To be presented at the International Symposium on the Physics and Chemistry of Finite Systems: From Clusters to Crystals, Richmond, Virginia, October 8-12, 1991, and to be published in the Proceedings.

ANL/CP--73227

DE92 000260

Atomic Structure of Clusters Through Chemical Reactions

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Abstract

Techniques for the probing of isolated metal cluster structure through adsorbate binding patterns will be described. The saturation of clusters with reagents such as ammonia and nitrogen provides information on the number of preferred binding sites for these reagents. The dependence of this number on cluster size can suggest particular structural themes. The equilibrium reaction with water can be used to identify cluster sizes having especially enhanced binding for the water molecule. Again, the sequence of cluster sizes showing such enhancement can point to specific cluster structure. The reaction with oxygen can identify cluster sizes having particularly high ionization potentials, and these can be compared to simple models for the electronic structure of metal clusters. Representative applications of these probes to iron, cobalt, nickel, and copper clusters will be discussed.

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1. Introduction

This paper will be primarily concerned with chemical probes of the geometrical structure of isolated clusters of transition metal atoms. There is little question that the structure of a metal cluster can be very important in determining its chemical properties, so, conversely, it may be no surprise that the tables can be turned and chemistry can be used to determine structure. The detailed interactions between a cluster and an adsorbate molecule, such as the number of binding sites and the binding energy, will depend on the microscopic arrangement of surface metal atoms in the vicinity of the binding site. With the use of appropriate adsorbate molecules and an understanding of how they bind to metal surfaces, it is often possible to determine cluster structure from a careful investigation of the dependence of binding patterns on cluster size.

The traditional method of probing the structure (both geometrical and electronic) of isolated clusters is via the observation of magic numbers in cluster mass spectra. These numbers correspond to cluster sizes having enhanced stability, hence enhanced intensity in the spectra. Classical examples include the alkali metals, where closed electronic shells dominate cluster stability, and rare gas clusters, where the closings of icosahedral geometrical shells and subshells produce clusters of enhanced stability. No such traditional magic numbers have ever been seen for transition metal clusters. This is because in order for cluster intensity to reflect stability, cluster growth must be under equilibrium or quasiequilibrium conditions. The most common method for transition metal cluster generation is laser vaporization in a flow tube, where cluster growth is kinetically, rather than thermodynamically, controlled. This leads to cluster size distributions

determined solely by the statistical probability of cluster-atom collisions, and cluster stability plays no role in cluster intensity.

An alternative probe of cluster structure uses the dependence of cluster chemical properties on cluster size. For example, the number of binding sites for a given adsorbate molecule can be determined by counting the number of molecules that saturate the cluster. Systematics in this number may point to a particular structural theme. For cluster-adsorbate reactions that are at equilibrium, the relative amount of a reaction product will be a strong function of the cluster-adsorbate binding energy, and this may be quite sensitive to cluster structure. Even for reactions that are kinetically controlled, electronic closed shells might be identified by cluster sizes that are relatively inert. Examples of such chemical probes will be presented here, taken from our studies of the reactions of iron, cobalt, nickel, and copper clusters with ammonia, water, oxygen, and nitrogen.

2. Experimental Methods

Clusters are generated by pulsed laser vaporization of an isotopically enriched metal target that is located in a flow-tube reactor (FTR). The vaporized metal atoms are entrained and cooled by a continuous flow of helium carrier gas, leading to rapid cluster growth. At a point downstream of the target where cluster growth has terminated and clusters have cooled to the ambient temperature, reagent gas is introduced into the FTR. Since the pressure of helium is 20 Torr or more, the resulting reactions are usually of the association type, because the excess energy of the reaction complex can readily be dissipated by collisions with the helium. At the end of the FTR, the clusters and their reaction products expand through a

nozzle into vacuum and are formed into a molecular beam. The beam traverses several stages of differential pumping, the clusters arriving at a time-of-flight (TOF) mass spectrometer where they are ionized by a second pulsed laser. Typical experimental spectra are averaged over several thousand laser pulses to provide adequate signal-to-noise ratios.

In the early days of transition metal cluster chemistry research, the most common experiment was a determination of cluster reactivity as measured by the kinetics of reaction with a single (i.e., the first) reagent molecule. Study of the prototypical system, the reaction of iron clusters with hydrogen, showed that reaction rate constants can vary substantially with cluster size, changing by two orders of magnitude with the addition of a single iron atom. Similar behavior has since been reported for many other systems. While such reactivity dependence points to substantial cluster structural changes, in general purely kinetics experiments do not provide any direct information on actual cluster structure, with the possible exception of electronic structure (see below).

