Phase Transitions in Metal Clusters and Cluster Catalysts†

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Received: February 24, 2009; Revised Manuscript Received: May 2, 2009

Comparing the phase transitions of metal clusters with those of dielectric clusters shows that although the relative energies of the phase transitions for metals is typically less than those of dielectrics, other parameters of the phase transitions such as the entropy jumps and the relative widths of the coexistence bands are comparable for the two kinds of clusters. The dominating special characteristic of metal clusters is the large number of isomers with low excitation energy, in contrast with dielectric clusters, whose liquid aggregate states, generated by configurational excitation requiring fairly significant energies (relative to the atomic bond energy), have a significantly smaller density. This is partially due to the contribution of low-lying electronic excited states of the metal clusters. We analyze hysteresis in the phase transitions of large metal clusters as a result of cluster heating and cooling. The experimental and theoretical aspects of metal clusters as catalysts are considered.

1. Introduction

Metal clusters can be very different from dielectric clusters in a number of observable ways because of their very different electronic structure. Indeed, electronic coupling through exchange interaction plays a very important role in the nature of the bonding, even more in bulk metals than in clusters. In reality, at small electron energies, coupling of electrons may be reduced to a pair interaction between atoms in both bulk metals and metal clusters, and various forms of modeling metal clusters are based on pair interactions between metal atoms,[1] much like the models for dielectrics. Therefore, a metal cluster can, to some extent, be treated much like a dielectric cluster, for which modeling is simpler. Hence, in analyzing the properties of metal atoms, we will initially base our approach on methods like those for dielectric clusters for which modeling is simpler and more reliable.

Understanding the nature of dielectric clusters and their solid−liquid phase transitions had its origins and derived many of its concepts from computer simulations, especially by molecular dynamics. The transition from the dynamic interpretation of cluster evolution to its description within the framework of thermodynamic parameters allows one to analyze the properties of dielectric clusters as systems of a finite number of identical bound atoms in a simple matter and to compare clusters and macroscopic systems of atoms. Phase coexistence for clusters near the melting point[2−5] is a principle characteristic for relatively small clusters, whereas this phase transition appears as a discontinuous jump in bulk atomic systems. Metal clusters are more complex because of their additional electronic degrees of freedom. The phase transition in dielectric clusters results from configurational excitation,[7] and this also has to be a major contributor to the phase transitions of metal clusters. Here we consider the special peculiarities and complexities of the phase transitions of metal clusters.

In contrast with dielectric clusters that have been the focus of most interest in the context of cluster phase changes, attention to metal clusters has turned very much to their role as catalysts. A general property of a catalyst is its capacity to enhance[8] some chemical process for a reacting molecule by reducing the energy or free energy barrier between reactant and product. The role of a surface is a typical example. Finding an appropriate type of metal surface to be a catalyst for a given chemical process is still very much an empirical process, Moreover, it is currently a major challenge to the theory of metal clusters to describe and predict their catalytic properties; progress is occurring at an increasing rate in this field, perhaps stimulated by the fact that clusters are typically significantly better catalysts than bulk materials. The first section following this introduction compares and contrasts clusters of dielectric and metallic materials, that is, of materials that are dielectrics and metals in their bulk forms but may be different in small clusters. (We shall refer to the latter as "metal clusters".) The next section is a brief description of the phase transitions of metal clusters. Two sections on cluster catalysis follow this, the first reviewing experiments and the second surveying theoretical studies.

2. Character of Configurational Excitations and Phase Transitions for Clusters

It is convenient to analyze properties of dielectric clusters on the basis of the behavior of their potential energy surfaces (PESs) constructed in a many-dimensional space of atomic coordinates.[9,10] The principal challenge of the PES of any but the smallest systems is the very large number of local minima,[10−16] each of which may be considered to be a configurational excitation. Distinguishing thermal (vibrational) from configuration cluster excitations,[6] one can represent the cluster aggregate state as a sum of configurational states with similar energies.[7] Correspondingly, a phase transition is a transition between these groups of configurational states.

