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PAPER

CO oxidation on Pt nanoclusters, size and coverage effects: a density functional theory study

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CO oxidation on Pt nanoclusters of approximately 1 nm in size was studied using density functional theory (DFT). Reaction barriers on various sites of a cuboctahedral 55-atom cluster and of several two-layer plane clusters representing (111) and (100) facets of the 147-atom cluster have been calculated at various coverage. The effect of atomic structure of various clusters was discussed. It was concluded that the 147-atom cuboctahedral cluster reveals properties of the Pt single crystal surfaces, while a 55-atom cluster cannot be fully described in terms of Pt single crystal surfaces. It was found that CO oxidation may occur faster at higher coverage and for cluster sizes up to a few nanometers, larger platinum clusters can be more efficient in CO oxidation than the smaller clusters. The size effect was found to depend upon coverage.

Introduction

Transition metals are well known for their catalytic properties. Reactions, such as CO oxidation, can be catalysed by single metal atoms, by small metal nanoclusters and by single crystal surfaces.[1-13] The metal nanoclusters represent a bridge between the molecular-like and solid state of matter. Their atomic and electronic properties change from discrete to bulk with increasing the size. In this way, the catalytic properties of nanoclusters change too. In the case of reactions on small, 'discrete' clusters, one needs to consider each atomic configuration individually,[14,15] while the surface large clusters can be seen as a combination of small pieces of single crystal surfaces with high coordinated adsorption sites, such as (111) and (100) terraces, and low coordinated sites, such as atomic steps and kinks.[6,7] Atomic and electronic structure of the cluster's facets, edges and corner sites resembles properties of the single crystal terraces, atomic steps and kinks.[4,5] Flat facets cannot always be distinguished on small clusters[14-16] but are present on larger particles, such as 55-atom and 147-atom cuboctahedral clusters (Fig. 1). A key question is whether the chemical properties of various sites on the clusters are similar to the properties of corresponding sites on single crystal surfaces? How far can one go with this simple model? To answer this question one needs to compare reaction occurring on the single crystal surface and on the cluster. In the present work, CO oxidation was examined on Pt nanoclusters. CO oxidation is one of the most studied reactions in heterogeneous catalysis and allows one to compare current results obtained for nanoclusters with the results of numerous previous experimental and theoretical studies.

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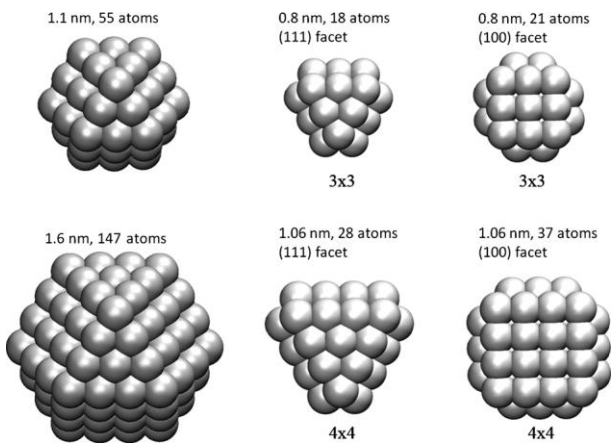

Fig. 1 Various platinum nanoclusters used in calculations. Top row: cuboctahedral 55-atom cluster and corresponding two-layer (111) and (100) clusters. Bottom row: schematic representation of the 147-atom cuboctahedral cluster and corresponding (111) and (100) two-layer clusters.

CO catalytic oxidation on single crystal surfaces is believed to occur through the Langmuir-Hinshelwood mechanism between adsorbed CO and atomic oxygen O formed in O_2 dissociations.[17-21] In some cases, such as reactions on small (n = 5 or 10-atom) clusters[15] or at saturated CO coverage,[6] the adsorbed CO was proposed to react with coadsorbed O_2 species.

The low coordinated sites on atomic steps on the surface are known to promote CO oxidation.[22-24] This effect was studied experimentally for CO and oxygen coadsorbed on platinum under ultra high vacuum conditions, and attributed to the longer residual time of reagents on the step rather than on the terrace,

which is due to a stronger adsorption on low coordinated sites of the step.

It was also proposed that the low coordinated sites on gold nanoclusters are more efficient in CO oxidation.[14,25] If so, smaller clusters should always catalyze CO oxidation better than larger ones. This rule works well for CO oxidation on gold nanoclusters, but breaks in the case of CO oxidation on Pt nanoclusters, where it was experimentally found that there is an optimum size of the cluster, approximately between 1 and 2 nanometers.[26-29] Larger or smaller clusters are less efficient in CO oxidation. This suggests that the high-coordinated sites on the facets of clusters can play an important role in CO oxidation if they are surrounded by the edges. To address this problem, CO oxidation should be studied systematically on various sites of clusters of one or a few nanometers in size.

Previously CO oxidation on small free clusters was studied theoretically by F. Schneider and co-workers[15] and on adsorbed small clusters by Rashkeev et al.[14] CO oxidation on selected sites of larger clusters and at high CO coverage was investigated by Neurock and co-workers. Calculated reaction barriers were used in description of the mechanisms of particular catalytic reactions.[6,7]

The current work presents a study of CO oxidation on the various sites of the 55-atom and 147-atom cuboctahedral clusters, which are approximately 1.1 and 1.6 nm in size. The cuboctahedral shape was chosen because it allows one to compare reactions on the (111) and (100) facets, while another stable configuration, the icosahedral cluster, contains only (111) facets.

