Charge Separation in CO Oxidation Involving Supported Gold Clusters[1]

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Abstract—The character of the catalytic oxidation of CO by supported gold cluster catalysts is analyzed with emphasis on the unique characteristics of this process. The scheme of this process used here has the reagent CO molecule captured in the interface between the cluster and support, with oxygen molecules or atoms located on the support surface to react with the CO. (Other models have also been presented.) The experimental data indicate that, together with configurational transitions that lead to the CO molecule joining an oxygen atom to form the CO_2 molecule, the charge separation due to capture of the CO molecule by the supported gold cluster is important. The process of release of the CO_2 molecule results in charge exchange; the time for this process is relatively long because of the large distance separating positive and negative charges, a distance exceeding the cluster radius. This provides a high efficiency of the oxidation of CO with this catalyst despite the relatively high activation energy for the configurational transition.

1. INTRODUCTION

The gold cluster is a particularly interesting physical object. Due to competition of interaction between $5d$ and $6s$ shells of valence electrons and relativistic effects, this cluster admits an unusual variety of structures [1]. Clusters of small sizes exhibit linear, zigzag, planar, and $3D$ structures; the transition between the planar and $3D$ groundstate structures of the negatively charged cluster Au_n^- occurs for $n = 12, 13, 14$, as shown by both experimental studies [2, 3] and calculations [4, 5]. For positively charged gold clusters Au_n^+, this transition occurs at $n = 7$ (see [4, 5]}. Larger clusters, in addition to the icosahedral structure, can have tetrahedral, cagelike, and tubular structures [3, 6, 7]. Next, in contrast to other metal clusters with the icosahedral structure, the gold cluster consisting of 55 atoms does not have such a structure [8]. The same rich behavior appears in the melting of gold clusters. The energy gap separating the solid and liquid aggregate states is significantly smaller for 13-atom gold clusters than for such clusters of other metals [9–13], if we express these parameters in reduced units where the measure is the binding energy of cluster atoms. Moreover, the melting points of gold clusters are anomalously low.

These properties of gold clusters make them especially good catalysts. To function, the catalyst must form bonds with substrate reagent molecules, and the molecules so attached may react with a lower activation energy than the uncatalyzed substrate, which of course leads to acceleration of the chemical process. In addition, reaction of the attached molecules may involve fewer intermediate stages than the uncatalyzed process. These general catalytic properties are characteristic of almost any catalyst; the catalytic process involves transitions between different binding states of the catalyst with reacting molecules. Hence, several lowest configurational states of the combined system of the catalyst and reagent molecules must have energies similar enough, and barriers low enough, for effective transitions to occur between these states in the course of the chemical process. Because lowest configurational states of gold clusters are similar in energy, these forms can be expected to play important roles in the bound states of gold clusters with reagent molecules.

A specific gold-based catalytic system that has attracted attention consists of clusters from 10 to 20 gold atoms attached to the surface of a metal oxide semiconductor. The number of suitable metal oxides for this purpose is restricted and includes Fe_2O_3, MgO, TiO_2, and CeO_2; other compounds as supports show only weak catalytic effects. These supports may be in the form of micron-size particles, macroscopic solids, or films. It is interesting that bulk gold is an ineffective catalyst, and it was perhaps surprising that only gold clusters (and some gold clusters with a foreign metal atom) induce oxidation of CO in atmospheric air at room temperature and moderate temperatures. This effect was discovered in 1987 by Japanese scientists

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[14—16], who extracted gold clusters or particles from solutions of their compounds on surfaces. This catalytic effect is strong for gold particles 1 nm in diameter (the Wigner—Seitz radius of gold is 0.17 nm); for a gold particle 5 nm in diameter or larger, the catalytic effect disappears. Moreover, the optimal size of gold clusters for CO oxidation is believed to be 10 atoms [17—20]; the 8-atom cluster is also quite effective [21].

As we indicated, the catalytic effectiveness of supported gold clusters is sensitive to the type of the support and to the cluster size; it is also sensitive to other conditions, for example, to the degree of covering of the support by oxygen molecules [22, 23]. This testifies to the selective character of the chemical process. Consequently, we cannot expect to find universal interpretations of the nature of this process, and our analysis of the character of the oxidation process of CO in air is therefore guided largely by experimental results.