Applying this understanding to metal clusters, we find that the ground configurational state is separated from excited configurational states by an energetic gap, by analogy to dielectric clusters. However, in contrast with dielectric clusters,

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10.1021/jp9017053 © 2009 American Chemical Society
Published on Web 06/19/2009

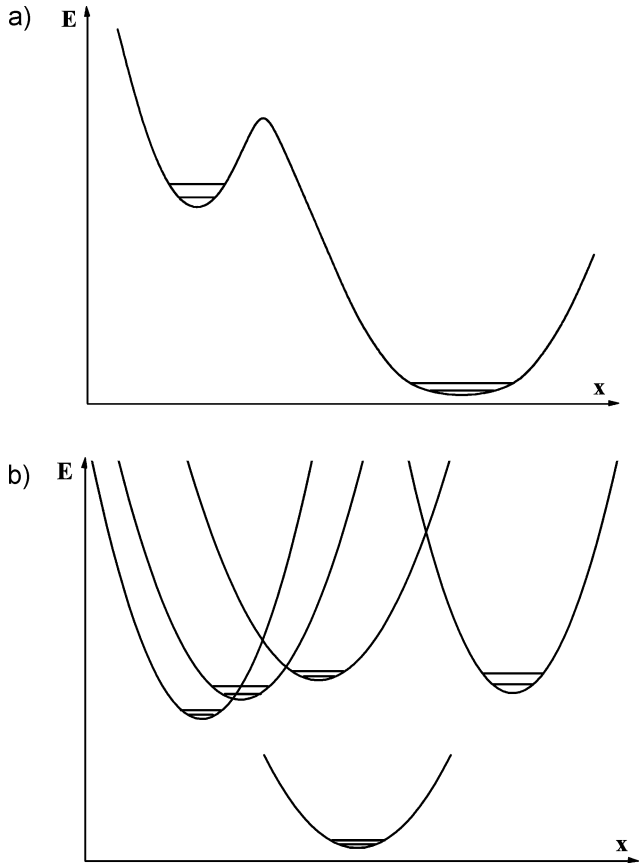

Figure 1. Character of cluster configurational excitation for a cluster consisting of inert gas atoms (a) with one PES and a metal cluster and (b) with many intersecting PESs. The schematic coordinate is chosen in a multidimensional space of atomic coordinates.

many configurational states with similar but somewhat different excitation energies are available in the threshold region for configurational excitation of metal clusters. (See Figure 1.) Therefore, although phase transitions between the solid and liquid aggregate states are observed for both dielectric and metal clusters, the nature of the liquid aggregate state is different for these two kinds of clusters.

Indeed, in the case of metal clusters, the number of isomers, configurationally excited state s, grows extremely rapidly with increasing excitation energy. In particular, Figure 2 shows the number of isomers, the number of configurationally excited cluster states, taking into account their degeneration, for metal clusters consisting of 13 atoms. For comparison, Figure 3 shows the way in which the lowest configurationally excited state forms for a 13-atom dielectric cluster in which interaction between nearest neighbors dominates. The number of configurationally excited states in this lowest set is $g = 12 \cdot 15 = 180$. (12 is the number of atoms on the surface atom shell, and 15 is the number of positions for a transferred atom if its position does not border the position of the vacancy.) Of course, the excited configurational level is split depending on the interaction potential between atoms because of interaction between a promoted atom and a new vacancy. The entropy of this transition, if we ignore the thermal motion of atoms, that is, at zero temperature, is equal to

$$\Delta S_{\mathrm{con}} = \ln g = 5.2$$

Taking the cluster entropy in the form

$$\Delta S = \Delta S_{\mathrm{con}} + \Delta S_{\mathrm{ter}} \tag{1}$$

with S_{con} due to configurational excitation and ΔS_{ter} arising from the different character of thermal atomic motion in the liquid and solid states, we have, in the case of the 13-atom Lennard-Jones cluster at the melting point[7]

$$\Delta S_{\mathrm{ter}} = 3.8 \pm 0.4$$

where the uncertainty indicates the dependence of this value on the way it is extracted from the results of computer simulation by molecular dynamics. We can see that the contribution to the entropy jump due to the different character of atomic vibrations in the liquid and solid states is comparable for dielectric clusters to that due to configurational cluster excitation.

Comparing metal and dielectric clusters, we note two distinctions: the relative energy of excitation for the dielectric cluster is significantly higher, whereas the relative number of configurationally excited states that are accessible in the liquid state is larger for metal atoms. As a demonstration of this, we give in Table 1 the ratio of the fusion enthalpy per atom to the binding energy per atom for bulk argon and metals; this value is significantly higher for argon by a factor of four or five.

To extract the special properties of metal clusters, we compare in Table 2 parameters of 13-atom metal clusters with those of the 13-atom Lennard-Jones cluster (LJ_{13}), basing the latter on the interaction parameters of argon atoms. Here E_b is the binding energy of a pair of the atoms, ΔE is the energy of excitation of the liquid aggregate state from the solid one, T_m is the cluster melting point (the temperature at which the free energies of solid and liquid are equal), and ΔS_o and ΔS_m are the entropy jumps for the solid−liquid phase transition at zero temperature and melting point, correspondingly. We take these parameters for the Lennard-Jones cluster from dynamic computer simulations under adiabatic[2] and isothermal[3] conditions and reduce these parameters to isothermal conditions.[7] The indicated uncertainty accounts for the differences of results of different evaluations.

