Pure & Appl. Chem., Vol. 62, No. 1, pp. 79–88, 1990.
Printed in Great Britain.

Recent advances in the chemistry of gas phase transition metal clusters

A. Kaldor and D. M. Cox

Corporate Research Laboratory Exxon Research and Engineering Co.

Abstract - Clusters containing a well defined number of transition metal atoms have unique chemical, electronic, and magnetic properties which vary dramatically with the number of constituent atoms, the metal, and the charge on the cluster. We have been developing experimental techniques to probe these properties for gas phase clusters. This report summarizes and briefly reviews some of these results.

INTRODUCTION

Clusters containing a well defined number of transition metal atoms have unique chemical, electronic, and magnetic properties which vary dramatically with the number of constituent atoms, the metal, and the charge on the cluster (Ref. 1). Compared to atomic and bulk materials our knowledge is surprisingly limited about these clusters in the 3-100 atoms size range. This is a challenging regime from both an experimental and theoretical perspective, because this is the transition from molecular description of matter to the solid, or liquid like. The size regime is also important from a technological perspective, because this is where unique properties are exhibited by materials in applications as diverse as catalysis and "writing" metal contacts on microscopic semiconductor devices. Interest in clusters is fueled both by the potential offered by their intrinsic unique properties and by what we can learn on the atomic scale about hard to probe, complex heterogeneous systems.

Honing our intuition is important since atomically rough heterogeneous systems are particularly difficult to study with atomic resolution due limitations of the available tools. Yet in this same size regime some catalysts are believed to exhibit strong size dependent behavior (Ref. 2), materials often are metastable and dynamic (Ref. 3), and nanoscale materials, inhomogeneous on the scale of a few atoms exhibit unique physical and chemical properties (Ref. 4). Some fundamental questions in catalysis, e.g. active sites, adatom effects, promotion, poisoning, etc. focus on effects localized on the atomic scale and these require models with similar specificity. It has been postulated that organometallic cluster compounds serve as atomic scale models for active sites in studies of surface catalysis (Ref. 5). Indeed, this approach does yield insight about the mechanism of surface reactions. Organometallic complexes provide structural, spectroscopic and thermodynamic data base for reaction intermediates and radicals bound to surfaces.

Much effort has been invested to synthesize cluster compounds with the right catalytic properties, either as homogeneous catalysts, or as supported, heterogeneous ones. A rich menu of multi-metal cluster compounds has been made, and much has been learned about the metal-metal bonding, cluster structure, coordination, etc., but only a few multimetal centered cluster compounds have emerged as interesting, catalytically active materials (Ref. 6). This is probably due to the coordinative saturation, and the high degree of symmetry inherent in many of these complexes. Often these complexes have not survived thermal activation, i.e. loss of ligands even when supported.

We have been interested in approaching this problem from the perspective of gas phase, "naked" metal clusters. These are at the outset free of support interactions, matrix effects, and coordinatively unsaturated. The objective is to discover their physical and chemical properties as a function of cluster size and to probe how these properties change as the degree of coordination is changed, i.e. at various stages of "dressing" of the clusters with ligands of differing properties. Finally, the ultimate challenge is to deposit the unique clusters on supports and explore the properties of these new materials. Recent advances have made it possible to perform such experiments in the gas phase using most metals and with a broad range of reagents. Now one can deposit monosized clusters of many metals on a variety of supports. In this report we plan to briefly review the emerging trends in the field.

Rules which define the chemical bonding of transition metal clusters when coordinately saturated (Ref. 7) need further development to deal with "naked" metal clusters, though they have been useful as the clusters adsorb ligands (Ref. 8). At this point we know little of the structure of these materials, and our scientific intuition is not well developed. With so few atoms involved one would expect that they are close-packed and globular. The cohesive energy of clusters as a function of the number of constituent atoms competes with other energetics. Clusters in the gas phase release energy by collision with rare gas carriers, vaporizing constituent atoms, reconstructing to different configurations and condensing onto a support. Some clusters are fragile upon ionization, some fragment/fission upon reaction, and some do not survive deposition onto a support. While we want to understand why these losses occur, we are looking for the survivors.

It has been exciting to find so many diverse examples of cluster systems which exhibit dramatic, non-monotonic, size selective reaction rates, as well as unusual levels of saturated coverage as a function of the metal, the charge on the cluster, and the reagent used (Ref. 1). But it has been very surprising and difficult to understand why only certain cluster sizes have definable isomeric forms and why some are essentially unreactive (Ref.9).

The fact that some clusters have isomers suggests that the simple globular, close packed structure is too simple a model. The small energy difference among possible structures encourages the concept of fluxional structural isomers, and in the limit conjures the image of a "molten droplet". This is not a novel concept. Surfaces of solids are mobile well below the melting point, in fact significant reconstruction of catalyst surfaces is known to occur at about 1/3 of the melting temperature of transition metals, known as the Huttig temperature (Ref. 10). The melting point of clusters is known to drop as a function of cluster size, thus reconstruction may become more facile the smaller the cluster. This would be similar to an equilibrated metal surface with no structure dependent reactive properties, though there could be size dependence due to electronic effects. Structure dependence would be superimposed on size dependence for cluster with stable, or metastable structures (Ref.11).