2. USING THE POTENTIAL ENERGY SURFACE FOR ANALYSIS OF CONFIGURATIONAL TRANSITIONS

We now turn to the potential energy surface (PES) of the combined system, which is a convenient tool for the interpretation and analysis of configurational transitions. For this, we construct the potential energy of a system of bound atoms at each fixed position of the nuclei, in accord with the Born—Oppenlieimer approximation, and vary the configuration of the nuclei. In this way, we obtain PES of this system in a $3N - 6$-dimensional space of atomic coordinates for N atoms with the coordinates of the center of mass and the orientation eliminated. The internal energy is the dependent variable. Then a configurational transition can occur either as evolution of this atom system from one local minimum to another on one PES or to a transition from one PES to another, corresponding to a different electronic state, with an associated change of the atomic configuration. The second channel is irrelevant for most discussions of dielectric clusters because of the large energy gap that separates the ground and first excited state of such systems. In contrast, for metal systems and metal clusters, the second type of transition is often favorable. Nevertheless, in spite of this basic difference between dielectric and metal systems, our experience in the analysis of dielectric clusters is useful for metal clusters because dielectric clusters are simpler [24—26]. An important property of the PESs for dielectric clusters is the large number of local energy minima; these are separated by energy barriers [27—30]. This is important for the phase transitions in clusters [25, 26]. Each local minimum of a PES corresponds to a locally stable cluster state because the configurational and oscillatory degrees of freedom are separable [31].

From the standpoint of the properties of the PES, the difference between a metal cluster and a dielectric one lies in the larger number of isomers for metal clusters, each isomer corresponding to a specific locally stable atomic configuration. Correspondingly, the liquid state of a metal cluster differs from that of a typical dielectric cluster by its much larger number of locally stable configurations. This number of course increases with increasing cluster excitation [32]. Successive occupation of many cluster configurations leads, in effect, to their mixing as a result of effective transitions between them. Hence, as we consider the chemical reaction of a bound system consisting of a metal cluster and reactant molecules and interpret it as a configurational transition on a single PES or between PESs of different electronic states, we find the catalytic process to be a sort of an analog of the phase transition in a metal cluster. Indeed, in both cases the transition includes several or many configurational states that may correspond to different PESs.

One more important property in the phase transitions of small clusters is the dynamic coexistence of phases near the melting point [33—38]. This means, in the simplest cases, that part of the time the cluster is found in the solid state that corresponds to the global minimum of the PES, and rest of the time, it is located in the liquid aggregate state[2]. This property marks the fact that near the melting point, cluster evolution leads to many transitions between different PESs or between different local minima of the same cluster PES. Because the gold clusters under consideration here contain only a few atoms, this property is important for catalytic processes involving these clusters.

3. CO OXIDATION WITH SUPPORTED GOLD CLUSTERS AS A CATALYST

We now consider oxidation of the CO molecule in reaction with the oxygen molecule O_2 that proceeds according to the scheme

$$2CO + O_2 \longrightarrow 2CO_2. \tag{3.1}$$

Because the energy to break the CO—O bond is 5.45 eV and the binding energy of the O—O bond is 5.12 eV, even the chemical reaction

$$CO + O_2 \longrightarrow CO_2 + O \tag{3.2}$$
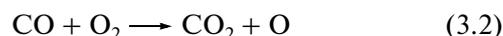
is energetically favorable and corresponds to an energy release of 0.33 eV if molecules before and after the process are in their ground vibrational states. Therefore, from the standpoint of the PES, a low rate for the total process in (3.1) at low temperatures may be the result of energetic or entropic barriers on the PES in the course of this chemical process in the gaseous phase. Catalysts may reduce or even remove these barriers.