For 13-atom metal clusters, the results of computer simulations[17−20] are used. Note that in the case of the Lennard-Jones clusters, computer simulations allow one to distinguish aggregate states because of the relative large energy of configurational excitation, whereas in the case of metal clusters, this distinction is not made. The small values of ΔE for metal clusters do not allow one to extract this value in a direct way, say, from the cluster's caloric curve. Therefore, we infer this value by assuming proportionality between this energy and the total binding energy of the cluster's atoms. But melting of 13-atom clusters and macroscopic systems of atoms of the same element are different because of the importance of surface melting for clusters and the overwhelming dominance of "volume melting" for a macroscopic system. Therefore, to account for this difference, it is necessary to introduce an additional proportionality factor. Indeed, in the case of bulk argon, we have $\Delta H_{\mathrm{fus}}/\varepsilon_o = 15\%$, whereas $\Delta E/E_b = 5.4\%$. Taking into account these ratios, we use the following relation for ΔE

$$\Delta E = 0.36 \frac{\Delta H_{\mathrm{fus}}}{\varepsilon_o} E_b$$

and the values given in Table 2 of ΔE are obtained from this formula. The melting points of metal clusters, T_m, are determined

TABLE 1: Parameters of Bulk Argon and Metals

bulk	ε_o, eV	ΔH_{fus}, eV	$\Delta H_{fus}/\varepsilon_o$, %
Ar	0.080	0.012	15
Ni	4.13	0.181	4.4
Cu	3.40	0.138	4.1
Ag	2.87	0.120	4.2
Au	3.65	0.130	3.6

TABLE 2: Binding Energy, E_b, of Cluster Atoms, Configurational Excitation, ΔE, Entropies, ΔS_{con} and ΔS_m, and Melting Temperatures, T_m, for the 13-Atom Lennard-Jones Cluster with Argon Parameters and Some 13-Atom Metal Clusters

	LJ_{13}	Ni_{13}	Ag_{13}	Au_{13}
E_b, eV	0.54	44.1	27.9	42.0
ΔE, eV	0.030 ± 0.001	0.70	0.42	0.54
$\Delta E/E_b$, %	5.4 ± 0.1	1.6	1.5	1.3
T_m, K	39 ± 1	860	420	440
$T_m/\Delta E$, %	11	11	8.6	7.0
ΔS_{con}	5.2	6.4	7.1	7.2
ΔS_m	9.0 ± 0.6	9.4	11.6	14.2
$\Delta S_{con}/\Delta S_m$, %	58 ± 4	68	61	51
δT, K	18 ± 2	420	180	140

from their caloric curves, and the entropy jump, ΔS_m, at the melting point is given by

$$\Delta S_m = \frac{\Delta E}{T_m}$$

The entropy jump for metal clusters at zero temperature associated with configurational excitation is $\Delta S_{con} = \ln g$, where g is the number of isomers with excitation energy below ΔE. Comparing the 13-atom Lennard-Jones and metal clusters shows that the contribution of atomic oscillation to the entropy jump at melting for metal clusters is significantly higher.

Here δT (kelvins) is the width of the observable range of coexisting phases, discussed below.

We now analyze the character of phase coexistence for metal clusters. Taking as a basis the fact that dynamic phase coexistence of clusters means that at some fractions of time, a cluster is found in the solid state, and at other times, it is in the liquid state.[2−5] This is a true thermodynamic equilibrium with the unfavored state still present in detectable quantities in an ensemble or in a time series of observations. (With such small systems, it is even quite possible for more than two phases to be present in thermodynamic equilibrium.) In considering a general principle of phase coexistence, we introduce the ratio $p = w_{liq}/w_{sol}$ of the probabilitiy for a cluster to be found in the liquid (w_{liq}) and solid (w_{sol}) states. In terms of thermodynamics, we have under isothermal conditions

$$p = \exp\left(-\frac{\Delta F}{T}\right) = \exp\left(-\frac{\Delta E}{T} - \Delta S\right) \tag{2}$$

where ΔF is the difference of the free energies of the aggregate states, ΔE is the internal energy change at the phase transition, ΔS is the entropy jump at a given temperature, and T is the current temperature.