Heterogeneous CO oxidation on platinum is important for many catalytic processes, such as cleaning industrial and automotive exhausts as well as the operation of fuel cells.[8-12] The Pt catalyst is usually used in the form of nanoclusters with size of a few nanometers or more. Since the platinum catalyst is expensive it is important to optimize the catalyst for this reaction, in particular, by determining the optimum size and shape of the Pt nanoclusters used in catalysis.

Another parameter which can affect the rate of catalytic CO oxidation is the CO and O reagent coverage. At high enough CO gas phase pressure the surface can be covered by CO molecules. In this case, adsorbed CO blocks oxygen adsorption and the rate of the reaction depends on the rate of CO desorption.[6,7] If oxygen is present on the surface, then the reaction may occur faster and a hyperactive state of the surface can be formed.[8-12] On small clusters CO oxidation is also promoted by the presence of extra oxygen atoms on the clusters.[30-32]

If CO and oxygen are coadsorbed on the surface, the CO oxidation rate can be determined by CO + O recombination on the surface. It was found that, the increase in CO and O coverage leads to a decrease in the activation energy of CO oxidation.[33-35] The decrease in the activation energy at higher coverage was explained by the increased repulsive interaction between adsorbates, which destabilizes equilibrium configurations of the coadsorbed CO and oxygen. The transition state, which is weakly bound to the surface, is affected by coverage to a lesser degree than the equilibrium structure.

An accurate description of the experiment requires the studies of CO oxidation at higher coverage and on large clusters.[6,7] In spite of large progress achieved during the last few years, such studies still present a challenge.

In the current work, elementary steps of CO oxidation, namely the $CO + O \rightarrow CO_2$ recombination reactions on various low and high coordinated sites were investigated at various coverage. The activation energies of the recombination reaction were calculated on the 55-atom cuboctahedral cluster and on two-layer platinum clusters which correspond to two-layer atomic slabs of the (111) and (100) facets of the 55-atom and 147-atom cuboctahedral clusters (Fig. 1).

While cuboctahedral clusters represent one of the stable forms of free platinum nanoclusters, the two-layer clusters may be formed on solid substrates. The properties of supported clusters are affected by the substrate, which can change the atomic and electronic structure of the clusters.[14,32]

The CO oxidation reaction was studied at several coverages: at low coverage, where only one CO-molecule and the O-atom are present on the cluster; at high coverage, where the corner sites of the cluster can be covered by the CO molecules while the O-atom can be adsorbed either on the edge or on the facet of the cluster; and at stoichiometric coverage where there is an equal amount of the CO-molecules and O-atoms on the cluster. In the case of high and stoichiometric coverage, the $CO + O \rightarrow CO_2$ recombination reaction occurs in the presence of the coadsorbed CO-molecules and O-atoms which play a role of spectators, and may influence the structure of cluster and reaction barriers. This effect is different for different adsorption sites and is discussed in detail below.

Computational details

Adsorption, transition state and gas phase energies were calculated using the plane wave DFT code DACAPO,[36] which was used in CO oxidation studies reported previously.[4,5] The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies up to 25 Ry, while Vanderbilt non-local ultrasoft pseudopotentials are used to describe the core electrons. The exchange-correlation (xc)-energy is described using the RPBE generalized gradient correction self-consistently.[37] The G-point calculations were performed with a unit cell containing at least 10 A of vacuum space between repeated structures. The structural relaxation was performed until a maximum force below 0.05 eV A^{-1} per each atom was obtained. Adsorption and transition state energies were calculated as a difference between the energy of the whole system and the sum of energies of the gas-phase CO_2 molecule and the Pt cluster with one CO-molecule and one O-atom removed. The energies were then recalculated with respect to the energies of the gas phase CO and $1/2O_2$ species as described elsewhere.[4]

Equilibrium and transition state configurations with the CO-molecules and O-atom adsorbed on the 55-atom cluster were calculated with all atoms unfrozen in all directions, while in the case of two-layer clusters equilibrium configuration, Pt-atoms of the bottom layer were aligned in one plane and then positions of all atoms were optimized with the bottom layer frozen in the direction perpendicular to its plane. The (100) two-layer cluster which corresponds to the 55-atom Pt cluster was cut from the (100) two-layer cluster representing

the 147-atom cuboctahedral cluster, and the positions of adsorbates and Pt-atoms from the top layer of the cluster were optimized. Transition state configurations were found by varying the distance between the adsorbed O-atom and the carbon atom of the CO-molecule, while the rest of the system was optimized with the bottom layer frozen in the equilibrium configuration. Activation energies were calculated as differences between the transition state energy and the energy of the most stable configuration of the system.

CO oxidation on the 55-atom cluster and on the two-layer plane clusters that correspond to the (111) and (100) facets of the 55-atom cluster

At low coverage (LC) the most stable equilibrium configuration on the 55-atom cluster was found in the case where the CO-molecule is adsorbed on a corner site and the O-atom on another edge of the cluster. This agrees with experimental results which suggested that CO-molecules are adsorbed in atop configurations on Pt nanoclusters.[38] Equilibrium and transition state energies of several configurations of the single CO-molecule and O-atom adsorbed on the edge are shown in Fig. 2.

