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R. S. BERRY and B. M. SMIRNOV

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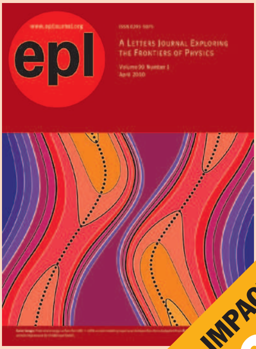

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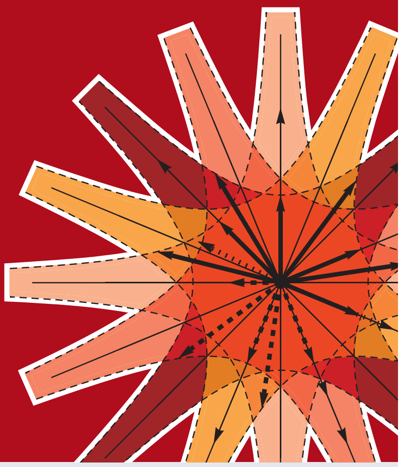

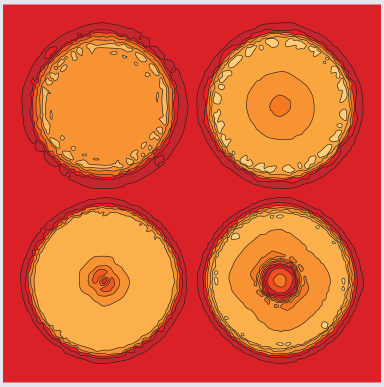

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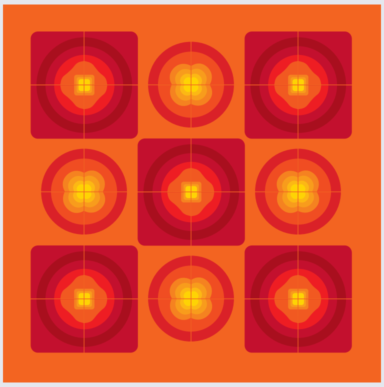

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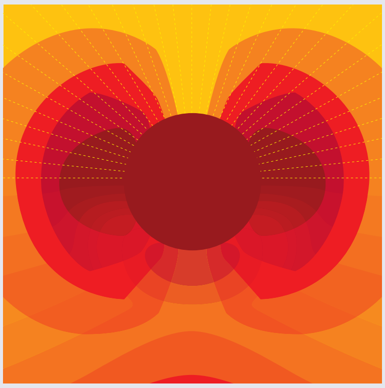

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Image: Ornamental multiplication of space-time figures of temperature transformation rules (adapted from T. S. Bíró and P. Ván 2010 *EPL* **89** 30001; artistic impression by Frédérique Swist).

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Charge exchange in CO-oxidation with supported gold clusters

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Abstract – The oxidation of CO molecules bound to supported gold clusters evolves through a series of configurational changes along the potential energy surface of the total system. The possibilities of theoretical approaches and models for description of catalytic processes are analyzed, and, in particular, the vulnerability of the DFT method is shown for such processes. The analysis of experimental data shows that the formation of the CO_2 molecule occurs via a straightforward chemical process, which competes with a charge exchange process involving formation of negatively charged gold clusters. The structure of the gold cluster for one pathway involves the planar form whereas the other pathway goes via the two-layer cluster structure. From this information, we can infer the selectivity and efficiency of the catalyst as functions of the cluster size and determine that the typical distance for the tunnelling electron transition to form negatively charged clusters is 1–2 nm that means that this electron is taken from the support.