Some clusters may be unreactive because with a highly symmetric, unusually stable configurations they cannot accommodate the reaction products. This is only one example of accommodation induced size selectivity, the notion includes not only the ability of the cluster to accommodate the reagent spatially, but also energetically, including the ability to handle excess energy resulting from the chemisorption process. If the product cannot be stabilized, the reaction will not be completed. These accommodation factors may be the reason why for several metals, clusters of fewer than 30 atoms are usually less reactive than larger ones.

The electronic structure of clusters differs from the bulk surface. The density of states is more sparse, and there are more surface orbital energy and symmetry restrictions. Valence electron binding energies vary non-systematically, cluster orbitals are oriented and have varying extension depending on the metal and orbital involved. In order for a reaction to occur there has to be a match between the energetics and symmetry of a cluster state and a reactant; there also has to be orbital overlap. This is a source of selectivity with cluster size, structure, and reagents. A further source of selectivity is the limited number of reacting states. Specific size selective reactivity will be observed if cluster valence electrons of the required energy, symmetry, and spatial extension are available and if the cluster can accommodate the reaction products, in the broadest definition discussed above. The complex interaction of all these forces explains why it is so difficult at this point to formulate a comprehensive description of the diverse, often bewildering observations of size selective reactivity reported to date.

This discussion will focus on work done in our laboratory, and except by some reference, will not do justice to some excellent work done by others. There are several recent reviews which have covered the field in more depth than we will do here.

EXPERIMENTAL APPROACH

The experimental apparatus and the data analysis have been described elsewhere and only a brief discussion is given here (Ref 1). Figure 1 shows the lay-out of the functional components. Laser vaporization in the throat of a supersonic pulsed valve has made studies of transition metal clusters much easier than conventional high temperature vaporization techniques. The pulsed valve introduces high pressure of helium over the metal target and at the right moment a doubled Nd-Yag laser, focused on the metal target is fired and generates a "cold" plasma. This is a soup of species at several thousand degrees which consists of atoms, positively and negatively charged ions, as well as electrons. The carrier gas sweeps this "soup" through a narrow channel causing nucleation and cluster growth by condensation and cooling. The length of this condensation zone can be adjusted to maximize cluster growth and bring the cluster temperature to equilibrium with the ambient. It is assumed in all experiments that the system had a chance to come to equilibrium and metastable structures, or states have all relaxed. Depending on the ion stabilities involved, not all charged clusters survive. For example, one is able to generate neutral, and positively charged iron clusters, but not negatively charged ones; positively charged

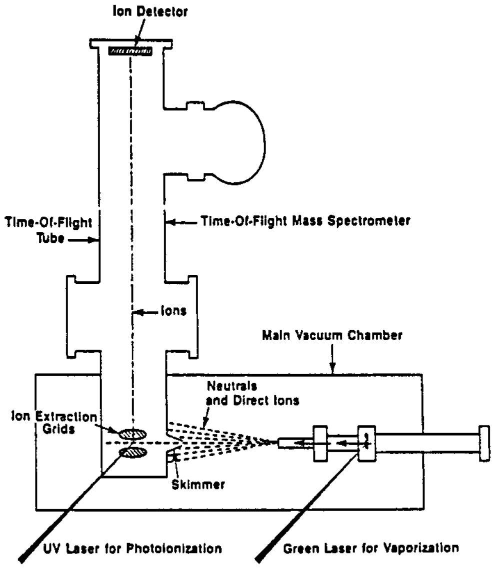

Fig. 1: Pulsed Cluster Beam Apparatus

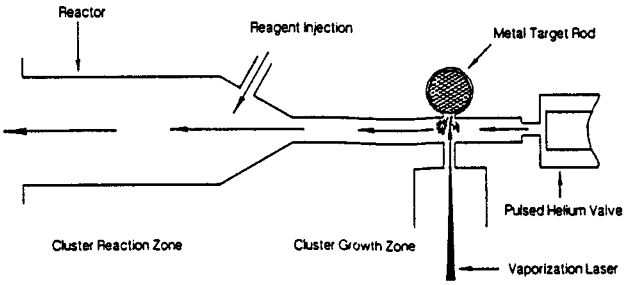

Fig. 2: Details of Cluster Source and Reactor

palladium clusters have not been produced. This is a complex and poorly characterized system, and while this source is an attractive, simple device for screening studies it needs to be further developed for other applications. A lot of work is going into developing continuous, or pseudo continuous sources to make experiments, such as EXAFS, which require high stability and high duty cycle doable.