We arbitrarily define the range of observable phase coexistence as that satisfying the condition

$$0.1 \le p \le 10 \tag{3}$$

which determines the width δT of the coexistence range[21]

$$\frac{\delta T}{T_m} \approx \frac{5}{\Delta S} \tag{4}$$

Table 2 gives the values of the coexistence range widths for the 13-atom Lennard-Jones and metal clusters. On the basis of data in Table 2, one can conclude that although the excitation energy for metal clusters is lower than that for dielectric clusters, the entropy jump at the phase transition, the contribution of cluster oscillations to the entropy jump, and the relative width of the range of phase coexistence has the same order of magnitude for dielectric and metal clusters.

Let us consider the dependence of the width of the phase coexistence range on cluster size. We represent it first for the Lennard-Jones cluster of 55 atoms with argon interaction parameters. Then, we have the melting point $T_m = 44$ K and the entropy jump at the melting point $\Delta S_m = 45 \pm 2^7$ for this cluster. Using formulas 3 and 4, we find that phase coexistence is observable in the range of 40−48 K for this case, and its relative value is less than that for the 13-atom Lennard-Jones cluster, as we expect. Next, the cluster melting point, T_m, grows slightly on average with an increase in a cluster size, whereas the entropy jump increases approximately linearly with an increase in the number, n, of cluster atoms, $\Delta S_m \approx n$. From this, we obtain that this width tends to zero for bulk atomic systems, and phase coexistence is important for small clusters when the number of cluster atoms is below 100.

As long as the thermal energy of electrons is small and insofar as the density of low-lying excited electronic states is small, one can consider the behavior of metal clusters by analogy to dielectric clusters. Therefore, under these conditions, the nature of phase coexistence and the role of thermal motion of atoms in the phase transition is nearly identical for both cases. We note that the results of computer simulations and experimental data for small metal clusters exhibit the coexistence of the solid and liquid cluster aggregate states, and we base our analysis of metal clusters on this. This means that the solid-state configuration of atoms is separated from the first excited configurational state by an energy gap. However, in contrast with dielectric clusters for which the configurationally excited state is separated from the next configurationally excited state by an energy gap (Figure 3), in many metal clusters, excited configurational states are near in energy, and insofar as they can all be populated, they may be joined conceptually into one aggregate state of the liquid. Therefore, in contrast with dielectric clusters, the configurations of atoms in the liquid aggregate state of metal clusters vary as the cluster is excited.

We give a simple model of the liquid state of metal clusters based on the results of computer simulations[17−20] for the 13-atom metal cluster. The liquid state includes all configurationally excited states with excitation energy below a chosen limit, and the connection between the excitation energy, E_{ex}, and the number of isomers, n, with excitation energy below that limit is represented in the form

$$E_{ex} = \Delta E + \varepsilon\frac{n - n_{max}}{2}, \quad n \le n_{max} \tag{5}$$

On the basis of this dependence, one can construct the partition function for the liquid cluster state as

$$Z_{\mathrm{liq}} = Z_{\mathrm{T}} \int \exp\left(-\frac{E_{\mathrm{ex}}}{T}\right) \mathrm{d}n = Z_{\mathrm{T}} \exp\left(-\frac{\Delta E}{T}\right) F\left(\frac{\varepsilon}{2T}\right), \quad F(x) = \frac{1}{x \cosh x} \qquad (6)$$

Here Z_{T} is the part of the partition function relating the thermal vibrational motion of atoms in the liquid state to that of the solid state. Treating the caloric curves from the results of computer simulations[18] for the isothermal case together with the above energy dependence of the isomer number, one can separate parts of the entropy jump at melting due to configurational excitation and thermal atomic motion in the liquid state; these data are given in Table 2. Note that the contribution of the thermal part to the entropy jump is greater for metal clusters than for the Lennard-Jones clusters. According to this model, properties of the liquid state vary sensitively with the cluster temperature, whereas classical thermodynamics would attribute constant parameters to the liquid aggregate state in the region near the melting point.

3. Hysteresis in Melting and Solidification of Metal Clusters

Above, we defined the liquid state of a metal cluster as a mixture of configurationally excited states. This mixture includes many configurational states with a small energy difference between neighboring configurations, whereas the lowest state of this group is separate from the ground configurational state by a relatively large energy gap. Assuming that transitions between excited states are realized effectively, one can join configurationally excited states into a common liquid aggregate state and, in this way, define the solid and liquid aggregate states of metal clusters. Experience with cluster investigations has shown that this definition is valid for small metal clusters. Metal clusters consisting of hundreds or thousands of atoms exhibit hysteresis in heating and cooling, which is a property determined by rates of transition between different structures.