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Introduction. – We examine the process of CO oxidation with supported gold clusters as a catalysts that proceeds according to the scheme

$$\widetilde{\mathrm{CO}} + \widetilde{\mathrm{O}} \to \mathrm{CO}_2, \qquad (1)$$

where $\widetilde{A}$ means that the particle A is bonded with a surface. It was shown more than 30 years ago by Japanese scientists [1–3] that this process proceeds efficiently at room temperature in spite of its high activation energy if the catalyst is a small gold cluster attached to the surface of any of certain semiconductors —metal oxides, in particular. Because of its practical importance, this process is the object of detailed experimental and theoretical studies. From these studies investigators have found a restricted number of effective supports which include Fe_2O_3, MgO, TiO_2, and CeO_2. The optimal size of gold clusters for CO oxidation is believed to be 10 atoms [4–7], although the 8-atom cluster is also quite effective [8]. In this process, oxygen molecules are captured by the support far from the cluster, while captured CO molecules are located at the cluster-support boundary [4,9–11]. One might expect to achieve a total description of this process from the density functional theory (DFT) [12] as a result of the transition between structures consisting of the support, cluster and reactant molecules. According to DFT, the uncertainty of the lengths of chemical bonds is estimated as 1% and the barrier height of chemical reactions is 25% [13]. In this paper we show on the basis of the analysis of similar processes that simplifications used in applying DFT lead to a loss of the principal features of the catalytic process. In particular, the DFT cannot explain the dependence of the process rate on the presence of water [10], on the extent of coverage of the support surface by oxygen [14,15], and other factors. Here, basing our analysis on experimental data, we can infer the mechanism of this process under optimal conditions.

The potential energy surface in the analysis of chemical processes. – We consider the process under examination within the framework of the traditional transition state theory for the kinetics of chemical reactions [16–19]. Here, the chemical process results from transitions between specific minima of the potential energy surface of the total system of colliding molecules. We use the Born-Oppenheimer approximation and the adiabatic concept according to which nuclei move in a self-consistent field of electrons and ions, whereas electrons redistribute instantaneously to each current nuclear configuration. This means that the evolution of an atomic system can be described in terms of the effective potential energy surface given by the total internal energy at each spatial configuration of the nuclei. Hence, to calculate the rates of chemical

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processes it is necessary to determine the potential energy surface (PES) as a multidimensional function of atomic configuration and represent the rate of the process as transition between the minima of the PES that correspond to the initial and final states of the chemical process. This scheme is the rougher, the more complicated the process is. For this model, and for a single reaction path, the rate constant of the process is given by the Arrhenius formula [20]

$$k_{ch} = A \exp\left(-\frac{E_a}{T}\right), \qquad (2)$$

where the temperature T is expressed in energy units, and E_a is the activation energy of this process. In the simplest picture, this is the height of the barrier from the initial state to the simple saddle between the initial and final states. In this case one can assume that the catalyst decreases the activation energy E_a of the process. In a more sophisticated approach, the catalyst may affect the entropy of the transition state as well.

In this scheme we use the following assumptions. First, treating the process at a finite temperature, we use, in the first approach, the PES at zero temperature, *i.e.* all the evaluations relate to motionless nuclei. In the following approach we deal with the effective PES which accounts for the motion of nuclei. Second, within the traditional scheme, we treat the chemical transition as evolution in the space of atomic coordinates (the configuration space) along a single PES, and assume that excited PESs do not partake in the chemical process. We check, in the discussion below, the validity of these assumptions for the process (1).

An important property of the potential energy surface for a system of many bound identical atoms is the large number of local minima for the potential energy surface of clusters; this was demonstrated first for Lennard-Jones clusters [21–23]. These local minima are separated by barriers, and evolution of clusters results in transitions between neighboring local minima [24,25]. This is a general property of atomic systems [26,27], and pertains to both chemical processes and the phase transitions in clusters.

The phase transition in clusters is the transition into configurationally excited states. The transition involves a change in energy ΔE, but it is also characterized by a large value for the ratio of statistical weights g of the excited (liquid) to ground (solid) configurational states. The traditional melting point T_m is the temperature at which the free energies of the two forms are equal, *i.e.* where

$$T_m = \frac{\Delta E}{\Delta S}. \qquad (3)$$

Here $\Delta S = \ln g$ is the difference of the entropies of the aggregate states of the transition. We note a bit of difference between the phase changes of dielectric and metal clusters [28]. In the case of dielectric clusters the lowest accessible form we would call a liquid state corresponds to a configurational state of one symmetry, typically a state in which one or a small number of atoms move onto the cluster surface where they have high mobility but may exchange with surface atoms. Then, at higher energies, eventually all the component atoms have high mobilities. In the case of metal clusters, even the lowest accessible liquid form exhibits a mixture of different configurationally excited states with a high mobility of atomic cores, and this mixture varies with increasing temperature [28].

