Catalytic behavior at the nanoscale: CO adsorption on Al_2O_3-supported Pt clusters

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ABSTRACT

The study of the adsorption and growth of metals on ceramics is a rapidly growing area, as these interactions are key to understanding many materials and processes used in modern technology. In particular, oxide-supported catalysts have been extensively studied, due to their widespread industrial applications. Knowledge of the role played by the underlying metal oxide in the reactivity of the metal catalyst can give insights into the design of more effective catalysts. Here, we use density functional theory (DFT) to investigate the adsorption of CO onto 1) bulk Pt, 2) Pt thin layers supported on an α-alumina surface and 3) Pt nanoparticles on α-alumina. Our results show strong binding for CO molecules on the surfaces of both the thin Pt layers and the 3-atom nanoparticles supported on alumina substrates. This enhanced binding can possibly lead to more reactive catalysts. Further calculations on reaction products are needed to determine the effectiveness of these new systems.

Keywords: nanoparticles, clusters,catalyst,oxide,metal,chemisorption,DFT, Platinum, CO, alumina, surfaces

1. INTRODUCTION

The study of nanocatalysts involves a diverse spectrum of surface science. In the examination of the properties of Pt nanoclusters on alumina supports, there is a need to draw upon knowledge of oxide surfaces, metal-oxide interactions, molecule-surface interactions, catalytic activity, and, of course, nanoparticles themselves. Quite aside from the potential industrial applications of these studies, the incorporation of such a broad range of topics makes the investigation of size-selected nanocatalysts a fascinating scientific inquiry.

Current catalyst technology involves the use of an active metal catalyst (such as Pt, Pd, and Rh). For example, Pt metal particles help to oxidize molecules such as hydrocarbons or carbon monoxide (CO), and Rh metal particles are often involved in reducing molecules such as NO_x . Studies on the interaction of molecules with the active metals have given insights into the reaction pathways for many of these systems.[1–3] Such studies are a starting point for tackling difficult problems such as catalyst poisoning, and can lead to the improvement of the catalytic activity of many systems.

The ability of nanostructures to enhance the properties of their bulk counterparts has led to an increasing interest in these systems for use as catalysts. For instance, gold nanoparticles have been shown to be superior to bulk for binding and dissociation of O_2 molecules,[4, 5] while Pt nanoclusters on alumina are more reactive substrates for the hydrogenation of propene than the standard alumina-supported Pt catalysts.[6] However, the growth of these nanostructures is not always trivial, and therefore much has been done toward creating more efficient and effective growth processes. Experimental and theoretical studies have revealed that the presence of surface vacancies and defects (such as water products) promote the growth and nucleation of metal nanoclusters on oxide surfaces[7, 8] and can be used to tailor the growth of such clusters, thus offering numerous possibilities to alter the reactivity of these systems.

Our investigation starts with the adsorption of CO on the Pt (111) surface, a well-studied model system. We then look at the effect of an α-alumina support on the adsorption of CO on Pt thin films, as the thickness of the Pt film is varied. Finally, we investigate the adsorption behavior of CO on Pt (111) clusters of various sizes on the alumina surface.

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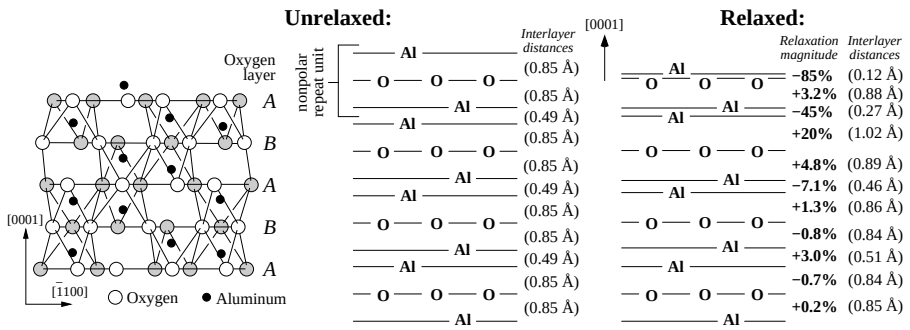