Two transition state configurations were investigated: one with the CO-molecule adsorbed atop on the corner Pt-atom and O-atom on the edge (1.9 A O-CO distance), and another where both the O-atom and CO-molecule are adsorbed on the edge of the cluster (2.1 A). Barriers for the reaction were found to be 1.32 eV and 1.49 eV respectively. This difference in energy may be due to the difference in atomic structures of the transition states. The energy of the system is the same if the CO and O-atom particles are adsorbed on various edges, regardless of whether these edges belong to the same facet or not. Energy goes up slightly if the adsorbates bound to the same edge.

The O-atom can also be adsorbed on one of the facets of the cluster. On the (111) facet it can be adsorbed at a 3-fold position and on the (100) facet at a bridge position, as shown in Fig. 3.

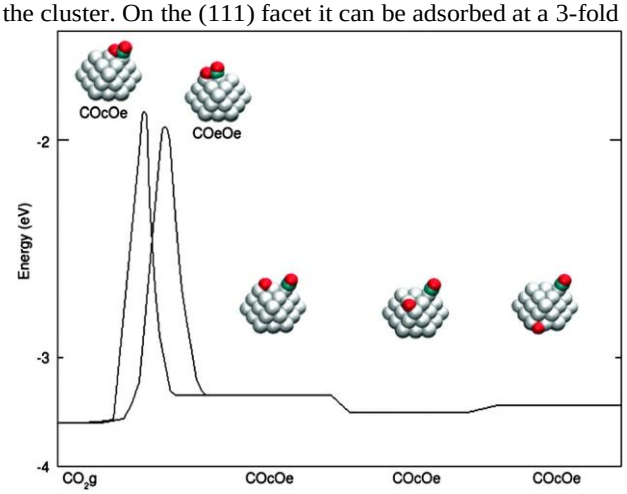

Fig. 2 Potential energy diagram of CO + O → CO_2 reaction on the 55-atom Pt cluster at low coverage (LC). Index g refers to the CO_2 molecule in the gas phase; e refers to adsorption on the edge; and c to adsorption on the corner site. The energy is given with respect to CO + $^2O_2$ in the gas phase.

In both cases adsorption is weaker than when the O-atom is adsorbed on the edge. From the 3-fold position on the (111) facet, the O-atom can react with the CO-molecule by migrating to the edge, where adsorption is approximately 0.5 eV stronger, and recombining there (most left peak in Fig. 3a and b). On the (100) facet, the O-atom can react with the CO-molecule adsorbed on the middle Pt-atom of the facet (most right peak in Fig. 3b).

Similar configurations were studied on the two-layer clusters, which correspond to the (111) and (100) facets of the 55-atom cluster. Transition state energies were found to be close to those on the 55-atom cluster, while energies of the equilibrium configurations may differ. The most stable equilibrium configuration on the (111) two-layer cluster is lower in energy than a similar configuration on the 55-atom cluster by approximately 0.3 eV. This difference may be due to the difference in the atomic structures and the absence of the charge transfer from the bulk in the case of the two-layer cluster.

The equilibrium and transition state configurations at higher coverage (HC) are shown in Fig. 3b for CO + O recombination that occurs on the 55-atom cluster containing two facets covered by the CO-molecules at corner sites. This model represents a case when the whole Pt cluster is completely covered by CO and oxygen with the excess of the CO reagent. The most stable configuration in this case occurs when all CO-molecules are adsorbed on the corner sites, while the O-atom is adsorbed on a (100) facet. From each of these equilibrium configurations the O-atom can react with the CO-molecule adsorbed on the adjacent corner site. This example shows that an increase in coverage may change an equilibrium configuration of the adsorbates on the cluster and force oxygen atoms to adsorb on the facets rather than on the edges of the cluster. In the case of the 55-atom cluster, coverage does not affect activation energies strongly: they are 1.48 eV on the (111) and 1.40 eV on the (100) facets.

Similarly to the low coverage case, transition states on the two-layer slabs are very close in energy to those on the 55-atom cluster. This agreement between the transition state energies suggests that the results obtained on the two-layer slabs can be used to compare CO oxidation conditions on various sites of larger clusters and to determine those with the lowest transition state energies.

In spite of the repulsion interaction between adsorbates, the structure of the platinum 55-atom cluster does not change strongly after the cluster is covered by CO and oxygen. A distance between two adjacent Pt corner atoms on the unoccupied cluster is 5.4 A. This distance would correspond to a 3.82 A bulk lattice constant of the Pt crystal, which is smaller than the previously calculated value of 4.0 A.[39] The presence of the adsorbates slightly disturbs the atomic structure of the cluster. If two CO molecules are adsorbed on adjacent Pt corner atoms, then the distance between the Pt-atoms increases to 5.6 A. At high coverage, where in addition, an oxygen atom is coadsorbed on the same edge, the distance increases to 5.7 A. The stretching effect was also found on the two-layer clusters, where Pt-Pt distance changes from 5.3 A on the unoccupied (111) cluster to 5.6 A at high coverage.