We now check the validity of assumptions in numerical simulations of clusters that allows us to estimate the reliability of DFT and other computer methods. Let us consider the phase transition in the 13-atom Lennard-Jones cluster LJ_{13}, which has a complete, closed-shell icosahedral structure for its ground configurational state. The configuration in which one atom moves onto the cluster surface is the first excited configurational state and can be considered the lowest-energy liquid form. Alternatively, one could also catalogue this as an excited solid configuration. At larger sizes, beginning at about 55 atoms, a size that has two icosahedral shells, Lennard-Jones clusters exhibit a well-defined phase-like form that has been called "surface-melted", a form in which the inner shell is clearly solid and the atoms of the outer shell exhibit high mobility [29]. For such clusters, the PES is based on the sum of the pairwise Lennard-Jones interaction potentials. The energy of configurational excitation of a single atom to the surface is $2.87D$ [30] where D is the binding energy of a diatomic, and the statistical weight for the 13-atom cluster is [31] $g = 180$, based simply on configurations, with no consideration of vibrations. According to formula (3), this gives the melting point of this cluster as $T_m = 0.55D$. One can describe the melting behavior of this simple LJ_{13} cluster at a finite temperature or at a fixed energy by computer simulation, using the method of molecular dynamics. Such simulations give the melting point of the isolated, constant-energy cluster as [32] $T_m = 0.30D$ and for isothermal cluster we have [33] $T_m = 0.27D$. This shows the error of the assumption that the cluster's behavior at zero temperature, with no consideration of atomic vibrational motion, can be used to describe the same system at its melting point. This shows what care is required in evaluating rate constants and dynamics for configuration transitions, and the danger of using a model based only on the PES at zero temperature.

In the characteristic behavior of a catalytic process, the reaction proceeds via the attachment of the reactants with simultaneous change the catalyst state, and the release of the reaction product or products proceeds on the following stage, at which the catalyst returns to its initial state. It is possible that if two electronic states of the total system are close in energy, the molecule capture step may lead to the catalyst making a transition into a nearby electronic state, with its own PES. Because DFT computer evaluations involve only one PES for the total system, the method is vulnerable to the error of neglecting the interaction of participating neighboring electron states.

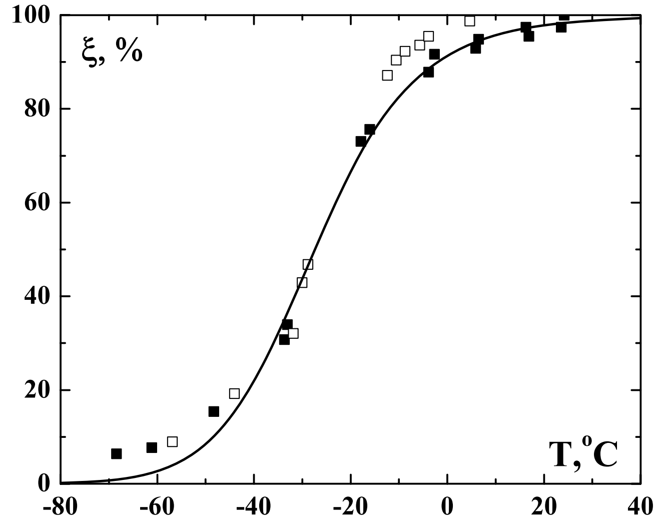

Fig. 1: The temperature dependence of the fraction P of the CO molecules ξ oxidized to CO_2 molecules in an air flow with an admixture CO and the catalyst Au/TiO_2 [4,10].