Once the clusters, or cluster ions are formed they can be subject to a variety of studies. These are all performed while the clusters are in flight to take advantage of the inherent sensitivity of mass spectrometric detection since the absolute number of clusters at a specific size can be very few indeed. The development of ultrasensitive measurement techniques have made it possible to detect as few as a hundred clusters of a specific size. Thus the experiments (see Ref. 1 and references therein) probe the reactivity, dynamics, energetics, structure, and electronic properties of the clusters. Ionization thresholds have been measured using tunable lasers. Stern-Gerlach type magnetic deflection experiments have been performed on some clusters, as have polarizability experiments. Negatively charged clusters have been used for electron affinity measurements as a function of cluster size, as well as to obtain photoelectron spectra on mass selected clusters and cluster adducts. Other physical characterizations have involved heating the clusters with lasers to measure the binding energy of metal atoms and adducts. Tunable infrared lasers have been used to thermally desorb molecules bound to the clusters, and in the process, using mass spectrometric detection, obtain the vibrational spectra in one measurement of chemisorbed species for the entire cluster distribution as a function of cluster size.

Experiments to study the chemisorption of various molecules by clusters as a function of cluster size follow two approaches. One approach aims to measure the rate of reaction by monitoring metal loss as a function of reaction conditions, and the other the products of the reactions, for example the degree of "surface coverage", or saturation achieved. Both approaches use the reactor configuration shown in Figure 2. The reactor is attached to the face plate of the cluster source. The "pulse" of helium with the cluster distribution imbedded flows into the tube reactor. This consists of a tube with two symmetric pulsed valves, similarly configured. One valve injects pure helium, the other helium with the reactant mixed into it. The idea is that the pulse from the first valve is used to measure the physical, e.g. mixing effects of the helium pulse on the cluster beam and the overall measurement system. This provides the base cluster concentration and data for the entire distribution is stored in the computer. The second pulse carries the reactant and this measurement is of the residual, unreacted cluster concentration. Cluster depletion can now be determined as a function of cluster size. This, as a function of reagent partial pressure, yields the rate of the depletion with a specific reagent as a function of cluster size. Figure 3 shows such data for clusters of neutral, and positively charged iron clusters for reactions (1) and (2), respectively

(1) $Fe_x + H_2$ ----> Fe_xH_2

(2) $Fe_x^+ + H_2$ -----> $Fe_xH_2^+$

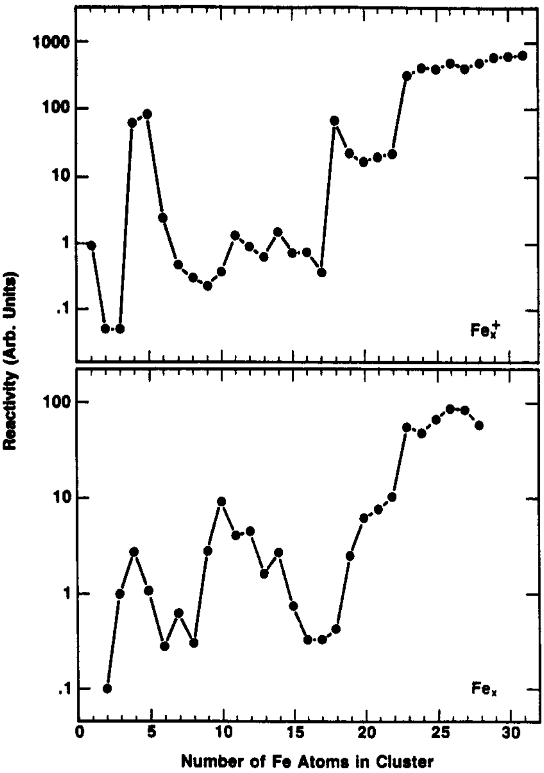

Fig. 3: Top - Reactivity of Fe_x^+ with H_2
Bottom - Reactivity of Fe_x^+ with H_2

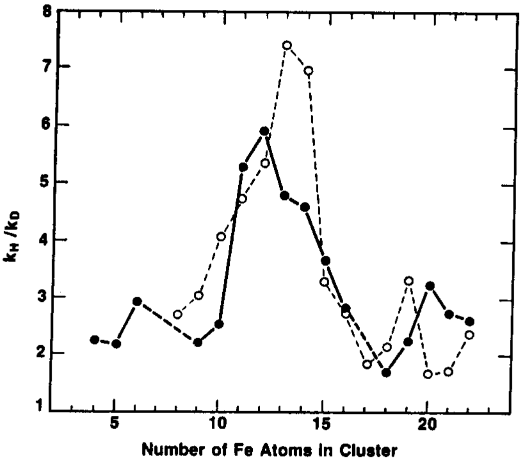

Fig. 4: H/D kinetic isotope effect for Fe_x (open circles), and Fe_x^+ (closed circles) as a function of cluster size.