More recently, a procedure for following the entire range of interaction between a cluster and an adsorbate has been developed. It consists of determining the coverage, as measured by the average number $\bar{m}$ of adsorbate molecules on a cluster, as a function of the partial pressure of reagent in the FTR. A plot of $\bar{m}$ vs log (pressure), an *uptake* plot, provides a map of the coverage dependence of the cluster-adsorbate interaction. For example, at low coverages it may be that the cluster-adsorbate interaction is sufficiently strong that the reaction is kinetically controlled. This region is characterized by a rapid increase in $\bar{m}$ with log (pressure). At some point, due to repulsive adsorbate-adsorbate interactions, the

adsorbate binding energy becomes weak enough that the reaction enters an equilibrium region, in which the uptake is much more gradual. Then a plateau may appear, a region where coverage does not depend on pressure. This implies the saturation of the primary binding sites. For a plateau to occur, the binding energy for the next site to be filled must be lower than that of the last site. Examples will be presented below.

This determination of cluster saturation can be an important clue as to cluster structure. If the preferred type of binding site for a given adsorbate is known, then saturation data provide a count of such sites. The dependence of this number on cluster size may display systematics that point to a particular structure, as will be shown below.

For reactions that are at equilibrium, the relevant quantitative measure of reactivity is the equilibrium constant K_{eq} . This can be calculated from the ratio of mass spectral intensities and the measured reagent partial pressure in the FTR. Since $RT\ln K_{eq} = -\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ$, variations in K_{eq} point to variations in $-\Delta H^\circ$, i.e., the cluster-adsorbate binding energy. In fact, with a systematic determination of the temperature dependence of K_{eq} , $-\Delta H^\circ$ and $-\Delta S^\circ$ can be extracted directly via a van't Hoff analysis. Again, the dependence of these thermodynamic quantities on cluster size can provide information on cluster structure.

3. Results and Discussion

Our studies have identified four simple reagents whose reactions with metal clusters can probe cluster structure, albeit in somewhat different ways. Ammonia and nitrogen are convenient reagents for cluster saturation: Since they are gases, high partial pressures are easy to

establish in the FTR. The equilibrium reaction with water can be used to probe changes in cluster-adsorbate binding energies. The reaction with oxygen can, in some cases, provide information on cluster electronic structure. Examples of the use of each of these reagents will be presented.

3.1. AMMONIA

Surface science studies on the adsorption of ammonia on metals have shown that the ammonia dipole binds nitrogen-end-down with the molecular axis normal to the metal surface. The binding is partly electrostatic, due to dipole-induced dipole forces, and partly due to σ donation of the nitrogen atom's lone pair electrons into the metal's d orbitals. The electrostatic forces are maximized over atop (single-atom) sites since for these the positive charge of the metal atom nucleus is directly below the molecule and the induced dipole is larger than for multiatom sites. Furthermore, the more exposed the metal atom, the stronger the metal-ammonia interaction, since electronic charge tends to be drawn away from such atoms into the surface. This attracts the ammonia dipole more strongly, and reduces the repulsive forces associated with the σ donation. Thus we conclude that as a cluster adsorbs ammonia molecules, the sites that will be preferentially filled first are those on the most exposed metal atoms, i.e., apex atoms or atoms that have minimum metal-metal coordination. If an uptake plot shows a clear plateau, then the number of ammonia molecules at the plateau provides a count of the number of apex atoms. Knowing this number, we can begin to suggest possible cluster structures.