Simulations of relatively small metal clusters are based on atomic pseudopotentials. Let us discuss this for small gold clusters for which the planar and 3D-structures compete for lowest energy. For example, according to both calculations and experiment [34,35], the ground-state structure of the isolated Au_{12}^- cluster is planar, while Au_{13}^- and Au_{14}^- clusters have 3D-structures. Let us consider the structure of the neutral Au_{13} cluster. Among 12 papers devoted to the ground-state structure of this cluster and are taken into account in a review [28], the icosahedral cluster structure is the lowest in 8 papers but the other 4 papers claim a different ground-state structure. This contradiction exhibits the uncertainty that can result from a proximity of electron structure energies. For clusters with structures at well-separated energies, simulations show no such inconsistencies or contradictions.

From this we infer that the computer DFT method is not likely to be reliable for the analysis of catalytic processes. Apart from any susceptibility to mathematic errors, we state that the use of DFT for the analysis of catalytic processes is likely to lead to errors because the processes take place at finite process temperatures and, particularly with metal cluster catalysts, generally involve participation of multiple electronic states whose proximity is a crucial element in the catalytic process, and hence whose omission may misrepresent the process, and have little resemblance to the actual experiments. Nevertheless, we note that DFT is useful in the analysis of catalytic processes because this gives us the atom configuration of the total system ground state in this complex process.

Model of catalytic process. – We now construct a model of the catalytic process (1) with a gold cluster catalyst, basing the model on experimental data and assuming optimal conditions for this process. The experimental data for the rate of this process, reduced to a common set of experimental conditions [10], is given in fig. 1; we will consider this as fixing the relative rate constant of the process (1) for the indicated catalyst.

It is clear that a change of the residence time of a CO molecule in a reactor or a change of the total catalyst mass leads to a proportional change of the process rate. Next, according to the nature of the catalytic process [36,37], the reagent molecules are captured by the catalyst, and then there is competition between the initial and final channels of the process. Specifically, the first channel corresponds to release of the unreacted CO molecule, and the second channel, to the formation of CO_2. Characterizing the (inverse) rates for these channels by τ_1 and τ_2, typical times corresponding to evolution of the system in a given channel, we obtain the probability of CO_2 formation as

$$P_1 = \frac{\tau_1}{\tau_1 + \tau_2}. \tag{4}$$

In accordance with the Arrhenius formula (2) for reaction rates, and with the barrier energies ε_1 and ε_2 for the two indicated channels, transition state theory gives us the typical reaction times of these two channels

$$\tau_1 = a \exp\left(\frac{E_1}{T}\right), \quad \tau_2 = b \exp\left(\frac{E_2}{T}\right). \tag{5}$$

From this we find the temperature dependence for the probability P_1 or P_2 of a given channel of the process. Hence, formula (4) for the rate P of reaction of the channel 1 is given by

$$P_1 = \frac{1}{1 + A \exp\left(\frac{E_a}{T}\right)}, \tag{6}$$

where the temperature T is expressed in energy units. Applying formula (6) to the experimental data of fig. 1, we can extract the activation energy and coefficient of the process, as $E_a = E_1 - E_2 = 0.50\,\mathrm{eV}$, and $A = b/a = 6.4 \cdot 10^{-11}$. We now analyze these obtained values. The activation energy E_a of the process (1) is a typical one for chemical processes, whereas the pre-exponent value is typically $A \sim 1$. Such an extremely small value of the pre-exponential factor indicates the unlikelihood of this process at room temperature. However the yield for the final product of this process depends strongly on the temperature. We next examine the basis of the small value of the pre-exponent with the nature of the process (1).