These results show dramatic variation of reaction rate with cluster size for both iron species. Similar measurements of the rates for deuterium, shown in Figure 4 as a ratio of k(H)/k(D) indicate a huge, size dependent kinetic isotope effect. Saturation levels are measured at progressively higher reagent partial pressure, and the product mass peaks are monitored (Ref. 11). As shown in Figure 5 multiple levels of surface coverage are observed, suggesting that intermediate stages of stable cluster structures may be present. One can also observe dehydrogenation reactions as a function of cluster size as shown in Figure 6. This is an example where the primary chemisorption reaction is not size selective, but the subsequent loss of hydrogen is (Ref. 12).

Once the clusters are made and have been reacted they are detected by time-of-flight mass spectrometry. The pulsed nature of the source is ideally suited for the detection of directly generated cluster ions, and products of cluster ion reactions. Laser photoionization is used to detect neutral species utilizing low fluence (<lmJ) excimer lasers operating at 7.87eV, or 6.42eV. Tunable lasers are used to measure IP-thresholds below 6.4 eV. Work is underway to push this to 12 eV using nonlinear mixing technology. Usually uJ level radiation is adequate for single photon ionization, and in fact one wants to avoid multi-photon ionization. MPI can cause other complications, such as photofragmentation, or photochemistry in the ionization zone. There are obvious limits to mass spectrometry, and use of isotopically pure metals is a great help. Other creative uses of mass spectrometry permeant the field. These include sophisticated use of FT ICR MS, and other mass selected ion reaction techniques.

<u>Chemical Reaction Studies</u> - Size selective dissociative chemisorption has been observed for several important reactions. These include activations of H-H, N-N, O-O, CO2, RO-H, R-H, RS-H bonds. We have been able to compare the effect of charge, addatoms such as oxygen, carbon, etc. and the role of the constituent metal atoms. Theory is evolving to provide a framework to organize the observed results, but it is not at the stage where it is able to predict the multitude of observed dramatic size selective effects. It is providing general guideline from a limited set of calculations (Ref. 13). Here we plan to discuss the chemisorption of hydrogen, methane and benzene as examples.

<u>Di-hydrogen</u> - One of the prototypical reactions is dissociative chemisorption of di-hydrogen. This reaction has now been studied for V, Nb, Ta, Fe, Co, Rh, Ni, Pd, Pt, as

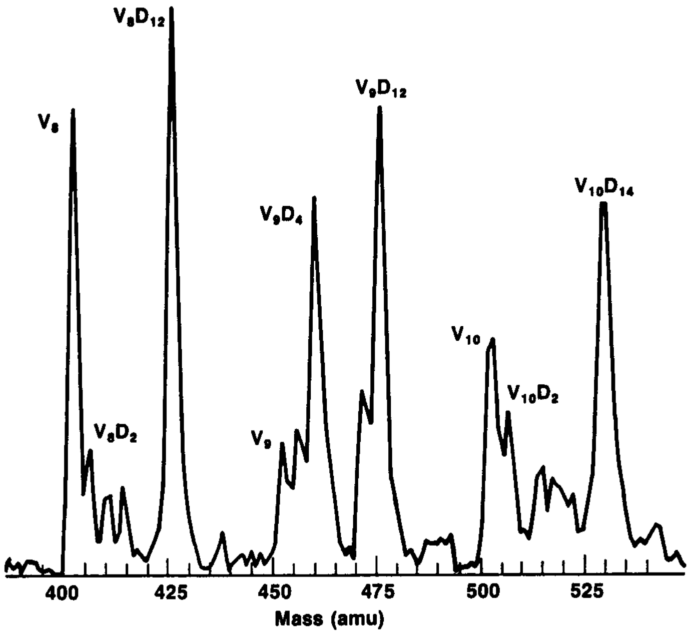

Fig. 5: Species observed in the mass spectrum upon saturated chemisorption of D_2 on V_x clusters.

well as Al. In all cases the reactivity varies non-monotonically with cluster size, and this size dependent reactivity is unique for each metal. As shown in Figure 7 several orders of magnitude variation is observed for the dissociative chemisorption of the first di-hydrogen on iron clusters. It is interesting to note that for iron clusters with more than eight atoms, the reaction rate is greater for clusters where the ionization potential, i.e. the binding energy of the least strongly bound electron is the smallest. For clusters smaller than eight atoms the correlation is direct; the larger the IP the faster the reaction. This correlation holds for reactions of niobium, vanadium, tantalum, palladium as well as aluminum, the systems for which some IP data now exists. Figure 3 compares the reaction rate of neutral with charged iron clusters as a function of cluster size. The effect noted for iron is much more dramatic than that observed for niobium. The case of iron is a rare one, it is one of the few examples where for several cluster sizes the ion reaction rates are slower than for a neutral species. It is also clear that by 25 atoms the effect of charge is dissipated and the rates are comparable.