Figure 1. Atomic layers for the stable surface of the α-alumina structure, before and after ionic relaxation, perpendicular to the [0001] axis. The interatomic distances for both structures indicate the large relaxation found in the alumina surface.[11]

2. METHODOLOGY

Our theoretical investigations were performed using the DFT[9] approach, as implemented in the CAPOS simulation package, with ultrasoft pseudopotentials[10] at a 400 eV plane-wave cutoff. The exchange-correlation energy was computed using the generalized gradient approximation (GGA). The atomic structure was optimized such that the forces on the unconstrained atoms were less than 0.01 eV/Å. Al_2O_3 supercells with five Al-O_3-Al trilayers were modeled, in which the bottom two trilayers were fixed at the corresponding Al_2O_3 surface positions, the middle trilayer was allowed to relax only in the direction perpendicular to the [0001] surface and the top two trilayers were allowed to relax in all three directions. Surface calculations were performed with at least 10 Å of vacuum between adjacent slabs. Potential energy surfaces (PESs) were constructed based on single Pt adatom adsorption data, incorporating the method of bicubic interpolation to approximate the surface between computed sites.

3. THE ACTIVE SUBSTRATE: ALUMINA

Alumina, Al_2O_3, occurs commonly in nature in the form of emery, sapphire, ruby, and other materials, most of which are insulators. There are more than twenty-five different phases of alumina, including the stable α- phase, and the numerous metastable transitional aluminas (κ-, γ-, θ-, etc.), called so because they undergo transition to α-alumina at high temperatures. The different aluminas can be found in numerous applications; for instance, as a result of their mechanical, chemical, and thermal-resistive properties, aluminas are used in cutting tools, dental implants, and spacecraft protection. Their optical properties are utilized in ruby lasers and optical windows, their electrical properties in circuit substrates, spark plugs and magnetrons, and their catalytic-support properties in automotive three-way catalysts.

The different alumina phases can be categorized into two major groups depending on the stacking of their oxygen atoms. In one group, including γ-alumina, the oxygen ions have a face-centered cubic packing. The oxygen atoms are hexagonally close packed in the other group, which includes both α- and κ-alumina. In either case, there are two possible sites in which to find the Al atoms; in the octahedral or tetrahedral sites formed by the oxygen packing. In the majority of the metastable aluminas, the Al atoms are found in both octahedral and tetrahedral sites, with the percentage in each type of site depending on the structure. On the other hand, in the stable α-alumina structure, the Al atoms are found only in octahedral sites, of which they occupy two-thirds.[11]

Figure 1 gives a side view of the stacking sequence, perpendicular to the (0001) surface, for the most stable α-alumina surface. As it shows, there is an AB stacking of the O_3 layers with an ABC stacking of Al bilayers between each oxygen layer. Due to the fact that the Al atoms in neighboring layers share octahedral faces, there are strong electrostatic repulsions between them, causing the Al atoms in a single layer to be slightly displaced from each other, forming two layers. Here we see large inward relaxations for the alumina surface which may persist up to nine layers.