Thus, we have competition of two channels of processes involving a captured CO molecule on the catalyst surface. The first is the chemical process in which an oxygen atom of (or attached to) the support attaches to the bonded CO molecule, and the newly formed CO_2 molecule leaves the gold cluster. This chemical channel is characterized by an activation energy of about 0.5 eV, whereas the other channel has very low probability, to the extent of being virtually inactivated. Because of the small probability of this channel ($\sim 10^{-10}$), we infer that it is a charge exchange transition, *i.e.* a tunnelling electronic transition through a distance significantly greater than a typical atomic size. Recently, [38] in analyzing this problem we dealt with the charge exchange transition between positive and negative ions. We now consider another charge exchange transition involving electron transport from the negative oxygen ion located on the support to form a negatively charged gold cluster with a CO molecule on the boundary of the cluster and support. This is based on the large electron affinities of gold clusters; the electron affinity of an isolated gold cluster consisting of 10–20 atoms ranges between 3 and 4 eV [39].

In the analysis of the tunnel electron transition, we use the rectangular potential barrier that separates electron states in the gold cluster and on the support and assume the distance between the well for an electron in the cluster and on the support to be l. Then the probability of tunnel electron transition between these two states is given by [40]

$$A = \exp\left(-\frac{\sqrt{2m_e B}\, l}{\hbar}\right), \tag{7}$$

where B is the barrier height that corresponds to electron affinity with each well with we assume to be identical, l is the length of this barrier, m_e is the electron mass, E is the energy of the reaction, and $\hbar$ is the Planck constant. Taking typical values for $B = 3\,\mathrm{eV}$ and $E = 4\,\mathrm{eV}$, we obtain the distances between charges $l = 1.6\,\mathrm{nm}$ and $l = 1.1\,\mathrm{nm}$ correspondingly at the transition probability $A = 6 \cdot 10^{-11}$. For comparison, the Wigner-Seitz radius for gold is $r_W = 1.65\,\text{Å}$ [41,42]). As is seen, the distance between wells for an electron exceeds a cluster size that is 1 nm. From this we conclude that the bound electron for formation of the negative cluster is taken from the support. As a result of this transition, the binding energy of the CO molecule with the gold cluster increased as well this may lead to a change of the electron structure of this molecule. As a result, the activation barrier for CO oxidation by bound oxygen atoms and molecules increases, and this process is absent practically at room temperature.

One can describe this version of oxidation of CO with a supported gold cluster as a catalyst by the following scheme of competing reactions, involving neutral, negatively and positively charged gold clusters:

$$\mathrm{CO} + \widetilde{\mathrm{Au}_n} \to \mathrm{CO}\text{-}\widetilde{\mathrm{Au}_n}, \tag{8}$$

$$\widetilde{\mathrm{O}} + \mathrm{CO}\text{-}\widetilde{\mathrm{Au}_n} \to \mathrm{CO_2}\text{-}\widetilde{\mathrm{Au}_n} \to \mathrm{CO_2} + \widetilde{\mathrm{Au}_n}, \tag{9}$$

$$\widetilde{\mathrm{O}^-} + \mathrm{CO}\text{-}\widetilde{\mathrm{Au}_n} \to \widetilde{\mathrm{O}} + \mathrm{CO}\text{-}\widetilde{\mathrm{Au}_n^-}, \tag{10}$$

where CO-$\widetilde{\mathrm{Au}_n}$ is the bound state of those particles and the second and third processes of this scheme correspond to stable states of this system and are competitive and depend on whether the oxygen atom attaches to the monoxide-cluster complex as a neutral or negative particle. Of course the cluster could also take on an electron from the substrate, which would give a process essentially equivalent to the third of these. At the level of our analysis here, these can be considered equivalent. A more detailed analysis of cluster-substrate interactions will be necessary to reveal any significant differences between the two processes of charging the cluster negatively.