Most clusters will adsorb several molecules of hydrogen, but the rate of chemisorption of the first molecule is quite interesting. As already noted this reaction exhibits a remarkable range of size selective behavior with most transition metal clusters, and cluster ions. Iron, cobalt, niobium, vanadium, tantalum, and aluminum show the strongest size selectivity, while nickel and palladium are an intermediate case. Rhodium, and platinum are relatively size independent. Equally interesting is the kinetic isotope effect shown in Figure 4 for iron which shows nearly identical size dependent kinetic isotope effect, k(H)/K(D) for the neutral and positively sized clusters, ranging from 2 to 7. This suggests that the reaction for both ions and neutrals has a similar potential surface as a function of cluster size. This is an important element in formulating a model for this chemistry. Palladium clusters show an inverse isotope effect $k(H)/K(D)<1$ as a function of cluster size, suggesting that other forces can interfere with the simple picture (Ref. 14).

A somewhat different measure of size selective chemistry is the maximum number of hydrogen molecules a cluster can chemisorb, as a function of size. Here the difference among the metals is quite significant. Iron will accept only one hydrogen atom/surface metal atom, even though there are other open surface sites that accept molecules such as ammonia. Niobium, vanadium, and tantalum will accommodate somewhat higher hydrogen content, up to an $H/M=1.4$. Small clusters of Pd, as shown in Figure 8, will accommodate up to $H/M=3$, with some variation with size, falling to $H/M=1$ for clusters larger than Pd(15). For cluster ions of Pt, Ni, and Rh the small clusters show $H/M=5,4$ and 8 respectively. The H/M is size dependent, falling toward $H/M=1$ for Ni_x^+ clusters with more than 13 atoms but $H/M = 1$ is not reached until >20 atoms for Pt_x^+ (Ref. 15). Reaction rate studies also provide insight about isomers. Figure 9 shows the reaction rate for di-hydrogen with niobium clusters and positively charged cluster ions. The data indicates that for the twelve atom cluster and cluster ion at least two isomers coexist, while for the six atom cluster only one species is

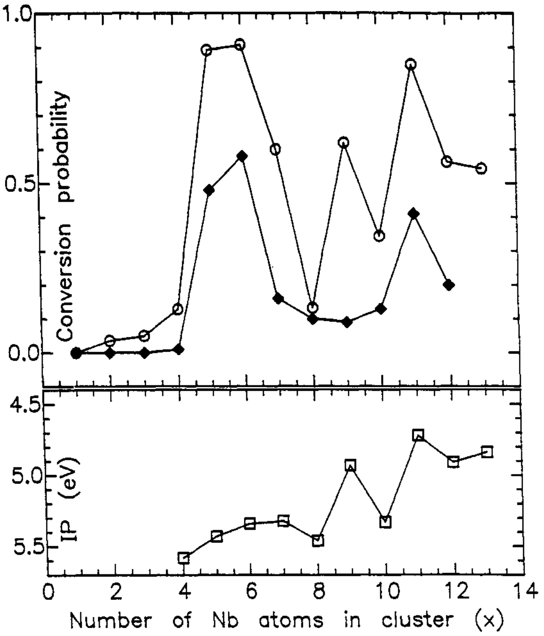

Fig. 6: Benzene chemisorbed on Nb clusters loses hydrogen to produce Nb$_x$C$_6$ species. Top panel - Conversion probability to Nb$_x$C$_7$ Bottom panel - IP variations with cluster size.

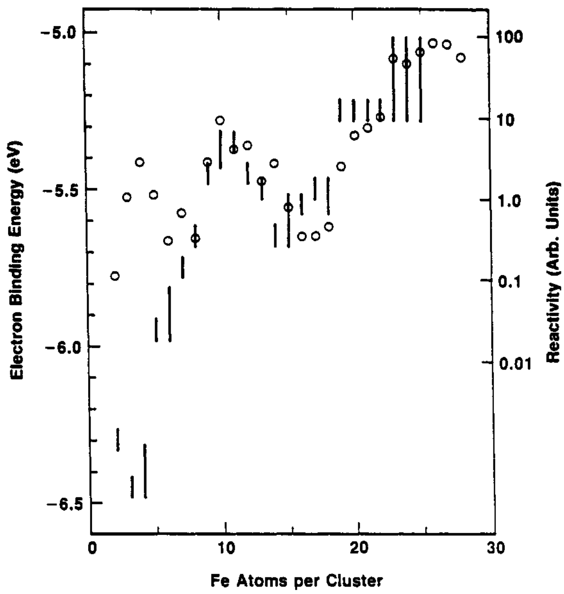

Fig. 7: Ø ionization potential of iron clusters (vertical lines) relative reaction rate measurement of iron clusters with dihydrogen (open circles)

present. It is interesting to note that the negatively charged twelve atom niobium cluster shows a linear reactivity pattern. Isomers of other niobium clusters have also been observed, e.g. Nb(9) and Nb(19)$^+$.

The effects of adatoms have also been explored. Figure 10 shows the variation of the di-nitrogen activation rate as a function of cluster size with and without an adatom of oxygen. By eight atoms the contribution of the oxygen atom is dampened, but for smaller clusters the effect is dramatic, nearly an order of magnitude "mirror image" of reaction rates. The adatom appears to act as if it was a tantalum atom, shifting reaction rates by one cluster size. For di-hydrogen, the activation rates of TaO and Ta$_x$ are similar.