Examples of such ammonia uptake data are shown in Figure 1 for Ni_{19} and Co_{19} . It is immediately apparent that the way these two clusters take up ammonia is quite different. Ni_{19} shows a plateau at $\bar{m} = 12$, while for Co_{19} there is a plateau at $\bar{m} = 6$. For a 19-atom cluster, there are two possible atomic configurations that provide a clear choice as to the number of apex atoms. These are the fcc octahedron and the double icosahedron. Models of such structures are shown in Figure 2. In this figure, the atoms having minimum metal-metal coordination are shown in gray. It is clear that the octahedron has six such sites, while the double icosahedron has twelve. This would suggest that a good candidate for Co_{19} would be the octahedron, and for Ni_{19} the double icosahedron. For the octahedron, the apex atoms have only four nearest neighbor metal atoms, while the other surface atoms have seven. This large difference in metal-metal coordination explains the extensive plateau in the Co_{19} uptake plot: The cluster-ammonia binding energy for a non-apex site is substantially lower than for an apex site. (In fact, the binding energy for the apex sites is so high that there is no obvious equilibrium region in the uptake plot.) For Ni_{19} , the 12 atoms on the caps have six nearest neighbors, while the atoms around the "waist" have eight. Also, the 12 preferred sites are quite close together, resulting in higher dipole-dipole repulsion between bound ammonia molecules than for the octahedron. This explains why a much higher ammonia pressure is required to saturate Ni_{19} than Co_{19} .

Similar ammonia saturation experiments have been done for larger cobalt and nickel clusters, and for cobalt and nickel clusters saturated with hydrogen. In many cases, for clusters in the 50- to 200-atom size range there is considerable evidence for clusters having icosahedral packing. The

evidence comes from a succession of magic numbers corresponding to the filling of icosahedral shells and subshells, just as for rare gas clusters. In the present case the magic clusters are characterized by a *minimum* in the number of ammonia molecules bound at saturation, and often this minimum is 12. An inspection of models of these icosahedral closed (sub)shell clusters explains why. Clearly, the closed icosahedral shell clusters at 55 and 147 atoms have 12 apex atoms, and these clusters would be expected to bind 12 ammonia molecules preferentially. The addition of another metal atom to the closed shell will provide a 13th ammonia binding site, since the new atom will sit outside the closed shell and in fact will have only three nearest neighbor metal atoms. The removal of an atom from the closed icosahedron will most likely be from an apex position, since these atoms have the lowest coordination. Although this might appear to reduce the number of ammonia binding sites, in fact in most cases it increases it, because the "hole" left at the apex position now has enough room around it to accommodate two ammonia molecules, for a total once again of 13. Thus the closing of an icosahedral shell provides a local minimum (12) in the number of binding sites. A consideration of the disposition of metal atoms on the surface of closed subshell icosahedral clusters shows that in many cases these clusters will likewise provide a local minimum, often 12, in the number of preferred ammonia binding sites. Thus the sequence of $\bar{m}$ minima for cobalt and nickel clusters, both hydrogenated and nonhydrogenated, points to cluster growth schemes based on icosahedral packing.

3.2. WATER

While the cluster-ammonia reactions discussed above provide evidence for icosahedral structure, there is certainly the possibility that saturation with ammonia might change cluster structure, i.e., the bare clusters (or the purely hydrogenated clusters) might not be icosahedral in structure. This would be the cluster analog of surface reconstruction, and in fact there is evidence for such effects for iron, cobalt, and nickel clusters in the 19- to 34-atom size range. There is, however, a less invasive structural probe, the reaction with water, that points to icosahedral structure for nonammoniated cobalt and nickel clusters in much of the size range covered by the ammonia probe. The important aspect of the reaction of water with these clusters is that the cluster-water binding energy is sufficiently low that under normal experimental conditions the reaction is an equilibrium one. This means that slight changes in the binding energy will result in large changes in the relative amount of cluster-water product, since the equilibrium constant is exponentially dependent on ΔH° for the reaction.

That such large changes occur can be seen in Figure 3, which shows a portion of the mass spectrum recorded when hydrogenated nickel clusters are reacted with 0.1 mTorr H_2O in the FTR. It is clear that certain cluster sizes, noted in the figure, have a dramatically enhanced propensity to bind water. In fact, an analysis of data such as this indicates that these special cluster sizes can have $-\Delta G^\circ$ values as much as 2 kcal/mol greater than other clusters. Furthermore, the sequence of these "magic" cluster sizes with water binding maxima is found in most cases to comprise clusters with just one metal atom more than the cluster sizes having *minima* in ammonia binding, in other words, the sequence of icosahedral closed

subshells. It would appear, then, that the pattern of water binding is also somehow related to the icosahedral sequence.

This relationship becomes obvious if we consider the nature of the cluster-water interaction. Like ammonia, water binds through the lone pair electrons, now on the oxygen, and is expected to prefer atop sites with metal atoms of lowest metal-metal coordination. As was pointed out above, a single atom outside a closed icosahedral shell or subshell will in fact have the lowest coordination of all atoms on the cluster surface, and in this case will provide the strongest binding site for the water molecule. Thus the sequence of "closed subshell plus one" clusters having enhanced water binding is consistent with icosahedral structure for these clusters, implying that for the most part saturation of the clusters with ammonia does not change cluster structure.