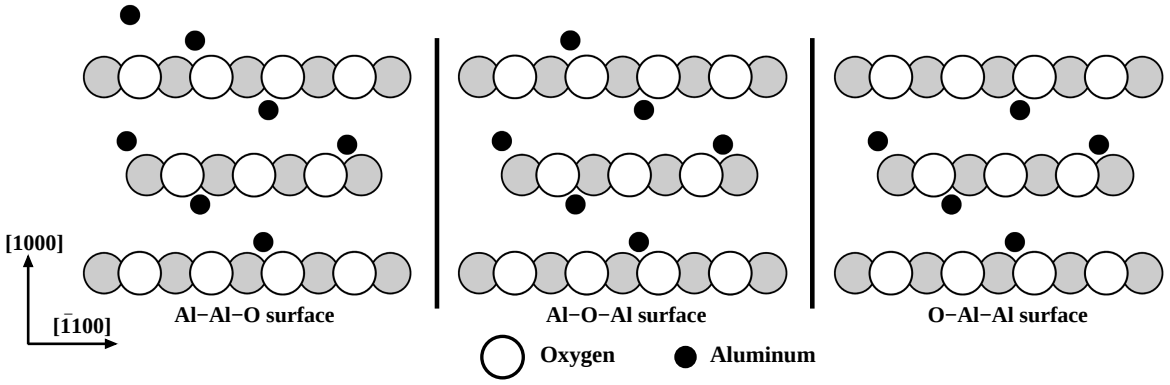

Figure 2. Possible surface terminations for α-Al_2O_3 surfaces. The surface could terminate at an Al bilayer (left) (Al-Al-O_3 surface), in between two Al bilayers (center) (Al_T surface) or at an O layer (right) (O_T surface).

There are several possible surface terminations for the α-alumina (0001) surface (Figure 2). The surface could terminate at an O layer (O_3-Al-Al surface), at an Al bilayer (Al-Al-O_3 surface), or in between two Al bilayers (Al-O_3-Al surface). Both the Al-Al-O_3 and O_3-Al-Al surfaces have strong surface polarizations, whereas the Al-O_3-Al surface, the most stable of the three, is nonpolar. Wang *et al.*[12] have shown that the Al-O_3-Al is the thermodynamically favored surface.

In our investigation, we first looked at the formation energy for the creation of the O_3-Al-Al and Al-Al-O_3 terminated from the stable Al-O_3-Al surface. In these calculations, the formation energy refers to the energy required to remove or to add an aluminum atom from the Al-O_3-Al surfaces, in order to create the desired surface. The surface terminated by two Al layers (i.e. Al-Al-O_3 surface) shows a formation energy of 0.53 eV. It is therefore likely that the extra Al will agglomerate into bulk Al, returning to the stable Al_T surface. While this may present some interesting physics, it is the basis of a separate scientific investigation, and the Al bilayer-surface will not be further considered. Our investigations will be centered around the O_3-Al-Al (oxygen-terminated; O_T) surface and the more stable Al-O_3-Al (aluminum-terminated; Al_T surface) surface. Even though the O_T formation energy is very high (11.45 eV), the O_T surface presents us with a surface which resembles that of many transition aluminas, and therefore can give us a means of comparing the effects of transition aluminas and α-alumina on the reactivity of Pt catalysts. Furthermore, the O_T surface can be thought of as a region of the stable Al_T surface in which surface Al ions have been etched away to create a defect. Therefore, comparing and contrasting O_T and Al_T α-alumina will give insight into the range of possible support effects.

4. CO ON PLATINUM(111) SURFACE

Before we investigate CO on Pt/alumina, we first look at the adsorption of CO on the bulk Pt(111) surface for later comparison. The adsorption of CO on Pt(111) has been extensively studied both theoretically and experimentally. Experimentally, numerous studies using diffraction, vibrational spectroscopy, and scanning probe microscopy have confirmed that CO binds preferentially to the top site on Pt(111) at low coverages, but binds equally at top and bridge sites at high coverage.[13] As Feibelman *et al.*,[14] pointed out, however, density functional calculations consistently find that CO prefers to bind in the more highly-coordinated hollow site on Pt instead. Grinberg, Yourdshahyan, and Rappe (GYR)[15] showed that the discrepancies between the experimental and theoretical results stem from the varying accuracy with which the GGA treats different bond orders. Their analysis showed that the top site chemisorption energy obtained by DFT-GGA is accurate, while that of the hollow site is not, resulting in the incorrect site preference. They suggested that a simple empirical correction to the chemisorption energy based on the reaction energy of small organic molecules would allow the accurate prediction of site preferences in many molecule-surface systems. This correction has recently been confirmed by hybrid density functional analysis, which suggests that the incorrect DFT values for the $2\pi^*$ orbital energy make the double and triple bonds inaccurate, thus leaving the single bonds quite accurate.[16] We consistently apply the GYR correction to all chemisorption energies in this paper.