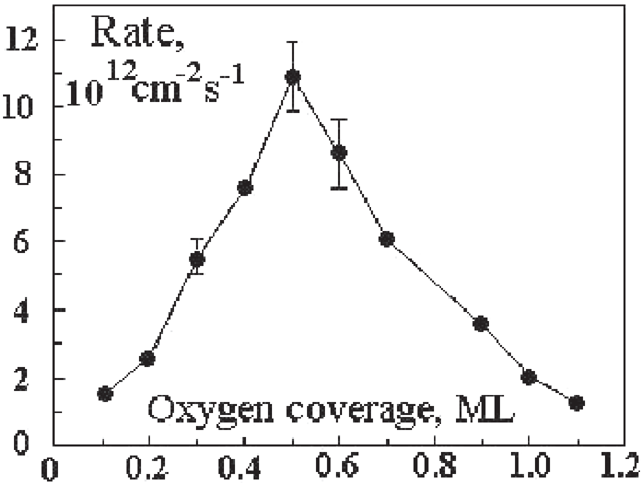

Fig. 2: The rate of $\mathrm{CO_2}$ formation by process (1) as a function of oxygen coverage of the substrate surface at temperature of 200 K [14,15]. ML is the number of molecular layers covering the support surface.

Let us analyze the negative ion states for this system. Evidently, in the negative ion state CO-$\widetilde{\mathrm{Au}_n^-}$, an additional electron is attached to the gold cluster, and the binding energy of the CO molecule to the negatively charged gold cluster bonded with the support is higher than that to the supported neutral gold cluster. This makes the bound state CO-$\widetilde{\mathrm{Au}_n^-}$ stable. In addition, formation of the cluster negative ion may lead to change of the electron state of the CO molecule. The contrasting negative ion state, in which the electron is bonded to the support may, in principle, have two forms, delocalized or localized. In the first case, the bound electron is distributed over a large area, *i.e.* it is bound simultaneously with many oxygen atoms of the support. In the second case the electron forms a bond with just one oxygen atom of the support. The latter must be associated with a nonuniform support surface, so that the excess electron is bound to some nonuniformity. Figure 2 shows the observed dependence of the rate of this process on the extent of covering of the support surface by attached oxygen molecules. This tells us to choose the second, localized picture of the surface negative ion for the following reason. If the excessive electron were distributed over a large area, the dependence of the rate of oxidation on the oxygen molecule coverage would be weak. However in contrast, the strong concentration dependence is quite apparent in fig. 2. According to the localized interpretation, the degree of coverage influences the character of chemical bonds involving surface oxygen. Therefore the rate of displacement of oxygen atoms over the support surface, as well as parameters of the negative ion depend on the extent of coverage. Similarly, the rate of the chemical process may depend on the presence of water molecules and other factors which influence parameters affecting attached molecules.

In addition, fig. 2 helps to understand the nature of the electron state, so that this electron transfers subsequently to the cluster and forms the $\widetilde{\text{CO-Au}_n^-}$ state. We assume the positive and negative ions of the support to be separated. Then a sharp dependence of the process rate on the oxygen coverage at low temperatures confirms the transfereed electron is bonded with an individual oxygen atom (or molecule) rather than being distributed over the surface as it takes place at higher temperatures.

Thus, the catalytic chemical process of CO oxidation with supported gold clusters of 10–20 atoms has two competing channels; these channels correspond to two different PESs for the atomic system which consists of the support, the isolated gold clusters bonded with the support, and CO molecules located on the boundary between the gold clusters and the support. This corresponds to the PES of the initial state. We note that from the standpoint of configurational states, a catalytic process has two such states similar in energy. The capture of a reagent molecule leads to transition of the catalyst from the PES of the initial (and presumably ground) state to the nearest state and corresponding PES of the combined system. For small isolated gold clusters, such configurational states correspond to the planar and 3D-cluster structures which are close in energy if the number of cluster atoms is close to 10. The transition between these structures can be found on the basis of measurements of the cluster mobilities in a gas [43] because the mobility of charged clusters depends on their structure. Small gold clusters have a planar structure for their ground state, whereas the ground state of larger clusters is characterized by the 3-dimensional structure. According to mobility measurements [44], the transition between the planar and 3d-structures of negatively charged clusters Au_n^- appears at $n = 12$. This is supported by calculations employing DFT (density functional theory) [45,46]. According to such evaluations, the negatively charged cluster Au_{12}^- is planar in its ground configurational state, whereas clusters Au_{13}^- and Au_{14}^- have 3D-structures in their ground states. For positively charged gold clusters Au_n^+ the transition from the planar to 3D-structure starts from $n = 7$ [47].