Similar studies of bare and hydrogenated cobalt and nickel clusters show that, just as for the ammonia probe, many clusters in the 50- to 200-atom size range are icosahedral in structure. There are notable exceptions, however, in particular the 147-atom nickel cluster, which does not appear to be the closed-shell icosahedron. In most cases the hydrogenated clusters show more pronounced icosahedral features in their binding patterns than the nonhydrogenated ones: They have deeper $\bar{m}$ minima and more enhanced water binding maxima. This most likely reflects the fact that the hydrogen atoms, while not competing directly for binding sites with the ammonia or water, do weaken the relative binding strength to the non-apex sites on the faces and edges of the clusters. Interestingly, these two probes provide no evidence at all that iron clusters in the 50- to 200-atom size range are icosahedral.

3.3. OXYGEN

As a general rule, the oxidation of transition metal clusters is a process quite different from the simple surface chemisorption reactions with molecules such as ammonia and water. Oxidation can result in a complete reconstruction of the cluster, yielding what is essentially a metal oxide cluster, and can be so exothermic that even etching of the cluster can occur. Earlier studies of transition metal cluster oxidation showed that a constant metal-oxygen ratio was established for remarkably small clusters, but provided no information on cluster structure. In fact, it is unlikely that oxidation would be sensitive to geometrical structure, since it is such a violent reaction. However, it would appear that in favorable cases cluster oxidation can be a probe of *electronic* structure.

This is illustrated by the oxidation of copper clusters. Figure 4 shows a portion of the mass spectrum recorded when copper clusters are reacted with 4.2 mTorr of O_2 in the FTR. [Actually, to generate this spectrum 0.9 mTorr of water was also added to the FTR. Since the mass of four oxygen atoms is close to that of a copper atom, the cluster oxide spectrum is very congested and difficult to interpret. The addition of water has the effect of spreading the products out over a large number of $Cu_nO_m(H_2O)_p$ peaks, since the oxides readily adsorb water.] The peaks that stand out in Figure 4 represent those cluster sizes that are unreactive with oxygen. It is most likely that the reactivity in this system is dominated by cluster electronic properties, in particular, ionization potentials (IPs). The reaction is probably governed by an electron transfer from the cluster to the oxygen molecule, so that the higher a cluster's IP the lower its reactivity. Thus the

pattern of unreactive clusters in Figure 4 reflects a pattern of clusters with maximum IPs.

The well-known spherical jellium model has been quite successful in explaining the magic numbers seen in mass spectra of alkali atom clusters. Based on the idea of electrons moving in a spherical well potential caused by the positively charged nuclei, it predicts filled electronic shells for clusters with, among other numbers, 20, 34, 40, 58, and 92 electrons. Such clusters have higher IPs and enhanced stability compared to other cluster sizes. As can be seen in Figure 4, copper clusters with these numbers of atoms likewise have locally high IPs, suggesting that copper clusters can also be explained by the spherical jellium model. However, there are at least two clusters, Cu_{14} and Cu_{48} , showing low reactivity that cannot be explained by the simple spherical model. At this point, the question of geometrical structure becomes important.

For alkali metals, there is evidence that under most experimental conditions clusters are highly fluxional, if not actually liquid. In principle the nuclei can adjust their geometry to accommodate closed electronic shells, if that results in the lowest total energy, and strong magic numbers are seen for spherical clusters. Copper clusters, however, have more rigid geometries. This is shown by the ammonia and water probe reactions. Water binding maxima are found for just those closed (sub)shell plus one clusters expected for icosahedral packing, at least in the 40- to 100-atom size range. This geometrical structure can impose on the system a nonsphericity that causes additional electronic subshell closings. For example, calculations show that there is a subshell closing at $n = 14$ associated with a spheroidal distortion. These calculations do not predict a

closing at $n = 48$, so the relative unreactivity of this cluster may represent a different type of distortion, or may result from a more complex interaction between geometrical and electronic structure that affects chemical properties. The copper cluster system is the first one in which information has been provided on both electronic and geometrical structure. A better understanding of the interplay between these structural properties will provide us with a fuller understanding of basic structure-reactivity relationships.