Our initial results for the site preference of CO adsorption on Pt(111) agree with previous DFT studies; i.e, we found that the hollow site was favored over the top site at all coverages. Applying the correction suggested by GYR yields correct site preferences for Pt at all coverages. For a $c(4 \times 2)$ unit cell at 1/4 coverage, we found the CO chemisorption energy to be 1.698 eV at the top site, in good agreement with the experimental value of 1.68 eV,[13] and at 1/2 coverage, the CO chemisorption energy at the top and bridge site was found to be 1.53 eV, again in good agreement with the experimental value of 1.55 eV.[13]

The deposition of a metal onto an oxide support which is not lattice matched can induce strain in the metal particle. For this reason we investigate the effects of purely mechanical strain on the adsorption of CO on the Pt (111) surface (without the electronic effects of a support layer) by both expanding and contracting the in-plane lattice constants of the system. These effects were monitored by observing the chemisorption energy of the CO molecule on the top site of a Pt(111) surface. Table 1 shows the chemisorption energy for CO adsorbed at 1/4, 1/2, and full coverages on a bulk Pt surface for systems under various strains. Here we see that for all cases tested an increase in the in-plane lattice constant results in stronger binding of CO molecules to the surface. This suggests that, without considering the electronic properties of the underlying oxide, the chemical adsorption properties can be tuned by changing between oxide supports with different lattice constants.

Table 1. Strain effects on the CO top site chemisorption energy (eV/CO) for 1/4 coverage, 1/2 coverage and full coverage on the bulk Pt(111) surface. The results show that an increase in the in-plane lattice constants give rise to an increase in the CO binding energy.

Strain	1/4 Coverage	1/2 Coverage	Full Coverage
2.5% Expansion	1.77	1.49	1.00
Unstrained	1.70	1.42	0.89
5.1% Constraction	1.66	1.35	0.78

5. CO / PLATINUM LAYERS ON ALUMINA SUBSTRATE

To study the effect of the alumina support on the adsorption behavior of CO on Pt(111), we examined the CO top-site adsorption energy for varying thicknesses of the Pt film on both the O_T and Al_T surfaces of α-Al_2O_3. Figure 3 shows the relationship between CO binding energy and the number of layers of Pt on both the O_T- and Al_T-alumina surfaces. For a single layer of Pt, the CO adsorption energy is similar for both alumina terminations, about three times higher than the value for bulk Pt. The CO binding energy returns to bulk values at four Pt layers.

The large CO adsorption energy on a monolayer of Pt on α-Al_2O_3 as compared to the bulk value suggests that there may also be an effect on the site preference for the observed systems. As Figure 4 indicates, we find that the adsorption behavior of CO dramatically changes as a function of the number of Pt layers for both alumina surfaces. When Pt forms a monolayer over the alumina, there is a very large preference of 0.95 eV for the top site over the hollow site for one monolayer of Pt on the oxygen terminated surface, and a smaller but still significant top site preference of 0.25 eV on the aluminum terminated surface. For a bilayer of Pt, there is almost no preference for the top or the hollow site on either alumina surface. As the number of Pt layers is increased, the adsorption behavior quickly approaches that of the bulk Pt, with a relatively small preference of 0.1 eV for the top over the hollow site.

6. BUILDING PLATINUM NANOCLUSTERS

To relate our model more directly to realistic catalytic systems, we study the effects of Pt nanoclusters on the chemisorption of CO. Before we can understand how nanostructures modify the properties of the catalysts, it is first necessary to examine the process by which these particles are formed on the alumina surface. This can be studied by investigating how, first, a single Pt adatom binds to the alumina surface. This will allow us to study

