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ADSORPTION ON NANOSURFACES: A DETAILED LOOK AT METAL CLUSTERS USING INFRARED SPECTROSCOPY

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A technique known as *infrared photodissociation spectroscopy* is being used at Argonne to probe the intimate details of how molecules and atoms adsorb onto metal clusters. Clusters of transition metal atoms, produced by laser vaporization of a metal target, are allowed to react with small molecules, producing cluster complexes whose properties mimic those of the small metal-containing particles that make up many industrial catalysts. A powerful infrared laser is used to excite the characteristic vibrations of the atoms or molecules adsorbed on the surfaces of the clusters, causing the complexes to fragment. The resulting photodissociation spectrum is capable of revealing whether the adsorbed molecules have undergone a chemical reaction after sticking to the cluster surface. This technique has been used to show that methyl alcohol molecules readily adsorb to the surfaces of small iron clusters, but do not undergo further reaction once they are there. This behavior is fundamentally different from that observed on macroscopic iron surfaces, where methyl alcohol readily reacts to form smaller fragment species. It is anticipated that these experiments will contribute to our understanding of particle size effects and their influence on reaction mechanisms and pathways in heterogeneous catalysis systems. This research, supported by the Department of Energy, Division of Chemical Sciences, was conducted by Mark Knickelbein of the Metal Cluster Chemistry Group of Argonne National Laboratory.

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ADSORPTION ON NANOSURFACES: A DETAILED LOOK AT METAL CLUSTERS USING INFRARED SPECTROSCOPY

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One of the most interesting and useful properties of metals is the ability of their exposed surfaces to adsorb and react with a wide variety of small molecules. It is this ability that makes metals (usually transition metals in finely divided form) so useful as catalysts in a number of important industrial processes ranging from gasoline production to specialty chemicals synthesis. The study of small, isolated clusters of transition metals using the modern methods of chemical physics has emerged as a powerful approach to understanding the fundamental physical and chemical properties of transition metal-based catalysts and how these properties vary with particle size and structure.

Clusters M_n (with n typically between 2 and 150 atoms) can be produced from any metal by pulsed laser evaporation from a solid target of that metal contained in a source through which a stream of inert carrier gas, usually helium, is flowed. A molecular reactant X can be added to the helium carrier gas in amounts sufficient that some of the clusters react, forming cluster-adsorbate complexes, M_nX_m . A molecular beam containing bare clusters and cluster-adsorbate complexes is formed by expanding the helium-cluster mixture into vacuum through a small nozzle. The distribution of cluster sizes, as well as the propensity of the metal clusters to form complexes with the added reagent, are monitored by time-of-flight mass spectrometry, using an ultraviolet laser to ionize the clusters and their complexes. What such studies usually show is that if a given molecular species chemisorbs onto a macroscopic transition metal surface, it will also react with clusters of that same metal, providing the cluster contains more than a critical number of atoms (usually less than ten). Although these reactivity experiments provide valuable information regarding the relative propensity of metal clusters to react with various molecular species, they tell us little about the structure of the

complexes M_nX_m , specifically whether the reactant X has adsorbed molecularly, or whether dissociative chemisorption, $X \rightarrow Y+Z$, has occurred, forming $M_nY_mZ_m$ complexes.

A technique known as *infrared photodissociation spectroscopy* is being used at Argonne National Laboratory to answer these fundamental questions. This approach employs an intense infrared laser capable of being tuned to one (or more) of the characteristic vibrational frequencies of the adsorbed species X contained in the M_nX_m complexes. At resonance, the chromophore X can absorb up to several tens of infrared photons while in the molecular beam, providing sufficient energy to fragment the complex: $M_nX_m \rightarrow M_nX_{m-1} + X \rightarrow M_nX_{m-2} + X$, etc. An infrared photodissociation spectrum is obtained by measuring the depletion of the M_nX_m parent species from the molecular beam by mass spectrometry as the infrared laser is tuned in frequency. The depletion bands obtained in this way are analogous to the absorption bands measured using traditional infrared spectroscopy and can be used to unequivocally identify the molecular chromophore X.

The utility of this technique is demonstrated in the study of $Fe_n(CH_3OH)_m$ complexes, formed by the reaction of iron clusters with methanol. Surface studies suggest that methanol will either bind molecularly to the iron clusters, or undergo dissociation to form surface-bound CH_3O (methoxy) and adsorbed hydrogen. Figure 1 shows the infrared photodissociation spectra of Fe_8 -methanol complexes formed using four different isotopic variants of methanol: $Fe_8(CH_3OH)_m$, $Fe_8(CH_3OD)_m$, $Fe_8(CD_3OH)_m$, and $Fe_8(CD_3OD)_m$. The observation that the spectra are all different from one another confirms that it is an adsorbate species on the surface of the cluster rather than the underlying metal cluster itself that is responsible for the infrared absorption bands.

Although all of the absorption bands exhibited in these spectra provide important structural information about these complexes, the identity of the chromophore is revealed most clearly from a detailed comparison of the spectral features of $Fe_8(CD_3OH)_m$ and $Fe_8(CD_3OD)_m$ near 950 cm^{-1} , shown in Figure 2. The spectra of the $Fe_8(CD_3OH)_m$ species display intense absorption bands with a maximum around 958 cm^{-1} , corresponding to the C-O stretch of either CD_3O ($\nu_{\text{gas}} = 1000\text{ cm}^{-1}$) or CD_3OH ($\nu_{\text{gas}} = 988\text{ cm}^{-1}$). If CD_3O were the chromophore in these complexes, it would be expected that the spectra obtained using CD_3OD as the reactant would be identical to those

obtained with CD_3OH , with no spectral shifts observed. However, this is clearly not the case. The band observed at 958 cm^{-1} in $\text{Fe}_8(\text{CD}_3\text{OH})_m$ shifts measurably to the red, to around 950 cm^{-1} in $\text{Fe}_8(\text{CD}_3\text{OD})_m$. This shift is of the same magnitude and direction measured in the gas phase for the C-O stretching frequencies of CD_3OH ($\nu_{\text{gas}} = 988\text{ cm}^{-1}$) vs. CD_3OD ($\nu_{\text{gas}} = 983\text{ cm}^{-1}$). This clearly indicates that methanol adsorbs onto these metal clusters molecularly, not dissociatively. This behavior is fundamentally different from that observed on macroscopic iron surfaces, where methyl alcohol readily reacts to form surface-bound methoxy, and at higher temperatures, carbon monoxide and hydrogen. Interestingly, no size selectivity was observed in cluster chemisorption behavior. Identical spectra are observed for all complexes containing 5-14 iron atoms.

The general applicability of the infrared photodissociation spectroscopy method will allow detailed study of adsorbate binding in a variety of metal cluster complexes. It is anticipated that the structural information obtained will not only be of fundamental interest, but provide a more detailed picture of the origin of particle size effects in metal-containing catalysts, and how these effects influence reaction mechanisms and pathways in heterogeneous catalysis systems.

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Fig. 1.

Fig. 2.

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