CHEMICAL REACTIONS OF TRANSITION METAL CLUSTERS

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Research Scope and Objectives

The objectives of this program are to determine fundamental properties of transition metal clusters via studies of their gas phase chemical reactions. Identification of the reaction products and measurement of the reaction kinetics provide information on the mechanisms of chemical reactions of clusters and of catalytic reactions on cluster surfaces.

Description of Research Effort

Metal clusters are generated by pulsed laser vaporization and nucleation in a continuous gas-flow channel. Gaseous reagents are introduced into this channel 3 cm downstream of the metal target, at which point cluster growth has terminated. Four cm further downstream the gas stream expands into vacuum, cooling the cluster species, and effectively quenching any further reaction. Reactant-cluster contact time is less than 0.5 msec. Typical channel pressures are 25 torr of buffer gas (He) and 50 μ of reactant. Further collimation yields a molecular beam which traverses several stages of differential pumping to a time-of-flight mass spectrometer. Ionization prior to mass analysis is via nonresonant multiphoton absorption of pulsed focused excimer laser radiation.

The reactions of small (to 60 atoms) iron clusters with oxygen produces iron oxide species with a nonstoichiometry strongly reminiscent of the bulk FeO. The principal oxidized products show an iron deficiency which rapidly approaches with increasing cluster size the composition $Fe_{0.9}O$. This nonstoichiometry is observed in clusters as small as Fe_9O_{10}. That such a metal deficiency appears in very small clusters raises questions about the bonding and ionicity of these species and about the theories of metal-deficiency that have been used to explain the structural, electrical, and magnetic properties of transition metal oxides.

Nickel cluster oxidation, on the other hand, appears to yield oxygen-deficient clusters with the approximate formula $NiO_{0.75}$. This finding may reflect the fact that surface Ni atoms are only partially oxidized, whereas for Fe clusters complete oxidative restructuring occurs, producing oxides with bulk-like composition.

Future Research

Clusters of any metal, no matter how refractory, can readily be generated via laser vaporization. Initial plans are to study oxidation of a series of transition metal-clusters to observe trends in metal deficiency or excess for comparison with bulk oxide properties. The tendency towards surface or bulk oxidation of small clusters may show a correlation to catalytic activity of the corresponding bulk oxides.

Cluster reactions with any gaseous species can easily be studied. Preliminary studies of the hydrogenation/deuteration of iron clusters have revealed the formation of a number of Fe_nH_m/Fe_nD_m species. This will be extended to investigate H_2-D_2 exchange on cluster surfaces. Reactions of Fe and Ni clusters with CO, H_2S, NH_3, halogens, hydrocarbons, and N_2 are just a few of the many systems to be studied in the near future.