Transferring to supported gold clusters, note that competition between two configurational transitions with small exponential factors of the Arrhenius formula (2) at room temperature may occur between a chemical reaction and a charge exchange process. From another standpoint, we can think of competition between the planar and 3-dimensional configurational states of supported gold clusters of atoms that provides the catalytic properties of these clusters with the number of atoms about 10 [4–7]. Extending the properties of free gold clusters to a system consisting of a support, isolated gold clusters and CO molecules located at the boundary between the gold clusters and the support [4,9–11], we recognize that this system has two energetically close configurational states. One configurational state corresponds to the planar cluster structure; the other is based on a bilinear, 3-dimensional structure. The gold cluster is neutral in one of these states, whereas the negative charge is distributed over the gold cluster in the other, negatively charged configurational state. These configurational states have very similar energies, which requires that the size of the catalyst we consider here is severely restricted to approximately 10 atoms [4–7].

Thus, one can recognize, in a realistic picture of the catalytic CO oxidation by supported gold clusters, that the charge exchange process competes with the chemical process and admits an alternative effective process at room temperature. Of course, the properties of the support are essential in this case, so that only a restricted number of supports (Fe_2O_3, MgO, TiO_2, CeO_2) are effective for the process (1). The support is a donor of oxygen atoms or electrons for the processes under consideration. Specifically, the support converts attached oxygen molecules into bound oxygen atoms which are consumed subsequently in CO oxidation. In addition, vacancies in the support lattice form both positively and negatively charged centers. Gold clusters are captured in these centers [11], and also these centers can provide a negative charge to a gold cluster holding a captured CO molecule.

Conclusion. – We consider the chemical process as a result of evolution on the PESs for reagent and product molecules. The oxidation of CO involves a change in the configurational state of the total atomic system, including the gold cluster catalyst. Moreover, CO oxidation with supported gold clusters as catalyst involves competition between two channels with different PESs. We infer that some standard computer models, including traditional DFT [12], are not suitable for this case because these methods, *e.g.* DFT, describe only one (usually ground) configurational state with no allowance for nuclear motion, while in this process the system must change its configurational state and potential energy surface.

Basing on experimental results, we demonstrate that the chemical process with a standard activation energy may be effective at low temperatures if it competes with the charge exchange process. This means that the ground state of a supported gold cluster with an attached CO molecule corresponds to a negatively charged cluster and exhibits the sensitivity of the supported gold cluster catalyst's activity to the cluster size. In addition, a typical distance for the tunnelling electron transition is about 1–2 nm that exceeds the size of the active gold clusters, but is comparable to this size.

From another standpoint, it follows that this system is working as a catalyst if the energies of the lowest configurational states of the catalyst are close. Using the analogy with free gold clusters, we infer that one of the relevant configurational states with low energy corresponds to the planar structure, whereas the other is that with the two-layer structure. Since the energies of these configurational states for supported gold clusters with attached CO molecules are close, the efficiency of the catalytic process depends strongly on the number of cluster atoms. From this structural consideration, it follows also that the rate of the oxidation process is sensitive to the composition of the support and the degree of its covering by oxygen molecules, as shown in fig. 2 for low temperatures. Probably, until oxygen atoms do not form on the support surface a continuous film, an excess surface electron is not spread over all the surface at low temperatures, but is bonded with a certain surface oxygen atom (molecule). In addition, the efficiency of this catalyst may be connected with the presence of various additives, in particular, water molecules. Thus, various experimental and theoretical analyses of CO oxidation with supported gold cluster catalysts show the complex character of this process. The confirmation of this is the dependence of the catalyst process efficiency on the support type, the degree of its covering by oxygen and the presence of water molecules. Introducing additional data in the model of this catalytic process, together with new experimental results may provide us with a deeper understanding of the nature of this process.

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