Methane - Clusters of platinum, positive platinum ions, and palladium dissociatively chemisorb methane, while iron, niobium, rhodium and aluminum do not. The strength of the C-H bond is comparable to that of di-hydrogen, but other factors may be also important. Platinum dimer through pentamer are the most reactive, as noted in Figure 11. A factor of four drop in reactivity is noted going from the five atom cluster to that with six. The other small clusters containing from 6 to 24 atoms are less reactive, though there is a small increase in reactivity at 11 and 12 atom clusters (Ref. 16). It is interesting to note that the primary effect of the positive charge on Pt clusters is to extend the larger reaction rate to the seven atom cluster ion, the slight reaction rate increase at 11 and 12 atom clusters noted above is also observed for the ions. The dominant products observed are Pt(x)C(1,2)H(y), with the larger clusters retaining more hydrogen. The decrease in reactivity with increasing cluster size is unusual, and in contrast to what we see for most di-hydrogen systems. A correlation is noted between reactivity and the ability for clusters to form compact structures with three, or less coordinated surface atoms in a close packed structure. This is consistent with the organometallic model, that coordinative unsaturation is critical for methane activation. Yet these strongly bound products may be analogues for poisoned sites for catalysis. Palladium clusters activate methane, but follow a size selective pattern quite different from that observed for platinum (Ref. 14). The maximum of reactivity is observed for the ten atom cluster, and the overall pattern of size dependence is similar to that with di-hydrogen. The deuterated methane reaction rate is significantly larger than that for methane, similar to what is observed for hydrogen isotopes.

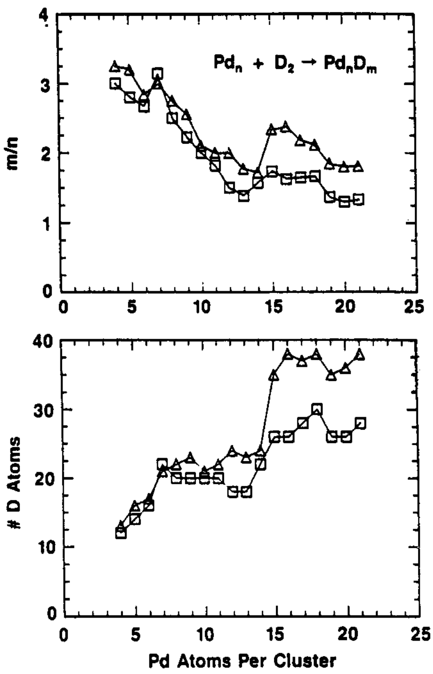

Fig. 8: Deuterium uptake as a function of cluster size.
Upper panel - The ratio of D/M plotted against cluster size.
Lower panel - The number of D atoms adsorbed on cluster versus cluster size. Squares refer to D_2 injected into reaction, triangles when injected upstream of vaporization laser.

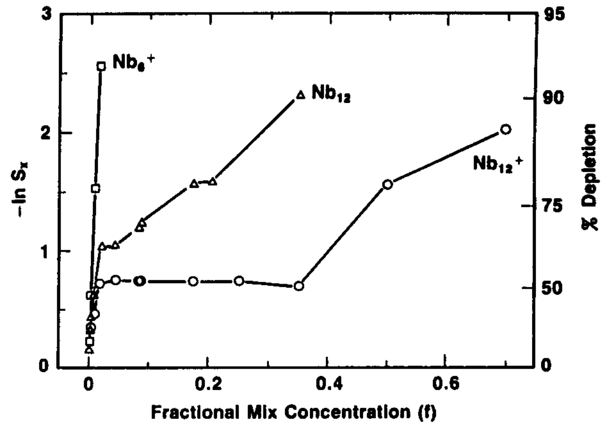

Fig. 9: Reactivity of Nb_6, Nb_{12}, and Nb_{12}^+ with D_2. S_x = survival fraction of injected metal cluster as a function of D_2/He fraction injected into reactor.