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[2] The real situation may be more complex. For example, there may be a temperature regime in which the cluster moves among a small number of solid-like isomers. Alternatively, there may even be more than two phases coexisting in dynamic, thermodynamic equilibrium.
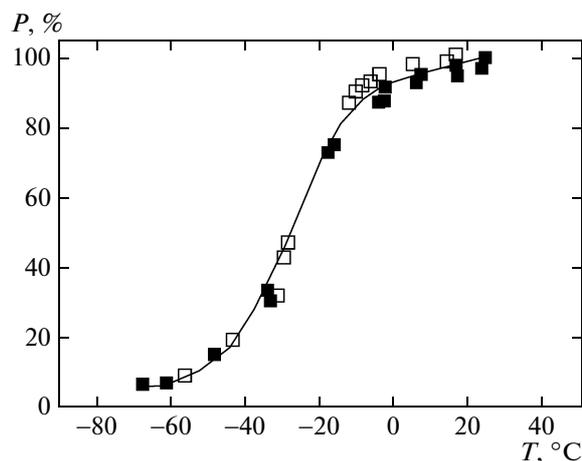
According to the general principle of heterogeneous catalysis [39–42], a catalytic chemical process involving two molecules proceeds on a surface with which the molecules are bonded and which in our case is a cluster surface. If bound molecules are in rapid equilibrium with free gaseous molecules, the process proceeds in a manner similar to that in the gaseous phase. But the parameters of individual stages of the chemical process are different, depending on whether it proceeds with free or bound molecules. The object of our analysis is process (3.1) with supported gold clusters as a catalyst. As shown in [14–16, 43], gold clusters supported by certain semiconductors, metal oxides, provide a high rate of this process. Moreover, a subsequent study of process (3.1) with supported gold clusters as catalysts demonstrated that the number of metal oxides effective as a support is restricted and includes only Fe_2O_3, MgO, TiO_2, and CeO_2. Furthermore, gold clusters function effectively as catalysts only if their size does not exceed 1 nm, approximately six times the Wigner–Seitz radius for gold. If the diameter of the gold particle exceeds 5 nm, the catalytic effect for supported gold particles disappears entirely. For this reason, less than 1% of the deposited gold contributes to the catalytic oxidation process if gold particles and clusters are prepared by traditional chemical methods [20]. One more conclusion from experimental research is that the CO molecules being oxidized are captured either in the boundary between a cluster and the support "on top" of a sufficiently small gold cluster [21]. Meanwhile, oxygen molecules are fastened to the support surface or oxygen atoms are taken for CO oxidation from the support [17, 44, 45]. (Clusters as small as Au_4 may bind O_2 "on top" of the cluster [46]). We use these peculiarities of gold clusters as catalysts in the subsequent analysis.

Fig. 1. The temperature dependence of the fraction P of the CO molecules ξ that are oxidized to CO_2 molecules in an air flow with an admixture CO and the catalyst Au/TiO_2 [17, 45].

4. PECULIARITIES IN THE STUDY OF CATALYSIS BY CLUSTERS

In the simplest version of a model of the catalytic process, the rate is determined by the Arrhenius formula [47]

$$k_{ch} = A\exp\left(-\frac{E_a}{T}\right), \qquad (4.1)$$

where the temperature T is expressed in energy units and E_a is the activation energy of this process. In this case, we can assume that the catalyst decreases the activation energy E_a of the process. We see that this case does not suitably describe process (3.1) under consideration here. Indeed, in this case, the rate of the catalytic process as a function of temperature has the so-called "volcano" form [39, 41, 42, 48], i.e., it has a maximum at a definite temperature that reflects the competition between the attachment process of molecules to the catalyst surface and the chemical process. Indeed, at low temperatures, the rate of the catalytic process is low because of the low rate of the chemical

process, but the overall rate becomes low again at high temperatures because the probability of molecular attachment to the catalyst surface is small. Hence, the rate of the catalytic process has a maximum at midrange temperatures. The simple Arrhenius version is not adequate to describe process (3.1) with supported gold clusters as a catalyst, as indicated by the experimental rate of this process given in Fig. 1.

Considerable progress in understanding catalytic chemical processes with supported clusters as catalysts has been achieved by computer simulations based on the density functional theory (DFT). However, it may be dangerous to overestimate the power of computer simulations for this problem. Because this computer simulation is meant to describe complex atomic systems, its accuracy is restricted. In particular, while the accuracy indicated in calculations [49] is 1% for the bond lengths, the accuracy of the barrier heights is estimated as only 25–30%. Although these accuracy estimates seem optimistic, the accuracy of these parameters of the PES may be gauged by comparing different calculations. But there is one more reason why we can consider evaluation of parameters of the static PES as only indicative model calculations. The fact is that thermal motion and rearrangements of atoms in this complex atomic system may change the parameters of the barriers to transition, because the calculations describe only the static system, whereas we have to deal here with a dynamic one.
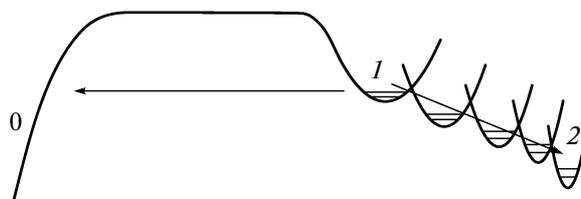
Therefore, the principal unique quality of the catalytic process by clusters lies in its dynamics, rather than simply in the structures formed in intermediate stages of the process. This has been called "dynamical fluctionality" [5, 50]), a property that characterizes the adaptability of a complex atomic system to find an optimal configuration or succession of configurations for effective transitions at each intermediate stage.
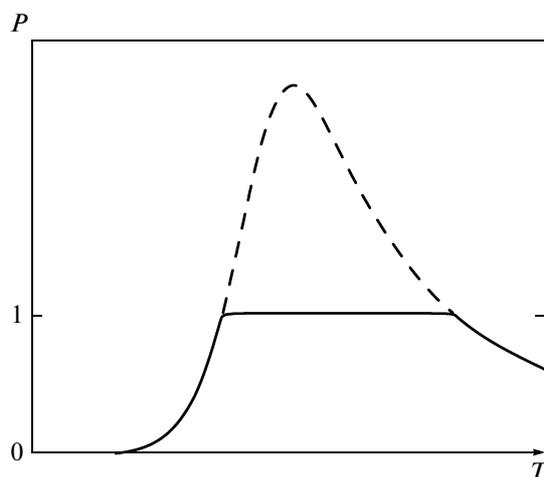
Fig. 2. The temperature dependence of the fraction of transformed molecules as follows from the "volcano" form for the rate of a catalytic process.