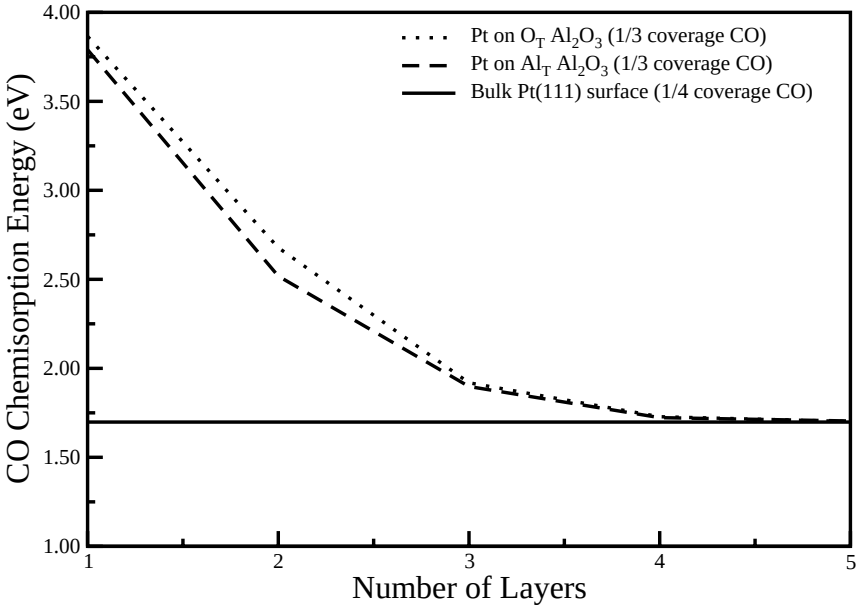

Figure 3. Top site binding energy for CO on a thin layer of Pt on Al_T- and O_T-alumina surfaces. Here we see that in both cases the CO binds strongly at monolayer coverage, returning to bulk values at 4 layers of Pt.

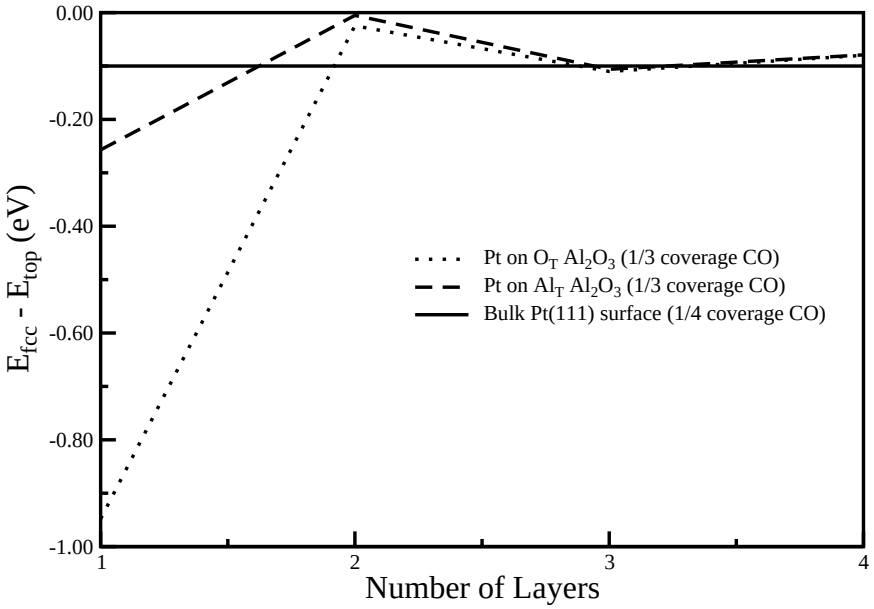

Figure 4. Site preference for CO on the Pt/α-alumina surface. Both surfaces investigated show a strong preference for the adsorption of CO at top site for monolayer, returning to bulk Pt values at 4 layers.(GYR correction applied.