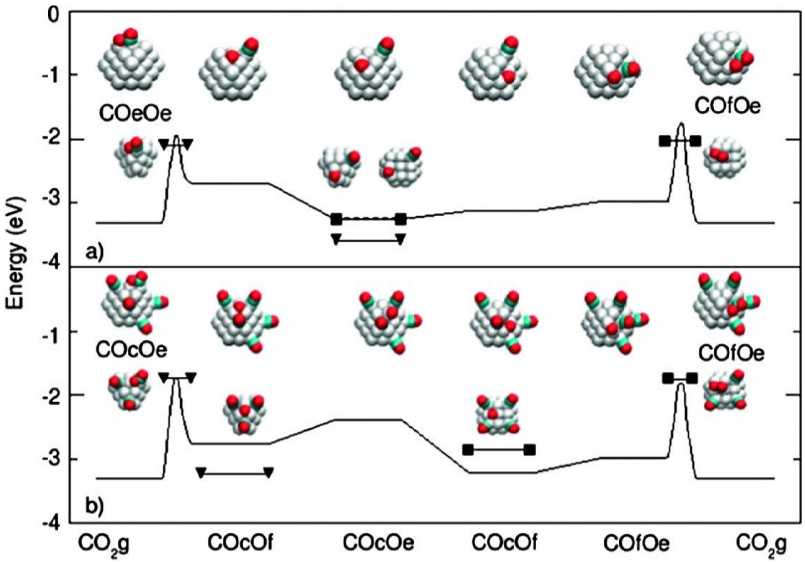

Fig. 3 Potential energy diagram of the CO + O reaction on the 55-atom Pt cluster: (a) low coverage (LC) and (b) high coverage (HC). The most stable adsorption and transition state configurations are also shown for the two-layer clusters, labelled with triangular (111) and square (100) symbols.

CO oxidation on the two-layer plane clusters that correspond to the (111) and (100) facets of the 147-atom cluster

To study CO oxidation on larger Pt nanoclusters, the energies of equilibrium configurations and transition states were calculated on the two-layer clusters, which correspond to the (111) and (100) facets of the 147-atom cuboctahedral cluster. One can see that there is a difference between atomic structures of the facets of the 55-atom and 147-atom clusters. Both (111) and (100) facets of the 147-atom cluster contain more Pt atoms than the facets of the 55-atom cluster. As a result, the facets of the 147-atom cluster provide more pathways for CO oxidation.

Various equilibrium and transition state configurations are shown in Fig. 4 for three types of coverage: (a) low coverage, (b) higher coverage with excess of CO, and (c) high coverage with a stoichiometric ratio between CO and oxygen. In each case, several configurations of the CO and oxygen particles have been tested to find the most stable equilibrium and transition state configuration on the given adsorption site. The transition state energies and energy of the most stable equilibrium configuration are given in Table 1.

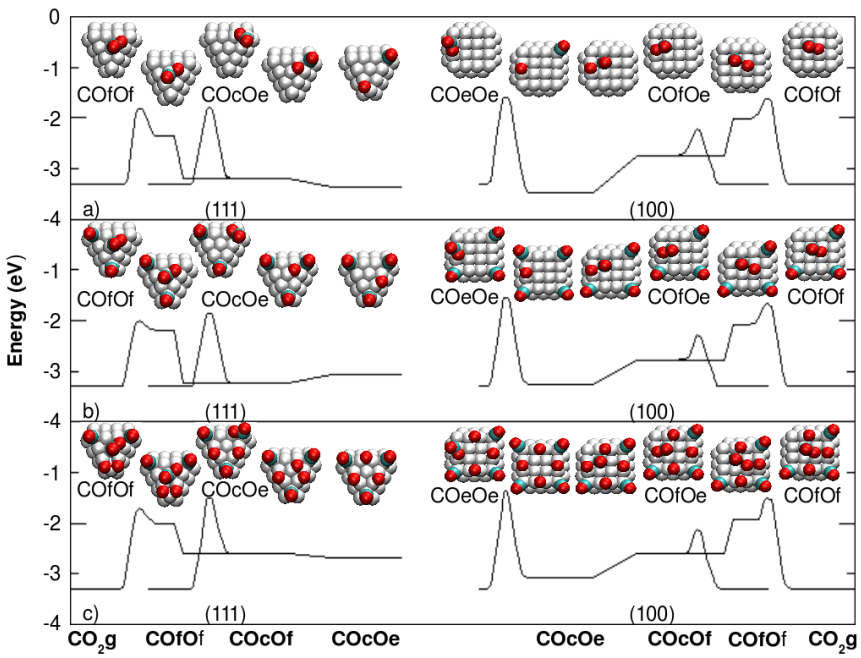

Fig. 4 Potential energy diagram of the CO + O reaction on the two-layer clusters. (a) showing reaction between a single CO-molecule and an O-atom (LC), (b) showing the CO + O reaction in the presence of CO molecules adsorbed on the corner Pt-atoms (HC), and (c) representing the reaction at stoichiometric ratio 1 : 1 (SC).