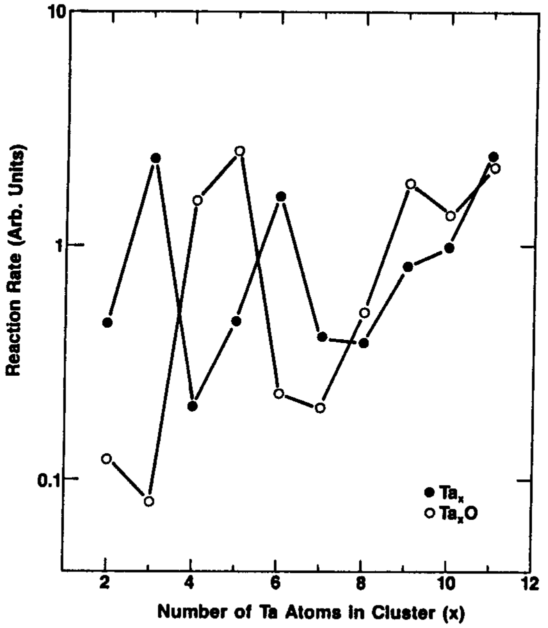

Fig. 10: Reaction rate Ta_x(o) and TA_xO(0) with H_2

<u>Benzene</u> Chemisorption of benzene on niobium and vanadium shows no size dependence, other than as a function of change in collision parameter with size, but an analysis of the reaction products is much more informative. Clusters of niobium containing 5,6, and 11 atoms not only chemisorb benzene, but there is also some dissociation and loss of hydrogen. Kinetic isotope effects have shown that this loss is subsequent to the chemisorption step, and is related to hydrogen activation. In this case, as can be seen in Figure 6 there is an anticorrelation to the measured IPs of the clusters, similar to observations made for di-hydrogen activation by niobium (Ref. 17, 18). Experiments with cluster ions confirmed these observations (Ref. 12).

Figure 12 shows the data for the dehydrogenation of benzene by vanadium cluster ions. Sequential dehydrogenation channels are observed for several cluster ions, in contrast to niobium ions where primarily only two species coexist, Nb(x)C(6) and Nb(x)C(6)H(6), we find dehydrogenation products with vanadium ions such as V(x)C(6)H(M) with M=2,4, and 6. Only V(5-7)+ produce completely hydrogen free species, M=0. There is a possibility that multiple oxidation states account for these products (Ref. 19).

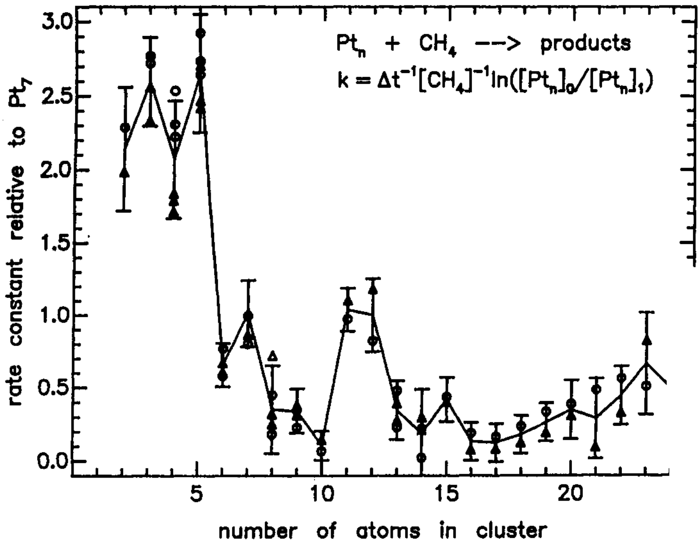

Fig. 11: Reaction rate of Pt_x with CH_4 normalized to Pt_7

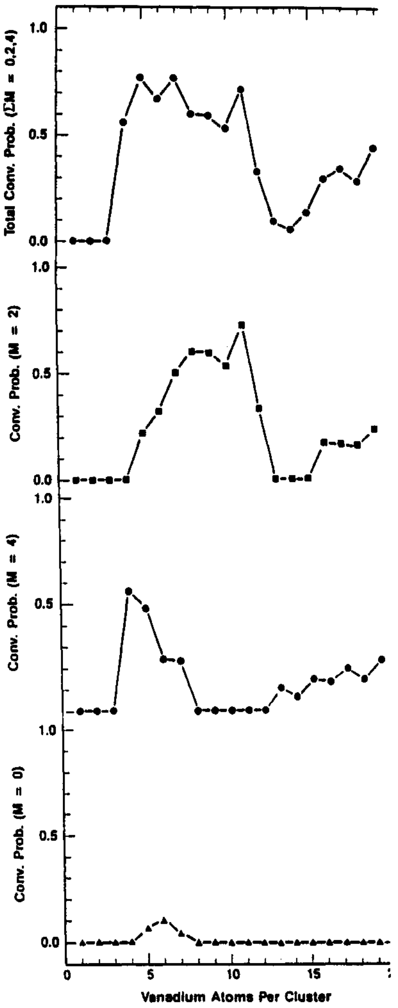

Fig. 12: Vanadium cluster ion size dependence for dehydrogenation of benzene; M= hydrogen content of vanadium benze adduct $V_xC_6H_M$. Lower panels show degree of dehydrogenation is size dependent.

DISCUSSION

The model that does explain a significant number of the observations discussed above invokes the donor/acceptor model of chemical reactions. This model has been used by a number of workers to explain surface chemical reactions, as well as reactions of metal complexes. Cluster reactivity is governed by a number of different factors, ranging from electronic and structural effects to thermodynamic and kinetic factors.