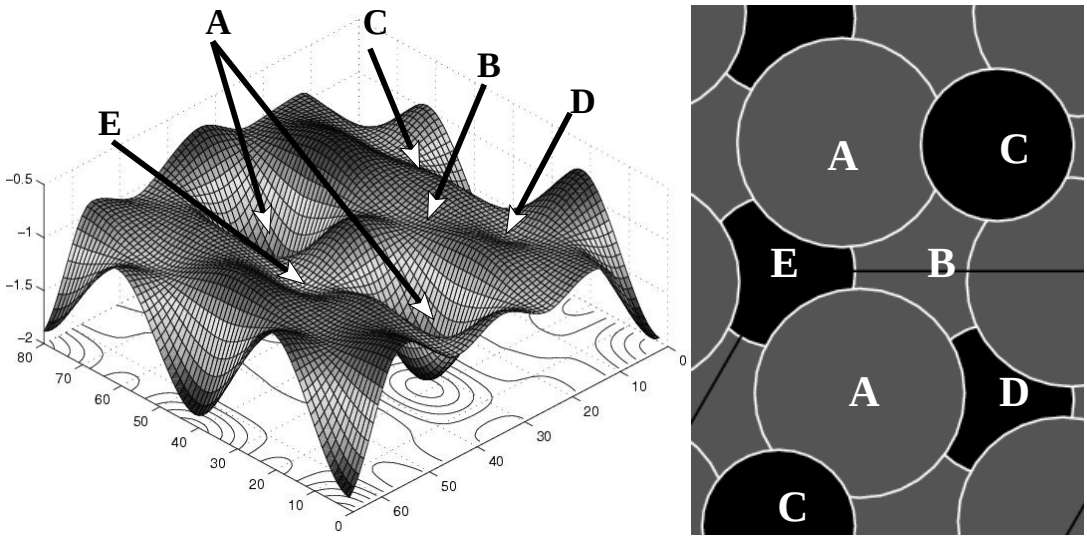

Figure 5. Single Pt adatom adsorption on to an Al-terminated surface. The Pt adatom prefers to adsorb on top of the surface oxygen sites (A), avoiding the surface Al ions. The Pt chemisorption energy is 1.92 eV.

the effects of nanocluster growth on the surface of the oxide support. Figures 5 and 6 show the PES for the adsorption of a single Pt atom onto the two alumina (Al_T and O_T) terminations. These PESs were constructed using 1×1 unit cells. The adsorption of Pt onto the Al_T surface results in an adsorption energy of 1.92 eV. In this case, the Pt adatom avoids the top Al atom and interacts most favorably with the top O atoms. Pt chemisorption results show an overwhelming preference for binding to the O_T-surface. Here, the Pt adatom will adsorb at the vacant Al site with a chemisorption energy of 7.80 eV. This creates a three-fold site interaction of the Pt adatom with the surface oxygen ions. This arrangement allows the Pt adatom to freely exchange electron density with the underlying oxygen layer, without the interference of a surface Al atom, thus producing more favorable bonding between the Pt and the neighboring oxygen ions.

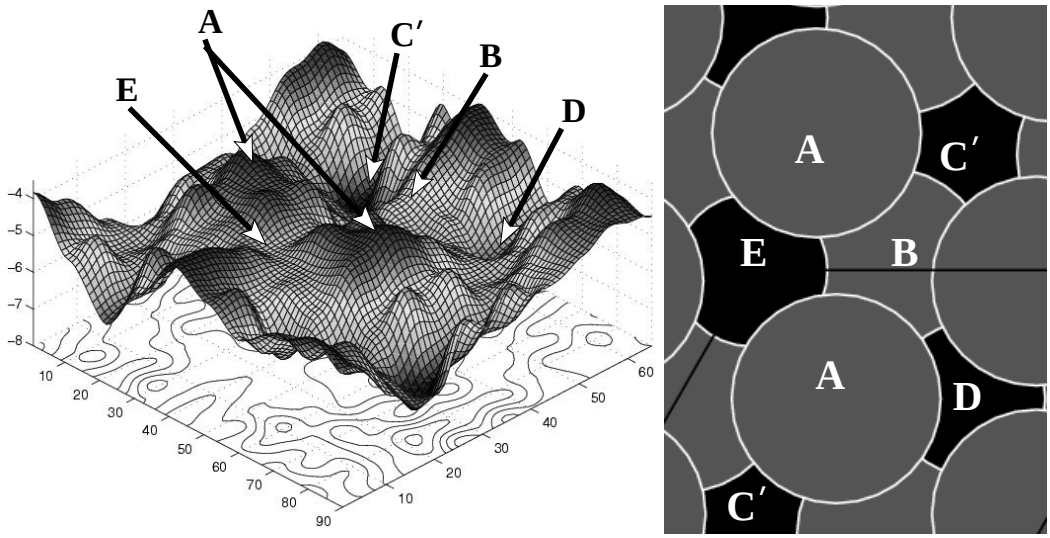

Figure 6. Single Pt adatom adsorption onto an O-terminated alumina surface. The Pt adatom prefers to adsorb into three-fold surface hollow sites (C′). The Pt chemisorption energy is 7.80 eV.