The thermodynamically favorable structure of most small metal clusters is based on the icosahedron. In particular, the icosahedral structure corresponds to the ground configurational state of practically all 13-atom clusters. On the contrary, for clusters containing more than 100 atoms, the ground-state configuration is typically based on the face-centered cubic lattice, as in the case of bulk metals; we conditionally call it decahedral. Nevertheless, computer simulation by molecular dynamics exhibits the preferential formation of the icosahedral structure for a wide range of cluster sizes,[22,23] even when the icosahedral structure is not the most favorable at thermodynamic equilibrium. It is possible that the reason for this apparent discrepancy for gold clusters lies in the character of the freezing process; this starts from solidification of the surface layer of the cluster, which forms a structure with five-fold symmetry.[23] Then, subsequent solidification of internal layers leads to the formation of the icosahedral structure, despite the fact that the icosahedral structure of large metal clusters is not the thermodynamically most stable form.

The finite rate of transition between the icosahedral and decahedral structures is precisely what leads to the hysteresis in the heating and cooling of metal clusters. Note that the research on which we base this inference was done primarily for gold clusters, and the properties of the metal clusters we consider below are largely based on the behavior of gold clusters. The transition between the icosahedral and decahedral structures results from realignment of cluster atoms, and this process requires an activation[24] through a cooperative slip-dislocation mechanism, whereas the solid−liquid transition as an order−disorder transition may not require activation. If the

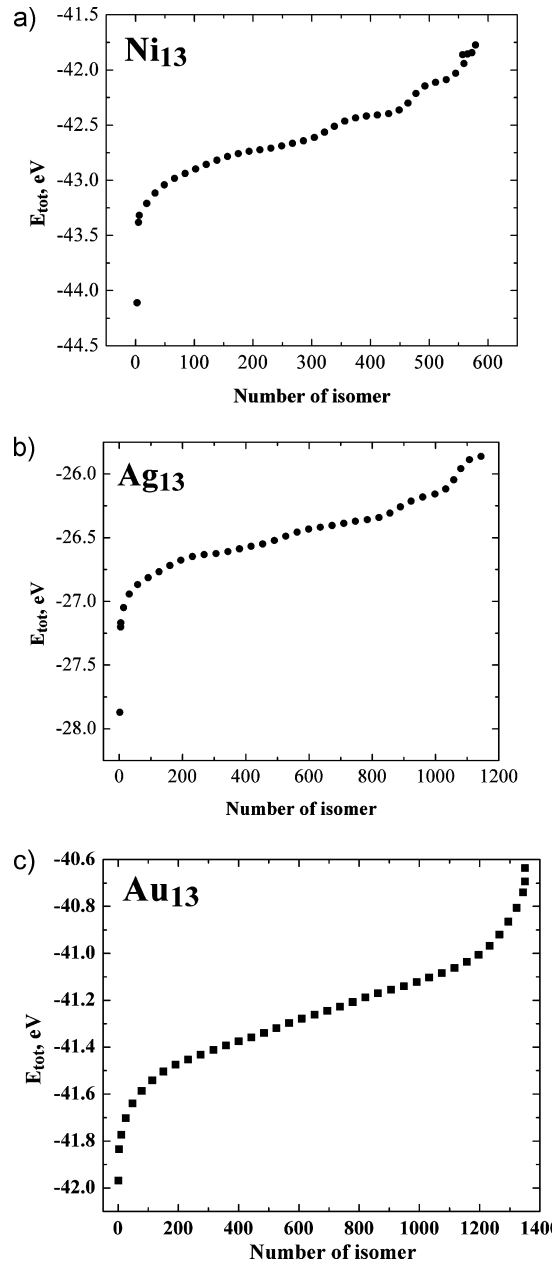

Figure 2. Number of isomers for metal clusters of 13 atoms[18] (a) Ni_{13}, (b) Ag_{13}, and (c) Au_{13}.

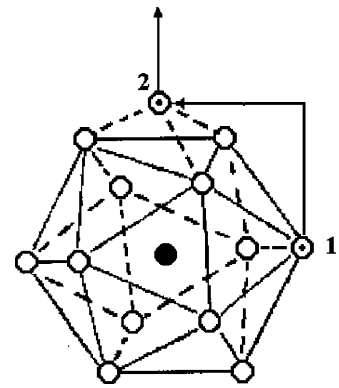

Figure 3. Configurational excitation of a cluster consisting of 13 atoms, where the interaction between nearest neighbors dominates.