Fig. 3. A scheme of process (3.1) as transitions between configurational states of a complex system consisting of a catalyst and reactant molecules. The cross section is taken for each transition along a line that joins local minima of the PES for this transition. The CO molecule from the initial free state 0 is captured in state *1* in which DFT calculations [21] indicate that it becomes positively charged, and hence the reversible transition with release of the Co molecule requires a tunnelling electron transition to neutralize the CO. Subsequent configurational transitions in direction *2* lead to formation of the CO_2 molecule.

Since a metal cluster may change the configuration of its atoms far more readily than can a macroscopic metal surface, clusters may be better catalysts in principle [51]. This possibility is especially important for metal clusters that have a large number of configurational states with low excitation energies [52–55]. One treatment of gold nanoclusters did take rearrangements into account [46]; this work addresses the attachment of O_2 molecules to the supported clusters, but does not consider binding or oxidation of CO. We can estimate the transition from a statistical description of the system to the dynamic one for the phase transition in the 13-atom Lennard–Jones cluster (i.e., with the Lennard–Jones interaction of atoms). The computer simulation of this cluster by molecular dynamics with focus on separation of its aggregate states in the course of cluster evolution [33, 34] allows describing cluster dynamics. These simulations demonstrate that the contribution to the entropy of the phase transition due to thermal motion of atoms is 30–40% near the melting point [26, 56]. This means that the transition from the static description to the dynamic one in this case corresponds to taking thermal motion (oscillations and large-amplitude displacements) of atoms in the cluster into account. This leads to a decrease of the calculated melting point for this cluster by 30–40%. This analysis shows that computer simulation of complex atomic systems based only on evaluation of the PES parameters with the assumption of motionless atoms, i.e., static calculations, are unrealistic, may be misleading, and must be combined with experimental results to determine the extent of their validity.

Therefore, in the analysis of process (3.1), we are guided primarily by experimental measurements, although computer simulation by the DFT method gives us some understanding of the character of this process. There are many measurements of the rate of

the chemical process, summarized in [45]. These measurements are based on a reactor with a catalyst through which a flow of air goes, with an admixture of CO (usually about 1%). The fraction of CO molecules that are transformed in CO_2 is measured. Measurements from different experiments are made under different conditions; these may be reduced to correspond to identical conditions for different air pressures, CO concentrations, and the time of residence inside the reactor, but the results cannot be compared if the catalyst properties are varied [45]. Nevertheless, if we restrict ourselves to certain conditions as is done in Fig. 1, we can obtain a qualitative understanding of the character of this process if we invoke also some results of DFT computer calculations.

5. CHARACTER OF CO OXIDATION WITH SUPPORTED GOLD CLUSTERS

We now base our discussion on the rate of process (3.1) according to Fig. 1 and infer the parameters of the main stages of this process when supported gold clusters are used as the catalyst. The dependence in Fig. 1 can be obtained from the volcano curve by cutting off the upper part of the curve, as it is shown in Fig. 2. This means that the time of residence of CO molecules inside the reactor exceeds the time required for the chemical process under the given conditions; under these conditions, the probability of attachment of the CO molecule to the catalyst surface is one.