The creation of a surface vacancy leaves the surface atoms with insufficient bonds to neighboring atoms. This can result in various instabilities within the surface layer. To accommodate for this unfavorable condition the atoms sometimes relax toward the underlying layers, therefore creating stronger bonds with these atoms. However, inward relaxations are sometimes insufficient to stabilize the dangling bonds within the system, and therefore this relaxation may be accompanied by an in-plane shifting of the surface atoms, which is referred to as a surface reconstruction.

Due to the periodic nature of DFT calculations, it is not possible to observe such reconstructions with a simple 1×1 surface. For this reason we examine the possibility for such events using a larger 2×1 unit cell. Although there is some slight relaxation of the oxygen ions toward the vacant aluminum site on the O_T surface, there is no significant surface reconstruction in either of the bare O_T or Al_T surfaces. Similar results were noted for the adsorption of a Pt atom on the bare Al_T surface.

The O_T surface differs from the previous cases in the fact that significant surface reconstruction is found in the larger 2×1 supercells. The 1×1 surface studies show that the Pt adatom prefers to adsorb into a three-fold oxygen site (Figure 7a) with a chemisorption energy of 7.80 eV. Further 2×1 surface studies have revealed that there is a surface reconstruction involved with this structural relaxation, which results in the formation of a four-fold adsorption site (Figure 7b). This reorganization of surface atoms allows for the Pt adatom to be embedded in the surface layer. Oxygen ions are now able to make stronger bonds with the Pt ions, lowering the energy of the system, and giving the two Pt adatoms in a 2×1 supercell adsorption energies of 8.20 eV/atom.

Our single Pt atom results show that even without considering the effects of surface reconstruction, the O_T surface is the energetically favored surface for the adsorption of Pt atoms. The strong chemisorption energy on these surfaces suggests that it will be a more suitable surface on which to observe the growth of nanoclusters. Using this surface, we were able to build 2D clusters of 3–6 atoms on a 2×2 α-alumina O_T surface. A typical six-atom cluster on the O_T surface showed a Pt chemisorption energy of 4.47 eV/atom, which was still more favorable than that of a single atom on the Al_T surface. The introduction of a seventh atom gave preference to the formation of a 3D nanostructure, with a chemisorption energy of 4.29 eV/atom, as opposed to epitaxial growth, which gives a chemisorption energy of 4.21 eV/atom. These preliminary results present a strong indication that the O_T surface will promote the formation of Pt nanoclusters and can be used to build larger clusters.

To get a preliminary indication of the chemical activity of the nanoclusters, a comparative study was performed between the adsorption of a CO molecule on the top sites of a three-atom nanocluster on α-alumina, bulk Pt, and thin film Pt layers on α-alumina. Table 2 lists the chemisorption energies for the three systems. Both the Pt monolayer film and the three-atom nanocluster present enhanced chemisorption energies over the bulk Pt system. The three-atom nanocluster gives further encouragement for the use of nanoclusters, as it further increases the CO binding energy. This increase in binding energy may correspond to more reactive catalytic behavior than previous systems or lead to new and interesting pathways.