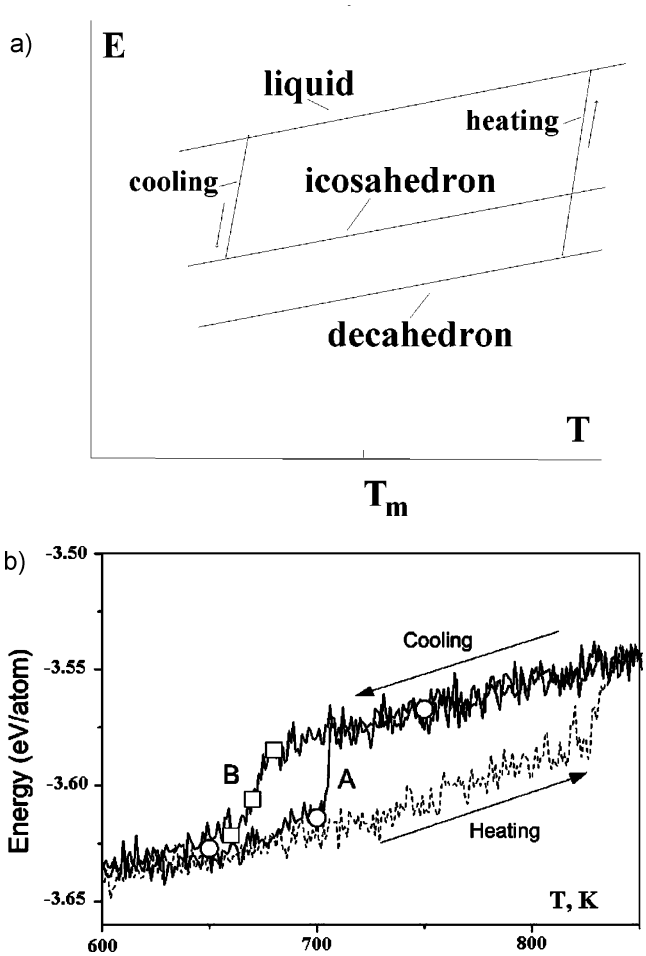

Figure 4. Temperature dependence of the potential energy of cluster atoms. (a) Schematic curves for the decahedral (low), icosahedral (middle), and liquid (upper) states. (b) Results of computer simulations for the 561-atom gold cluster at the heating and cooling rates of 10^{11} K/s.

melting point is above the temperature of the decahedron–icosahedron transition barrier, then both of these structures can, of course, participate in melting and solidification processes.

Figure 4 contains the analogs of the caloric curve for clusters under consideration (a) and the heating and cooling curves for gold clusters of 561 atoms according to computer simulations[23] when the heating rate is higher than the transition rate. Another consequence of this character of transitions are precursors of melting according to computer simulation[25] of clusters Au_{146} and Au_{459} with the truncated decahedron structure for the ground configuration state.

4. Experimental Aspects of Cluster Catalysis

The development of experimental techniques and diagnostics for the analysis of small metal clusters paves the way for applications of clusters as catalysts. The task of a catalyst is acceleration of a chemical process. In many such processes involving more than one reactant, one of the reactants attaches to a catalyst and reacts with other molecule in this attached state. The essence of the rate enhancement of the process may be due to a decrease in the activation energy and to a consequent acceleration. If the process consists of several stages, then the catalyst may decrease the number of stages, or it may open altogether new pathways from reactant to product. Of course, one cannot state beforehand that a given metal may be a catalyst for a certain chemical process. Nevertheless, one can expect the coinage metals to be particularly attractive candidates for this role because of the competition between the electronic structures of atoms and clusters.

Let us consider the peculiarities of metal catalysts for the simple chemical process

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2 \qquad (7)$$

for which palladium clusters Pd_n with 4 to 30 atoms are used as catalysts.[26,27] One can describe a simple scheme for this process such that two molecules of NO bond with the cluster surface, with the nitrogen atoms attaching to the surface, and these atoms of the NO molecules also bond with each other. Then, as a result of collision with CO molecules, they lose oxygen atoms, and a newly formed nitrogen molecule may lose its bonds to the cluster surface. The palladium clusters are also bonded (or at least are deposited) in these experiments with a MgO surface. Mass spectrometric cluster size selection enables deposition of clusters of a given size on the surface, and because clusters occupy a small part of the surface (below 0.5%), one can ignore interactions between clusters.

Study of this process shows that it proceeds if the number of cluster atoms exceeds five; in this situation, the reaction corresponds to the process just described because two nitrogen atoms must bond to each other. Next, the rate constant of this process as a temperature function has a maximum in the temperature range $T = 400$ to 500 K; the explanation of this is that molecules do not bond with the cluster surface at high temperatures.