We analyze the character of the process under consideration. In the framework of the PES concept, the transition is a sum of transitions between different PESs, as shown in Fig. 3. We note that the transition

between neighboring PESs is efficient if the Massey parameter [57] for this transition is small:

$$\xi = \frac{a\Delta E}{\hbar v} \ll 1. \tag{5.1}$$

Here, a is a typical distance that characterizes a recognizable change of the system energy, ΔE is the energy change or the barrier energy height for a given configurational transition, and v is a typical velocity of atoms in this transition. If the Massey criterion is small for all the configurational transitions of this process, an effective equilibrium is established in this system, and the populations of the initial and final states are determined by the statistics. Correspondingly, in this case, an equilibrium between configurational and vibrational states, for both free and bound reagent molecules, is subjected to the thermodynamic laws, rather than the dynamics of evolution of this system.

In this case, we have the competition of two overall processes; in the first, the state of CO bound with the catalyst results in release of the unreacted CO molecule. The other channel is the formation of CO_2. The probability of CO_2 formation is given by

$$P = \frac{\tau_1}{\tau_1 + \tau_2}, \tag{5.2}$$

where τ_1 and τ_2 are typical times corresponded to evolution of the system in a given channel. Assuming the transition in a given configurational state to be determined by the barrier energies ε_1 and ε_2, we have the typical times of realization of a given channel

$$\tau_1 = a\exp\left(\frac{\varepsilon_1}{T}\right), \quad \tau_2 = b\exp\left(\frac{\varepsilon_2}{T}\right).$$

From this, we find the temperature dependence of the probability P_1 of a given channel of the process. Hence, the yield for the final product of the chemical process may depend strongly on the temperature.

This scheme of the catalytic process as a result of sequential transitions between configurational states of this system allows understanding some features of this process. In particular, on a sufficiently long time scale, this process is reversible, and the rates of the direct and inverse processes are connected by the principle of detailed balance. But the dynamics of this process are important for shorter time scales, and the rate of a catalytic process is determined mostly by the slowest stage, whose rate is expressed through the barrier height separating the corresponding local minima of the PES.

Then the probability P of realization of channel 1 is given by

$$P = \frac{1}{1 + A\exp(E_a/T)}, \tag{5.3}$$

where the temperature T is expressed in energy units, the activation energy is

$$E_a = \varepsilon_1 - \varepsilon_2 = 0.50 \text{ eV},$$

and

$$A = \frac{b}{a} = 6.4 \times 10^{-11}$$

under standard conditions of the experiment given in Fig. 1.

Based on these data, we can compose the following picture of the process (3.1), represented in Fig. 3. The configurational transitions include both variation of the PES as a result of changes of the atomic configuration and a change of the charge distribution in this system. We assume, as calculations have indicated, that capture of the CO molecule by the supported gold cluster proceeds through formation of the CO^+ ion, in which the valence electron eventually transfers to an oxygen atom located at some distance from this ion. Then the reversible process of release of the CO molecule consists in a tunnelling electron transition that reneutralizes the CO, while formation of the molecule CO_2 results in transport of O^- toward CO^+ up to the point of their joining. That may include many subsequent transitions between neighboring PESs with the total activation energy E_a of all these transitions.

Our analysis is based on the cited experimental results and some results of calculations. In particular, a supported gold cluster may be better as a catalyst than a free gold cluster because it becomes charged on the support surface, and this opens additional possibilities for a chemical process, adding charge exchange processes to it. Indeed, a small gold cluster on a support surface of the type under consideration may be positively charged [1, 58–60], which supports our conclusion. But we must also note that atomic gold has a very large electron affinity, comparable to that of halogen atoms, and hence we might presume that small gold clusters would behave similarly. Nevertheless, a conclusion that the bilayer cluster structure leads to its optimal efficiency as a catalyst [17, 20, 44] cannot be inferred from this consideration.

We now base our discussion on the scheme given in Fig. 3, with parameters of the experiment in Fig. 1. In this case, there is competition between the processes of charge exchange and the activation transition. If we assume that the charge exchange process is without barrier, we obtain $A = 6.4 \times 10^{-11}$ for the probability of the tunnelling transition. We calculate a typical distance between an electron and ion that provides this probability. Assuming the potential energy to be constant, we obtain the probability A for the tunnelling electron transition as [61]