Table 1 Activation energies (eV) and adsorption energy of the most stable equilibrium configuration on the given cluster (global minimum, GM). Activation energies are given with respect to the GM configuration. The adsorption GM energy is given with respect to CO and $1/2O_2$ in the gas phase. The clusters are labelled as shown in Fig. 1. The LC stands for low coverage; HC for high coverage; SC for stoichiometric coverage; and VHC stands for very high coverage. Subscript f refers to adsorption on a facet, subscript e to adsorption on the edge, and c to adsorption on the corner

	Activation energy				E_{ads}
Facet	(111) CO_fO_f	(111)/(100) CO_eO_e	(100) CO_fO_e	(100) CO_fO_f	(111)/(100) GM
Cluster					
55 LC	—	1.32 (CO_cO_e)	1.52	—	3.26
3 3 LC	—	1.48	1.21	—	3.58/ 3.23
55 HC	—	1.48	1.40	—	3.21
3 3 HC	—	1.15	1.10	—	3.23/ 2.85
4 4 LC	1.52	1.65/1.88	1.25	1.87	3.36/ 3.48
4 4 HC	1.21	1.40/1.72	0.98	1.60	3.32/ 3.27
4 4 SC	0.97	1.19/1.70	0.94	1.56	2.68/ 3.07
4 4 VHC	0.34	—	—	0.22	1.87/ 1.79

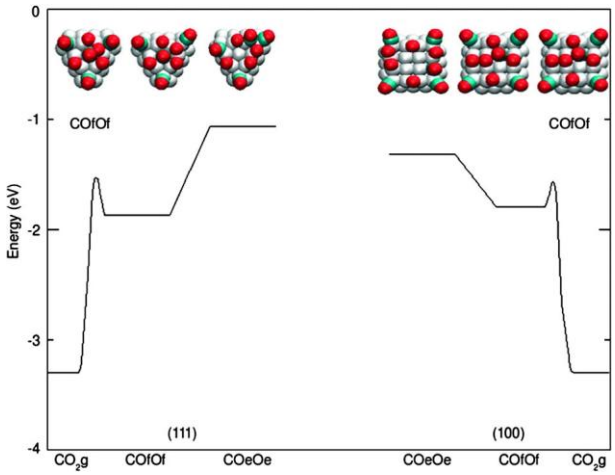

Fig. 5 Potential energy diagram of the CO + O reaction at very high coverage (VHC), when all corner sites are covered by the CO-molecules, and each edge contains at least one O-atom.

Among all studied adsorption sites, the lowest barrier for the reaction was found on the 'near edge' sites on the (100) facet, where the O-atom is adsorbed near the edge at a two-fold bridge position, and the CO-molecule is adsorbed atop on a Pt atom on the facet. This site is labelled CO_fO_e in Fig. 4. The barrier of the reaction on these sites varies from 1.25 eV to 0.94 eV, depending upon the coverage.

Another transition state was found with the CO-molecule on the same adsorption site and the O-atom adsorbed in the middle of the (100) facet. This configuration is labelled CO_fO_f in Fig. 4. Both equilibrium and transition state energies found in the CO_fO_f configuration are higher in energy than those of the CO_fO_e, while atomic structures of these two configurations are close to each other. Therefore, the difference in energies must be due to the influence of the low-coordinated sites on the edge on the electronic properties of the cluster. Observed correlation between equilibrium and transition state energy agrees with Brønsted-Evans-Polanyi rules, similarly to previous studies of CO oxidation on platinum.[4,5] Transition state energy on the edge of the (100) facet is much higher, however (1.88 eV at low coverage and 1.70 eV at higher coverage). This difference in energy can be due to the difference in atomic structures of the transition states on the (100) facet and on the edge.

On the (111) facet the most stable equilibrium configurations were found in the case when the CO molecules are adsorbed on corner sites and the O-atoms on the edge (Fig. 4a and c), and, in the case of high CO coverage, the O-atom preferentially adsorbs on the (111) facet rather than on the edge. A new pathway, which does not exist on the 55-atom cluster, was found on the (111) facet of the 147-atom cluster. In this case, recombination of the O-atom and the CO-molecule occurs on the middle Pt-atom, which resembles a Pt-atom on the (111) terrace of the single crystal surface. The CO-molecule is adsorbed in atop configuration, similarly to adsorption on the Pt(111) surface, where this configuration has been found experimentally and confirmed theoretically after long discussion.[40] One cannot, however, directly compare activation energy obtained in this work (1.52 eV) on the (111) facet of the cluster with that reported in the literature for CO oxidation on the Pt(111) single crystal surface,[14,19] or on the facet of a large cluster[7] because starting configurations of the reaction are different. In this work reaction starts from the CO and O-atom adsorbed on the corner site and edge of the cluster, where adsorption is stronger than on the (111) facet. In calculations on the (111) single crystal surface, starting configuration corresponds to the CO and O-atom adsorbed on the terrace far from each other. As a result, activation energy reported for the Pt(111) surface at low coverage (0.85 eV,[4] or 0.74 eV[19]) is much lower than calculated on the cluster in the current work. For rough estimation, the barrier on the Pt(111) surface can be compared with 0.54 eV reaction barrier for the CO-molecule and O-atom coadsorbed on the (111) facet of the cluster (Fig. 4a, configuration CO_fO_f).

More realistic modeling of the reaction however, requires taking into account the coverage effect, since experiments on clusters were performed at moderate or high coverage. Similarly to the CO oxidation on the single crystal surface, activation energy on the facets decreases with coverage. The activation energy decrease from 1.52 to 0.97 eV on the middle (111) sites mainly results from destabilization of the initial equilibrium configuration due to repulsion between adsorbates, as one can see in Fig. 4.