Now let us discuss why clusters as catalysts may be better than a macroscopic surface of the same material. In catalysis by a metal, the key property used is the capture of a reacting molecule by the surface and, thereby, a reduction of the barrier of the intended reaction. Evidently, such possibilities are greater for a cluster than for a macroscopic surface because of the larger and much more curved surface of the small clusters. Another factor may be the large number of isomers, configurationally excited cluster states, with low excitation energies. The possibility of changing the atomic configuration of a cluster in the course of a reaction also gives the cluster a kind of adaptive capability, a way to make a choice of the optimal cluster configuration both for the initial reaction stage when a reactant molecule is captured by the cluster and for the intermediate or final process stages when a change of cluster configuration may lead to a decrease in the reaction barrier. These conditions hold true for an atomic system in which transitions between configurational states are possible when a reacting molecule forms a bond with this atomic cluster. Both the surface of a cluster and the surface of a macroscopic atomic system may be suitable as a catalyst. However, the cluster is simply more adaptable and more capable of achieving different ways of interacting with the reacting molecules than is the bulk material. The cluster simply cannot only offer a potential surface different from that of the macroscopic surface; it can change structure and offer multiple surfaces for different stages of the reaction. The cluster could, for example, change the distance between potential wells of reacting molecules during the course of passage from reactants to products. Then, metal clusters that admit a larger number of configurations in the course of a chemical reaction are likely to be better catalysts than a macroscopic metal surface.[28] Obviously, a cluster catalyst is more complicated than a comparable metal surface because,

among other reasons, cluster catalysts must fasten to a macroscopic substrate and form bonds with it and still preserve their individuality. The previous example (process 7) is not a good one to illustrate the comparison of cluster and surface catalysts because both large palladium clusters and bulk palladium are good catalysts for the NO + CO process.[29−31] Nevertheless, this example is convenient for explaining the character of the process because of its simplicity.

To argue that clusters are typically better catalysts than macroscopic metal surfaces, we will base our discussion on the example of oxidation CO when gold clusters deposited on an oxide iron surface are the catalyst.[32] Then, the oxidation reaction is selective with respect to cluster size; an optimal cluster size corresponds to the order of 10 atoms. An analogous result[33] corresponds to the low-temperature oxidation of CO that is formed in oxidation of hydrocarbons. This process may be considered to be a result of structural transitions for a gold clusters when they bond with CO molecules.[34] One more example of this type relates to a fuel cell with a platinum catalyst in which the oxidation of hydrocarbons (and possibly hydrogen) creates an electric potential; that is, chemical energy is converted to electrical energy. Then, the addition of gold clusters to a platinum surface increases the lifetime of the catalyst without its becoming contaminated.[35,36]

Let us draw attention to the technological aspect of this problem. To prepare the catalyst under consideration, it is necessary to have a specific experimental technique that includes a cluster generator with mass spectral cluster size selection, such as an atomic force microscope, a scanning electron microscope, or a mass-selecting and -separating device,[37] to deposit and study the cluster's behavior on a surface and a diagnostic tool to analyze the chemical process under consideration. Although such a technique may be available, such investigations are likely to be expensive. In addition, it requires high technical qualification for specialists to carry out these investigations. Therefore, the challenge of doing them is nontrivial, to say the least.

5. Theoretical Aspects of Cluster Catalysis

In considering the possibility of using metal clusters as catalysts, we note that the theory is not yet advanced enough to allow us to choose an appropriate catalyst for any given process, that is, the stage of development of the theory is behind that of the experiment. There are, however, examples that demonstrate that such theoretical analyses can be done.[38,39] Moreover, within the framework of simple models, we cannot always choose between a cluster or surface as the more effective catalyst, so that in this analysis we might consider the cluster surface to be analogous to that of the bulk. Nevertheless, the theory gives a general insight into the problem to analyze peculiarities of its certain aspects and is already in a stage showing its very considerable potential.

We consider a chemical process that proceeds according to the scheme

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} \tag{8}$$

and will be guided by process 7. In the course of this process, molecule A attaches to the surface and in this state reacts with molecule B. Dividing the process 8 into stages, we express it in the form

$$A + \mathrm{Sur} \leftrightarrow \mathrm{A} - \mathrm{Sur}, \quad \mathrm{B} + \mathrm{A} - \mathrm{Sur} \rightarrow \mathrm{C} + \mathrm{D} - \mathrm{Sur}, \quad \mathrm{D} - \mathrm{Sur} \rightarrow \mathrm{D} + \mathrm{Sur} \tag{9}$$

where A−Sur is the bound state of molecule A with the surface.

