distribution gains approximately the same amount of energy from the external field. The extreme ionization of the targeted clusters produced ions of Ti^{10+} , V^{9+} , Cr^{8+} , Nb^{11+} , Ta^{11+} , and O^{6+} , requiring up to 216 eV of energy to create these maximum charge states via sequential ionization. Systematic investigations on the influence of cluster size and ionization laser pulse width indicate enhanced ionization contributions from the ionization ignition and charge-resonance enhanced ionization mechanisms.

Our coulomb explosion experiments of narrow distributions of small (<40 atoms) heteronuclear clusters composed of transition metal (Ti , V , Cr , Nb , or Ta) and carbon atoms reveal the presence of enhanced ionization during exposure to the ultrashort (~ 100 fs) pulse resulting in the formation of ions possessing significantly higher charge states than those expected to be possible for atomic species. Regardless of the transition metal species, we observe

the absorption of similar amounts of energy from the external field, as indicated by the maximum observed charge states in each experiment. We observe identical maximum observable charge states for each of the transition metal species resulting from both metal oxide and metal carbide clusters.

Publications sponsored by this DOE Grant during the period

(*the first three entries provide updated information about prior submissions while the remainder constitutes new publications during the present grant period)

- *617. “The Reactivity of Gas Phase Metal Oxide Clusters: Systems for Understanding the Mechanisms of Heterogeneous Catalysts”, N.M. Reilly, G. E. Johnson and A. W. Castleman, Jr., book chapter in, “*Model Systems in Catalysis: From Single Crystals and Size-Selected Clusters to Supported Enzyme Mimics*”, R. M. Rioux (ed.) 293 – 317, 2010 DOI 10.1007/978-0-387-98049-2_14, Springer Science

- *639. “Reactivity Trends in the Oxidation of CO by Anionic Transition Metal Oxide Clusters”, G. E. Johnson, J. U. Reveles, S. N. Khanna and A. W. Castleman, Jr., *The Journal of Physical Chemistry C, Barbara J. Garrison Issue*, **114**, 5438-5446 (2010).

- *648. “Generation of Radical Centers in Binary Neutral Metal Oxide Clusters for Catalytic Oxidation Reactions”, M. Nöbller, R. Mitrić, V. Bonačić-Koutecký, G. E. Johnson, E. Tyo, A. W. Castleman, Jr., *Angewandte Chemie Int. Ed.*, **49**, 407 (2010).

- 650. “Ultrafast Ionization and Fragmentation of Molecular Silane”, S. G. Sayres, M. W. Ross and A. W. Castleman, Jr., *Physical Review A*, **82**, 033424 (2010).

- 653. “Strong-Field Ionization and Dissociation Studies of Small Early Transition Metal Oxide Clusters”, D.E. Blumling, S.G. Sayres and A.W. Castleman, Jr., *Int. J. Mass Spectrom.*, **300**, 74-80 (2011).

- 670. “Strong-Field Ionization and Dissociation Studies on Small Early Transition Metal Carbide Clusters via Time-of-Flight Mass Spectrometry”, D. Blumling, S. Sayres and A. W. Castleman, Jr., *J. Phys. Chem. A*, **115**, 5038-5043 (2011).

- 681. “Cluster Structure and Reactions: Gaining Insights into Catalytic Processes”, A. W. Castleman, Jr. *Invited Perspective for Catalysis Letters*, **141**, 9, 1243-1253 (2011).

Personnel Supported by this Program

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