Finally, the Fig. 5 represents a high coverage regime, where all corner sites are covered by the CO-molecules, and each edge is occupied by at least one O-atom. An extra pair of the CO-molecule and O-atom can be adsorbed on the facet, where adsorption becomes stronger than on the edges at this coverage. From this equilibrium position the CO-molecule and the O-atom can recombine with very low reaction barriers: 0.34 eV on the (111) facet and 0.22 eV on the (100). Since desorption energy (1.87 eV) is still much higher than the recombination barrier, CO oxidation may occur.

Discussion

Calculated in the present work energies of the equilibrium and transition states, allow one to discuss various pathways of the

CO oxidation reaction on Pt nanoclusters of various shapes and at various coverage. Discussion can be done using the following model. Prior to the reaction, all CO-molecules and O-atoms are adsorbed in their most stable configuration. This configuration depends upon the cluster shape, size and coverage of the CO and oxygen. The CO-molecules always adsorb on the corner sites, while the O-atoms can be adsorbed on the edges at low coverage, and on the facet at high coverage. From this original configuration, one of the CO-molecules and an O-atom migrate to the site with the lowest transition state energy, recombine there and form a CO_2 molecule. The newly formed CO_2 molecule is weakly bound to the surface and desorbs immediately after the formation. To apply this model to analysis of CO oxidation on a particular cluster, one needs to know the transition energies on various adsorption sites at various coverage. These barriers of the reaction are discussed below.

In a discussion of chemical reactions on clusters, the surface of the cluster can be considered as a combination of small pieces of (111) and (100) terraces of a single crystal surface. Edges of the cluster can be seen as steps on the surface, and corner sites as kinks.[4,5] The relative probabilities of CO oxidation on various sites can be expected to be the same on clusters and single crystal surfaces. Oxygen and CO adsorption on platinum has been studied elsewhere.[41-46]

It was experimentally observed that on the Pt(111) surface CO-molecules and O-atoms react preferentially on low-coordinated sites at the steps, where adsorption is stronger.[22-24] Given this fact, small clusters can be expected to provide better conditions for CO oxidation, since they have higher ratio between low coordinated sites at the corners (CN_{corner} = 5), edges (CN_{edge} = 6) and high coordinated sites on facets ($CN_{(100)}$ = 8, $CN_{(111)}$ = 9). If this was the case, the catalytic properties of the Pt nanoclusters would be similar to that of gold nanoclusters, where CO oxidation was proposed to occur on the corner sites.[25] Small Au clusters are experimentally known to be always more efficient in CO oxidation than larger ones. However, it was observed experimentally that platinum nanoclusters smaller than 1 nm can be less efficient in CO oxidation than larger clusters.[26-29] This suggests that CO oxidation on facets of the clusters play an important role in CO oxidation on small clusters.

To understand better CO oxidation on small platinum nanoclusters, around 1 nm in size, the analogy between facets of the clusters and the terraces of the single crystal surfaces should be examined in more detail. This similarity can be straightforward for rather large clusters with thousands of atoms, but may break for smaller clusters. The clusters of several atoms or few tens of atoms may exhibit a variety of forms[16] and can be strongly affected by the oxide substrate.[14]

One can see, that the similarity between atomic structures of the terraces and facets breaks also in the case of the 55-atom cluster. Neither the (111) nor the (100) facet of the 55-atom cluster represents exactly a flat part of the single crystal terrace. There is no Pt atom on the (111) facet, which would correspond to the Pt atom from the (111) terrace, and which would provide an adsorption site for the CO-molecule similarly to adsorption on a flat (111) terrace. On the (100) facet there is no adsorption site for an O-atom, which would correspond to the flat (100) surface far from the step. Due to these differences in atomic structures, the 55-atom cluster and clusters of smaller size may behave differently in CO oxidation compared with the larger clusters.

The facets of the 147-atom cluster resemble the (111) and (100) single crystal surfaces better than the facets of the 55-atom cluster. On the (111) facet of the 147-atom cluster the O-atom adsorbed at a 3-fold position can react with the CO-molecule adsorbed on top of the middle Pt-atom, which resembles a Pt-atom on the (111) single crystal surface. The initial and transition state structures calculated in the present work, are close to those reported previously for the Pt single crystal surface.[17,19] On the (100) facet of the 147-atom cluster, there is another adsorption site for O-atom in the middle of the facet, which resembles an adsorption site on the (100) terrace far from the step. Barriers for CO oxidation on all adsorption sites decrease with coverage as shown in Fig. 3 and 4. Studied coverages are far from saturation. In the case of high coverage (HC) where all corner sites are covered with CO molecules the coverage is 0.5 ML on the 3 × 3 cluster (111) two-layer cluster and 0.4 ML on the 4 × 4 cluster (111), if a monolayer (ML) is defined as the coverage where each Pt atom on the surface is covered by a CO molecule. In the case of the 55-atom cluster the CO coverage is 0.4 ML.

The activation energy can become especially low in the case of a very high coverage (VHC) regime with CO molecules adsorbed on each corner site and O-atoms on each edge (Fig. 5). For example, on the (111) facet three CO-molecules occupy the corner sites, where adsorption is stronger and the fourth CO-molecule can adsorb on the middle Pt-atom. The (111) cluster can still accommodate two oxygen molecules, which adsorb by dissociating into four O-atoms. Three of them preferentially adsorb on the edges, while one O-atom can adsorb on the (111) facet near the middle CO-molecule. From this configuration, the O-atom and the CO-molecule adsorbed on the middle sites can react with each other. Activation energy of the reaction, 0.34 eV is much lower than the adsorption energy of the CO-molecule, which is 1.15 eV. This suggests that CO oxidation would occur rapidly on the middle sites of the facet. The same conclusion can be made about CO oxidation on the (100) facet.