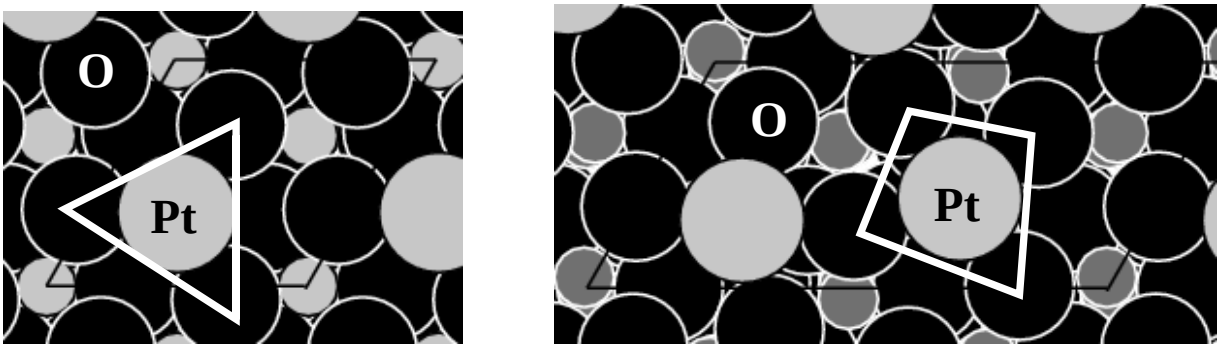

Figure 7. Surface reconstruction of O_T-surface. a) (left) Depicts the 1×1 unit cell three-fold coordinated adsorption site of the Pt adatom. This site has produces a chemisorption energy of 7.80 eV/atom. b) (right) Shows the surface reconstruction observed using a 2×1 unit cell surface. Here the production of a four-fold adsorption site increases the chemisorption energy of the Pt atom to 8.20 eV/atom making it a more suitable surface for the adsorption of Pt atoms.

Table 2. CO binding energies for three Pt systems. The nanocluster and 1-Pt layer systems both result in stronger chemisorption energies than the bulk Pt system.

System	CO chemisorption energy (eV)
3-atom nanocluster	3.92
1-layer Pt thin film / α-alumina	3.87
Bulk Pt	1.70

7. CONCLUSION

Our investigation has shown that the adsorption of CO depends significantly on both the physical characteristics and the environment of the metal. Properties such as the size and shape of the Pt metal and the thickness of the Pt layers from the surface can greatly change the binding energy of CO molecules as compared to the model system of CO adsorbed on the bulk Pt(111) surface.

First, we showed that a purely mechanical interaction like applying a strain to expand or contract this surface, and thereby creating a lattice mismatch of a few percent between the Pt surface and bulk atoms, resulted in the increase (expansion) or decrease (contraction) of the CO adsorption energy. This suggests that the CO adsorption can be tuned by switching between oxide supports with differing lattice constants

Next, we examined the effects of CO adsorption to α-alumina supported Pt thin films. In this case, we found that the CO adsorption energy varied with the thickness of the Pt on the alumina surface. For a single layer of Pt on the alumina support, the CO binding energy is more that twice as large as that of CO adsorbed on the bulk Pt(111) surface; for greater than three layers of Pt, however, the CO adsorption behavior is very similar to that of CO on the bulk Pt(111) surface. In addition to the thickness of the Pt on the alumina support, the alumina surface itself influenced the adsorption of CO to the Pt surface, CO binding much more strongly to Pt on the O_T alpha-alumina surface as opposed to the Al_T surface for one layer of Pt.

Finally, we studied the growth of Pt nanoclusters on the α-alumina surface and began to study the effects of nanocluster size on the adsorption of CO molecules. We found that the adsorption energy of CO on a three-atom nanocluster was greater even than that on a monolayer of Pt on α-alumina, suggesting that such nanostructures may show even greater catalytic activity.

Together, these results present good evidence that the atomic level size and shape of metal catalysts significantly affect their catalytic properties. Furthermore, they suggest that by controlling the size and shape of catalysts on this level, we will be able to alter these properties to achieve enhanced activity and better selectivity of catalysts in the future.

While the thin Pt films and nanoclusters exhibit a strong effect on the CO binding energy, which may lead to more favorable catalytic activity, there is the possibility that the CO will be bound too tightly and instead effectively poison the catalyst. This is something that should be examined. Nevertheless, the dramatic change in CO adsorption behavior with the number of Pt layers is indicative of the exciting possibilities for catalyst design presented by the interactions between metals and oxides in metal/oxide catalysts.

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