From a simple frontier orbital point of view the key features of the activation of oxidative coupling as amplified by di-hydrogen are 1) attractive metal cluster donor interactions between the high-lying unoccupied hydrogen sigma antibonding orbital and the highest occupied molecular orbital of the cluster, 2) attractive metal acceptor interactions between the occupied hydrogen sigma bonding orbital and the lowest unoccupied cluster orbital, and 3) Pauli repulsion between the filled hydrogen sigma orbital and the filled cluster valence orbital. Interactions 1) and 2) are attractive,leading to H-H bond weakening and M-H bond formation. In 1) charge density is transferred into the antibonding sigma orbital, and in 2) charge density is transferred out of the sigma bonding orbital. The repulsive interaction, 3) is directly responsible for the activation barrier to dissociative hydrogen chemisorption and dominates the dynamics in the approach to the transition state. The size selectivity of the reaction rate arises primarily from 3) and 1). The energetic cost in overcoming the activation barrier is expected to be the smallest when the binding energy of the electron involved in the charge transfer is the lowest, assuming that the metal cluster orbitals are of the appropriate symmetry to interact with the hydrogen sigma and sigma star orbitals, respectively.

The same charge transfer model has been invoked for metal surfaces, but if the reaction is site specific the effect is going to be magnified for metal clusters. For small metal clusters with high IPs the donation from hydrogen sigma orbitals to the metal cluster will start to dominate. Similarly, symmetry considerations are also expected to play an increasingly important role as there is an increasing sparsity of states near the Fremi level as the cluster gets smaller. Indeed, for iron clusters with fewer than eight atoms a direct correlation of reaction rate with ionization potential is observed. Similar situation is found for vanadium, niobium, and tantalum.

The chemisorption rate levels off at some maximum value for clusters with more than 25 atoms. This is what one would expect for a nonactivated process. For all metal clusters examined so far hydrogen chemisorption leads to an increased ionization potential. This follows from interactions 1) and 2) directly since the creation of the new metal hydride-bonds removes two electrons from the cluster valence manifold. This oxidative addition process suggests that as the cluster grows the shift in IP diminishes. The addition of other reagents, such as ammonia is a reductive addition process with respect to the metal cluster, resulting in an increase in the Fermi level, and a reduction in IP.

We have explored other tests of the reactivity model by considering the role of charge on reaction rates and find that if one accounts for the induced polarizability of the reagent the model holds. Also if one includes in the model reduction, as well as oxidation the model is predictive for small clusters as well. We are still in search of a model that is consistent with the non-reactive clusters, though as discussed in the introduction structural stability associated with high degree of symmetry may be an overriding factor. Also, the saturation level coverages are surprisingly large and require further insight.

The transition metal cluster reactivity area is quite fertile and there is every reason to expect significant continued progress in the future.

REFERENCES

1. A. Kaldor, D. M. Cox, and M. R. Zakin, Molecular Surface Chemistry: Reactions of Gas-Phase Metal Clusters, in Evolution of Size Effects in Chemical Dynamics, part 2 Advances in Chemical Physics Vol. XLXX, I. Prigogine and S. A. Rice eds, J. Wiley and Sons, New York, 1988
2. M. S. Spencer, Nature, V.323, 685, (1986)
3. G. C. Bond and X. Yide, JCS Faraday Trans. I, 80, 969 (1984)
4. JMRS report
5. M. R. Albert and J. T. Yates, The Surface Scientist's Guide to Organometallic Chemistry, American Chemical Society, 1987
6. Metal Clusters in Catalysis, B. C. Gates, L. Guczi, and H. Knozinger eds, Studies in Surface Science and Catalysis, V. 29, Elsevier, New York, 1986
7. Metal Clusters, M. Moskovits ed, J. Wiley and Sons, New York, 1986
8. P. Fayet, M. J. McGlinchey, and L. Woste, J. Am. Chem. Soc., 109, 1733 (1987)
9. M. R. Zakin, R. O. Brickman, D. M. Cox, and A. Kaldor J. Chem. Phys., 88, 3555 (1988)
10. G. F. Huttig, Arch. Metallk, 2, 93, (1948)
11. M. R. Zakin, R. O. Brickman, D. M. Cox, and A. Kaldor J. Chem. Phys., 88, 6605 (1988)

12. M. R. Zakin, R. O. Brickman, D. M. Cox, and A Kaldor J. Chem. Phys., 88, 5943 (1988)
13. T. H. Upton, D. M. Cox, and A. Kaldor, Activation and Chemisorption of Hydrogen on Aluminum Clusters, Physics and Chemistry of Small Clusters, P. Jena, B. K. Rao, and S. N. Khanna eds., Plenum, New York, 1987 and other contributions therein.
14. P. Fayet, A. Kaldor, and D. M. Cox, J. Chem. Phys. in press
15. Work in progress
16. D. J. Trevor, D. M. Cox, and A. Kaldor, J. Am. Chem. Soc., in press
17. M. R. Zakin, D. M. Cox, and A. Kaldor, J. Phys. Chem., 91, 5224 (1987)
18. R. J. St. Pierre, E. L. Chronister, and M. A. El-Sayed J. Phys. Chem., 91, 5228 (1987)
19. M. R. Zakin, D. M. Cox, R. O. Brickman, and A. Kaldor J. Chem. Phys., in press