$$A = \exp(-2S), \quad S = \frac{\sqrt{2m_e\varepsilon}l}{\hbar}, \tag{5.4}$$

where ε is the barrier height that corresponds to the electron binding energy, l is the length of this barrier, and m_e is the electron mass. Taking typical values for $\varepsilon = 2$ eV and $\varepsilon = 4$ eV, we obtain the respective distances $l = 1.6$ nm and $l = 1.1$ nm between charges. Figure 4 gives the surface charge distribution under these
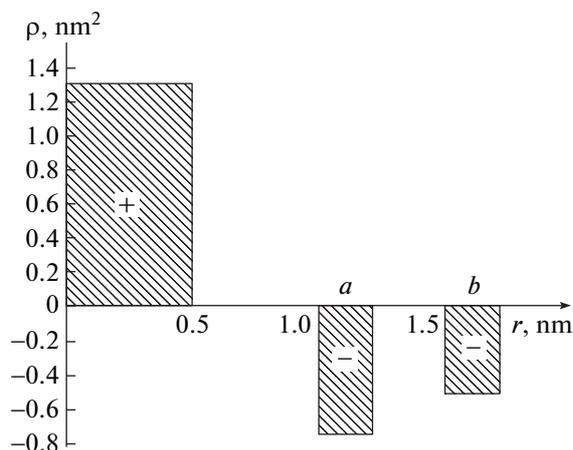
Fig. 4. The schematic charge density distribution after the capture of the CO molecule in process (3.1) that provides the probability $A = 6.4 \times 10^{-11}$ for the tunnelling electron transition for separated charges of the positive and negative charges. Version "a" corresponds to the barrier height $\varepsilon = 4$ eV, and version "b" relates to the case $\varepsilon = 2$ eV.

conditions if we assume axial symmetry of this distribution and also assume that the positive charge is distributed uniformly over the cluster surface. We see that a typical distance between the positive and negative charges exceeds the radius of the Au_{10} cluster for both examples.

We consider this process from another standpoint. If the charges of CO^+ and O^- are separated in accordance with Fig. 4 and formation of CO_2 from them proceeds in the optimal way, we find the optimal rate constant for a typical time of this process for bound particles at room temperature as

$$\tau = \frac{1}{\nu}\exp\left(\frac{E_a}{T}\right) \approx 2 \times 10^{-5} \text{ s},$$

where $\nu \sim 10^6$ cm/s is a typical velocity of a bound oxygen ion on the surface, $l \sim 1$ nm is a typical distance between charges, $E_a = 0.5$ eV is the barrier height, and in this case we have $\exp(E_a/T) \approx 19$. A typical lifetime of the bound CO molecule on the surface has the same order of magnitude. We note that this is a rough estimate and gives only a scale of times. Here these times are short compared with a typical residence time of free molecules inside the reactor for these measurements, but in reality the lifetime of a bound molecule may exceed the residence time for free molecules.

6. CONCLUSIONS

In the foregoing analysis, we have neglected many aspects of the process under consideration, such as the influence of water on this process, the dependence of its rate on the degree of support covering by oxygen, and so on. Various aspects of this are contained in book [45] and testify to the complexity of this process.

Moreover, within the framework of the above scheme, we cannot explain many facts of this problem, for example, why only the bilayer structure of the supported gold cluster provides an efficient catalyst for this process and why only a restricted group of supports are suitable for this. Nevertheless, this analysis exhibits the uniqueness of this process, in particular, how the separation of charges for reacting molecules exceeds the cluster size.

Fortunately, there is a large body information for this problem that allows us to indicate appropriate directions for subsequent research, as well as to bring it to the present stage. This problem is important because of its potential applications (see, e.g., [1, 45, 62–64]). A particularly fruitful direction for development of experiments is likely to be changing from the chemical processes for preparation of gold clusters to physical processes [20, 65]. This allows increasing the efficiency of the use of gold. Moreover, we may also ascertain ways to change the support surface to increase the yield parameters of this catalyst, e.g., by introducing vacancies in the oxygen sites [21]. As regards computer simulations of the process under consideration here, in addition to the mathematical challenges for this complex system, there is also a lack of truly appropriate contemporary calculations because those available deal with a static system, while in reality this catalytic process involves a dynamic system, and the nature of that dynamic development of the system is important especially for catalytic properties related to transitions between configurational states of the system. We note that there have been some efforts to include this in the total problem, in particular, the effect of dynamic structural flexibility [17] that has been introduced to account for a change of the structure of the system as a result of molecule absorption. Nevertheless, we want to point out the importance of dynamic effects, because the involvement of effective transitions between configurational states appears to be a central characteristic of this catalytic process, and presumably of others involving metal clusters.

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SPELL: 1. groundstate, 2. icosahedral, 3. cagelike, 4. uncatalyzed, 5. entropic, 6. fluctionality, 7. reneutralizes