One may now qualitatively discuss CO oxidation on larger clusters. This discussion requires taking into account both the difference between various adsorption sites and the coverage effect. Let us consider CO oxidation on the near-edge CO_fO_e sites located on the perimeter of the (100) facet. Activation energy of the reaction on these sites is lower than on other sites at any coverage. The fraction of these sites decreases with an increase in the size of the cluster. This is one reason why CO oxidation on large clusters may be slower than on the clusters of smaller size.

One also should take into account that, as has been discussed above, activation energy on the facets decreases with coverage. This decrease is due to the presence of the adjacent occupied low-coordinated adsorption sites on the corners and edges of the cluster. On the larger clusters the fraction of the occupied near-edge sites on the (100) facet is less, since the facets provide more sites located far from the edges and corners. The adsorbed CO and oxygen can migrate to these

CO oxidation reaction on Pt nanoclusters of various shapes and at various coverage. Discussion can be done using the following model. Prior to the reaction, all CO-molecules and O-atoms are adsorbed in their most stable configuration. This configuration depends upon the cluster shape, size and coverage of the CO and oxygen. The CO-molecules always adsorb on the corner sites, while the O-atoms can be adsorbed on the edges at low coverage, and on the facet at high coverage. From this original configuration, one of the CO-molecules and an O-atom migrate to the site with the lowest transition state energy, recombine there and form a CO_2 molecule. The newly formed CO_2 molecule is weakly bound to the surface and desorbs immediately after the formation. To apply this model to analysis of CO oxidation on a particular cluster, one needs to know the transition energies on various adsorption sites at various coverage. These barriers of the reaction are discussed below.

In a discussion of chemical reactions on clusters, the surface of the cluster can be considered as a combination of small pieces of (111) and (100) terraces of a single crystal surface. Edges of the cluster can be seen as steps on the surface, and corner sites as kinks.[4,5] The relative probabilities of CO oxidation on various sites can be expected to be the same on clusters and single crystal surfaces. Oxygen and CO adsorption on platinum has been studied elsewhere.[41-46]

It was experimentally observed that on the Pt(111) surface CO-molecules and O-atoms react preferentially on low-coordinated sites at the steps, where adsorption is stronger.[22-24] Given this fact, small clusters can be expected to provide better conditions for CO oxidation, since they have higher ratio between low coordinated sites at the corners (CN_{corner} = 5), edges (CN_{edge} = 6) and high coordinated sites on facets ($CN_{(100)}$ = 8, $CN_{(111)}$ = 9). If this was the case, the catalytic properties of the Pt nanoclusters would be similar to that of gold nanoclusters, where CO oxidation was proposed to occur on the corner sites.[25] Small Au clusters are experimentally known to be always more efficient in CO oxidation than larger ones. However, it was observed experimentally that platinum nanoclusters smaller than 1 nm can be less efficient in CO oxidation than larger clusters.[26-29] This suggests that CO oxidation on facets of the clusters play an important role in CO oxidation on small clusters.

To understand better CO oxidation on small platinum nanoclusters, around 1 nm in size, the analogy between facets of the clusters and the terraces of the single crystal surfaces should be examined in more detail. This similarity can be straightforward for rather large clusters with thousands of atoms, but may break for smaller clusters. The clusters of several atoms or few tens of atoms may exhibit a variety of forms[16] and can be strongly affected by the oxide substrate.[14]

One can see, that the similarity between atomic structures of the terraces and facets breaks also in the case of the 55-atom cluster. Neither the (111) nor the (100) facet of the 55-atom cluster represents exactly a flat part of the single crystal terrace. There is no Pt atom on the (111) facet, which would correspond to the Pt atom from the (111) terrace, and which would provide an adsorption site for the CO-molecule similarly to adsorption on a flat (111) terrace. On the (100) facet there is no adsorption site for an O-atom, which would correspond to the flat (100) surface far from the step. Due to these differences in atomic structures, the 55-atom cluster and clusters of smaller size may behave differently in CO oxidation compared with the larger clusters.

The facets of the 147-atom cluster resemble the (111) and (100) single crystal surfaces better than the facets of the 55-atom cluster. On the (111) facet of the 147-atom cluster the O-atom adsorbed at a 3-fold position can react with the CO-molecule adsorbed on top of the middle Pt-atom, which resembles a Pt-atom on the (111) single crystal surface. The initial and transition state structures calculated in the present work, are close to those reported previously for the Pt single crystal surface.[17,19] On the (100) facet of the 147-atom cluster, there is another adsorption site for O-atom in the middle of the facet, which resembles an adsorption site on the (100) terrace far from the step. Barriers for CO oxidation on all adsorption sites decrease with coverage as shown in Fig. 3 and 4. Studied coverages are far from saturation. In the case of high coverage (HC) where all corner sites are covered with CO molecules the coverage is 0.5 ML on the 3 × 3 cluster (111) two-layer cluster and 0.4 ML on the 4 × 4 cluster (111), if a monolayer (ML) is defined as the coverage where each Pt atom on the surface is covered by a CO molecule. In the case of the 55-atom cluster the CO coverage is 0.4 ML.