3.4. NITROGEN

Nitrogen is found to react with small nickel clusters via a nondissociative chemisorption process. Studies of nitrogen chemisorption on bulk nickel surfaces likewise suggest that chemisorption is nondissociative, and that the N_2 molecules are oriented perpendicularly to the metal surface and bind to single-atom sites. Saturation studies of nitrogen on nickel clusters also suggest that the N_2 binds to atoms, and furthermore each surface metal atom can accommodate a nitrogen molecule. This is illustrated by Figure 5, which shows portions of mass spectra recorded for nickel clusters reacting with 553 mTorr N_2 at 20 °C (upper spectrum) and with 985 mTorr N_2 at -40 °C (lower spectrum). At these pressures and temperatures, clusters in these size ranges are essentially saturated with nitrogen. As is highlighted in the figure, Ni_7 is seen to saturate with seven N_2 molecules, Ni_{13} with 12, and Ni_{19} with 17. Such saturation levels are consistent with the pentagonal bipyramid for Ni_7 , the icosahedron for Ni_{13} , and the double icosahedron for Ni_{19} , assuming each surface metal atom can bind an N_2 molecule. This result for Ni_{19} is consistent with the ammonia probe, as discussed above. Notice also that if the 19-atom cluster were the

octahedron (Figure 2) we would expect a saturation at 18 N_2 molecules, since the octahedron has 18 surface metal atoms. Furthermore, a detailed uptake plot of N_2 on Ni_{19} shows plateaus at both $\bar{m} = 12$ and $\bar{m} = 19$, suggesting that the first 12 sites, just those cap sites preferred by ammonia, are more strongly bound than the last five waist atom sites.

As can be seen in Figure 5, something interesting happens at Ni_{14} , which saturates at 14 N_2 molecules. If this cluster were simply the 13-atom one with an additional metal atom on the surface, it might be expected to bind 13 or possibly 12 molecules, but not 14. The binding of 14 suggests that the 14-atom cluster, at least when saturated with N_2 molecules, adopts some completely different structure in which there is no central metal atom. Such a structural change is suggested by our theoretical simulation studies of nickel clusters, which show that Ni_{14} is substantially more fluxional than the icosahedral Ni_{13} . The exothermicity of the reaction with N_2 may well be sufficient to heat the cluster enough to allow a restructuring that "pulls out" the central metal atom, allowing the binding of the maximum number of N_2 molecules. This type of restructuring might, in fact, be quite common for non-closed-shell clusters, and may play a dominant role in determining the actual structure of many metal clusters with adsorbates bound to their surfaces.

4. Conclusions

This paper has presented an overview of chemical probes of metal cluster structure. To date, these probes have been applied to iron, cobalt, nickel, and copper clusters, and have shown evidence for icosahedral packing in the latter three of these metals. There is every reason to expect these

probes will work for other metals, particularly those of the second and third rows of the periodic table. However, it must be noted that probes such as these have yet to reveal binding pattern sequences characteristic of nonicosahedral structure. This may mean that the differences in numbers of nearest neighbor metal atoms between atoms in a closed (sub)shell and those outside it are not great enough for crystalline packing schemes for binding energy differences to be significant. Or, it may mean that for metals not showing icosahedral structure, such as iron, clusters have several isomers, effectively hiding magic numbers. Clearly additional work will be needed before we have a complete picture of the geometrical structure of isolated transition metal clusters.

Acknowledgments

We thank Dr. E. K. Parks for being the driving force in these studies, and for a critical review of this manuscript. This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

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Figure Captions

Figure 1. Uptake plots for the reaction of Ni_{19} and Co_{19} with ammonia.

Figure 2. Models of the 19-atom octahedron and double icosahedron clusters. Primary ammonia binding sites are shown in gray.

Figure 3. Portion of the mass spectrum recorded when hydrogenated nickel clusters are reacted with 0.1 mTorr water. The mass peaks corresponding to cluster sizes having enhanced binding for water are annotated with n, m values.

Figure 4. Mass spectrum resulting from the reaction of copper clusters with 4.2 mTorr O_2 and 0.9 mTorr H_2O . Labeled intense peaks correspond to unreactive bare clusters. Asterisks denote peaks due to product copper cluster oxides.

Figure 5. Mass spectra illustrating the saturation of small nickel clusters with nitrogen.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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