We formally consider the attachment of molecule A to the metal surface to be a Langmuir isotherm.[40] This means that the metal surface contains active centers, sites ("knots") at which molecules readily attach. These knots may correspond to defects or to specific atoms such as corners on a step or to sites between the surface metal atoms that form a crystal lattice. From properties of metal clusters, one can see the likely greater reactivity of metal surfaces than those of dielectrics. Indeed, as we have seen, metal clusters may form various structures with similar excitation energies. From the standpoint of interaction between attached molecules and a metal surface, this means that the cluster may exhibit a large number of bound states of the attached molecule and metal surface. Because different atomic configurations correspond to different distances between some nearest atoms, after the formation of a bound state A−Sur between an attached atom or molecule and the metal surface, the distances between this molecule and nearest metal atoms can change, and the potential well for this molecule may become deeper.

Therefore, in process 8, according to the scheme 9, the first stage is attachment of a reacting molecule to a metal surface, which we take to be a dynamic equilibrium between molecules bound to the metal surface and free molecules. Then, the probability, f, that a given active center on a metal surface is occupied by molecule A, is given by the relation for the Langmuir isotherm[40]

$$f = \frac{[A]}{[A] + N_\mathrm{o} \exp(-\varepsilon_\mathrm{o}/T)} \tag{10}$$

where $[A]$ is the number density of free molecules A, ε_0 is the chemical potential for a bound molecule A that corresponds to the binding energy of this molecule to the surface, and the parameter N_o is on the order of an atomic number density ($N_\mathrm{o} \approx a_\mathrm{o}^{-3}$).

Let us simplify scheme 9 to reduce it to a form that indicates the fact that the bond with the surface is lost after the chemical reaction of a free molecule $[B]$ with the bound molecule $[A]$; that is, the process proceeds according to the scheme

$$\mathrm{A} + \mathrm{Sur} \leftrightarrow \mathrm{A} - \mathrm{Sur}, \quad \mathrm{B} + \mathrm{A} - \mathrm{Sur} \rightarrow \mathrm{C} + \mathrm{D} + \mathrm{Sur} \tag{11}$$

Then, the rate of the total process is the product of the flux of molecules B to the surface and the density of molecules A on the surface

$$\nu = j \exp(-E_\mathrm{a}/T) fs = \sqrt{\frac{T}{2\pi m_\mathrm{B}}} \exp(-E_\mathrm{a}/T) fs \tag{12}$$

where j is the flux of molecules B onto the surface, T is the temperature expressed in energetic units, m_B is the molecular mass, E_a is the activation energy of the second process (eq 12), f is the probability of location of a molecule A on the metal surface, s is the area around an attached molecule in which the chemical reaction of A and B can occur, and E_a is the activation energy of the chemical process. By extracting the temperature dependence for the rate of the chemical process for a bound molecule A, one can rewrite the rate constant, k, of the chemical process as

$$k = \frac{\nu}{[B]} = \frac{k_o \exp(-E_a/T)}{1 + \frac{N_o}{[A]} \exp(-\varepsilon_o/T)} \tag{13}$$

where k_o is of the order of the rate constant for an elastic collision of the two molecules. One can see that the effective rate constant, k, of the reaction between a bound and free molecules has a maximum if $\varepsilon_0 > E_a$, in which case the maximum temperature, T_{max}, at which $dk/dT = 0$, is determined by formula

$$T_{max} = \frac{\varepsilon_o}{\ln\left(\frac{N_o}{[A]}\frac{\varepsilon_o - E_a}{E_a}\right)} \tag{14}$$

Let us apply this formula to process 7,[27] whose rate constant has its maximum in the temperature range of 420−450 K when clusters Pd_8 and Pd_{30} are used as the catalysts for this process. The reaction proceeds at the partial pressure of the active component $p_{CO} = 5 \cdot 10^{-7}$ mbar; then, formula 14 gives for the binding energy of molecules $\varepsilon_0 \approx 1.2$ eV. Therefore, the theoretical analysis allows us to get a deepened understanding of the chemical process by using the catalyst.

6. Conclusions

This analysis exhibits the specific behavior of clusters in the course of a phase transition. Phase coexistence is a general phenomenon related to a system of a small, finite number of atoms that occurs for a truly attainable hierarchy of typical cluster times. The hysteresis form of the apparent caloric curves of metal clusters corresponds to their different melting and solidification temperatures, resulting at least partially from the character of the transition between icosahedral and decahedral structures of these clusters. Both effects testify to the complexity of cluster properties and processes.

Acknowledgment. We would like to express our long-standing admiration and friendship for Vicenzo Aquilanti, to whom this issue of the *Journal of Physical Chemistry* is dedicated. We look forward to many more years of stimulating interaction with him.

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JP9017053