The activation energy can become especially low in the case of a very high coverage (VHC) regime with CO molecules adsorbed on each corner site and O-atoms on each edge (Fig. 5). For example, on the (111) facet three CO-molecules occupy the corner sites, where adsorption is stronger and the fourth CO-molecule can adsorb on the middle Pt-atom. The (111) cluster can still accommodate two oxygen molecules, which adsorb by dissociating into four O-atoms. Three of them preferentially adsorb on the edges, while one O-atom can adsorb on the (111) facet near the middle CO-molecule. From this configuration, the O-atom and the CO-molecule adsorbed on the middle sites can react with each other. Activation energy of the reaction, 0.34 eV is much lower than the adsorption energy of the CO-molecule, which is 1.15 eV. This suggests that CO oxidation would occur rapidly on the middle sites of the facet. The same conclusion can be made about CO oxidation on the (100) facet.

One may now qualitatively discuss CO oxidation on larger clusters. This discussion requires taking into account both the difference between various adsorption sites and the coverage effect. Let us consider CO oxidation on the near-edge CO_fO_e sites located on the perimeter of the (100) facet. Activation energy of the reaction on these sites is lower than on other sites at any coverage. The fraction of these sites decreases with an increase in the size of the cluster. This is one reason why CO oxidation on large clusters may be slower than on the clusters of smaller size.

One also should take into account that, as has been discussed above, activation energy on the facets decreases with coverage. This decrease is due to the presence of the adjacent occupied low-coordinated adsorption sites on the corners and edges of the cluster. On the larger clusters the fraction of the occupied near-edge sites on the (100) facet is less, since the facets provide more sites located far from the edges and corners. The adsorbed CO and oxygen can migrate to these

remote facet's sites, where a reaction barrier is higher than near the edge. Therefore, the net CO oxidation rate on larger clusters can be slower than on the facets of the 147-atom cluster.

Now, let us consider clusters of smaller size, where CO oxidation also can be slower than on the 147-atom cluster. This happens, because the 55-atom cluster does not provide high coordinated CO adsorption sites on the (111) facets with low activation energy. Due to this fact CO can only react with oxygen on (100) facets or on the edges, where barriers for reaction are high.

Thus, comparison of CO oxidation on large and small clusters suggests that an optimum size of the cluster should exist at which CO oxidation occurs fastest. This result agrees with experimental observations.[26-29] In the experimental work of Haruta and co-workers an optimum size was found to be 1.3 nm,[26] which falls between the size of the 55-atom cluster (1.1 nm) and 147-atom cluster (1.6 nm) studied in the current work.

The net rate of CO oxidation depends also upon the total coverage and the ratio between adsorbed CO and oxygen. These parameters depend, in turn, upon the conditions of the experiment, such as temperature and partial pressure of CO and oxygen. It may be necessary to conduct the CO oxidation reaction in a high oxygen/CO ratio to avoid covering the surface with CO molecules.[6-10] Determining the best conditions for the reaction requires detailed analysis of the reaction kinetics and goes beyond the scope of the current work.

Conclusions

CO oxidation was studied on various platinum clusters containing from 18 to 55 atoms, with atomic structures resembling flat terraces and atomic steps on the (111) and (100) single crystal surfaces. It was found that the similarity between the surface of clusters and single crystals may break in the case of small particles, containing 55 atoms or fewer. The size of such nanoclusters is equal to or less than 1.1 nm.

In the case of the larger 147-atom clusters (1.6 nm in size) the high-coordinated CO adsorption sites on the (111) and (100) facets of the clusters can play an important role in the oxidation reaction. The low activation energy on these sites is due to the presence of adjacent low-coordinated oxygen adsorption sites on the edges of the cluster.

On clusters much larger than 1 nm in size, the effect of the low-coordinated sites on the edges becomes less pronounced, and therefore such clusters are less efficient in CO oxidation. This suggests, that the clusters of approximately 1 or 2 nm in size would be the most efficient in CO oxidation, in accordance with previous experimental studies.[26-29]

On the 147-atom cluster, it was found that the (100) facet provides lower reaction barriers than the (111) facet. This suggests that the clusters containing a larger (100) surface area, such as cuboctahedral clusters, could be more efficient in CO oxidation than the clusters which do not have the (100) facets, such as icosahedral clusters.

It was also found that activation energy of CO oxidation on clusters decreases with CO and oxygen coverage. The size effect also depends upon coverage and may vary with experimental conditions. These results qualitatively agree with previous experimental and theoretical studies.

The main finding of this work is that the high-coordinated sites on the facets provide low activation energy for CO oxidation if these sites are surrounded by the low-coordinated edges and corner sites. The clusters containing large fraction of such 'surrounded' high-coordinated sites can be more efficient in CO oxidation, compared with smaller or larger clusters.

Though this paper was devoted to heterogeneous catalytic CO oxidation on Pt nanoclusters in the gas phase, the findings may also be useful in analysis of other cases, where reactions on facets of nanoclusters may occur. Examples of such reactions are CO oxidation in electrochemistry, or other oxidation reactions on transition metal nanoclusters.

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