DFT+U Study on the Oxygen Adsorption and Dissociation on CeO₂-Supported Platinum Cluster

Tien Quang Nguyen¹, Mary Clare Sison Escaño^{1*}, Hiroshi Nakanishi¹, Hideaki Kasai^{1†},
Hiroyoshi Maekawa², Kazuo Osumi², Kaoru Sato²

¹*Department of Precision Science & Technology and Applied Physics, Graduate School of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

²*ISUZU Advanced Engineering Center, Ltd., 8 Tsuchidana, Fujisawa, Kanagawa 252-0881, Japan*

Abstract

We investigated the reactivity of CeO₂- supported Pt₄ cluster (denoted as Pt₄/CeO₂(111)) towards O₂ adsorption and dissociation as well as the geometry/electronic properties associated with such metal oxide supported cluster system using Density Functional Theory and on-site Coulomb interaction correction via the Hubbard-like term, U (DFT+U). It was found that Pt₄ binds strongly to CeO₂(111) via Pt-O-Ce bonds which act as “anchors” between the surface and the cluster, confirming its non-sintering as found in experiments. The adsorption of the cluster involves net electron transfer to CeO₂, however, charge redistribution also happens within the cluster (from Pt atom bonded to the surface to the Pt on top of the cluster). This charge couples to the top Pt leading to reduce its spin moment as compared to that of unsupported cluster. When O₂ adsorbs on Pt₄/CeO₂(111), while it prefers Pt vertex site near the CeO₂ surface, the O-O bond elongation is more profound at the Pt-Pt edges. The energy barrier for dissociating O₂ from this edge site precursor state is smallest. A correlation between the O-O bond length at the precursor state and the stability at the transition state is revealed. Finally, the barrier for dissociation in unsupported Pt₄ is lower, indicating suppression of the cluster’s reactivity due to the support. We

**Present address: Graduate School of Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui, 910-8507, Japan*

†*Corresponding author’s e-mail: kasai@dyn.ap.eng.osaka-u.ac.jp*

attribute this to the hybridization of Pt-5d orbitals with O-2p orbitals in CeO₂(111) leading to the broadening of Pt- 5d states near the Fermi level.

1. Introduction

Air pollution from automobile exhaust is one of the major environmental problems in the modern civilization. In order to reduce harmful emissions from diesel engines, the Diesel Oxidation Catalyst (DOC) has been widely investigated. In DOC systems, carbon monoxide (CO) and hydrocarbons (HC) are oxidized to harmless chemical substances such as H₂O and CO₂, while nitrogen oxide (NO) is converted to NO₂ for easy treating in Selective Catalytic Reaction (SCR) - another stage of Diesel Catalytic Converter [1-4]. DOCs have a honeycomb-like, monolithic structure. The monolithic support is made either from metallic (stainless steel) or ceramic material and is coated with high porous oxides, such as γ -Al₂O₃ (alumina), CeO₂ (ceria) and precious metals (on top), such as Pd, Pt, and Rh to increase the catalytic activity or to stabilize the structure of the catalyst. In DOCs, ceria provides multiple functions, one of which is to store excess oxygen under oxidizing (fuel lean) conditions and release it in reducing (fuel rich) conditions to oxidize CO and HC, where the transformation between Ce⁴⁺ and Ce³⁺ occurs. This process allows the catalyst to operate over wide air-to-fuel ratio [5-7]. On the other hand, CeO₂ is also widely used for stabilizing precious metal particles [8]. Experimentally, it has been reported that Pt particles in Pt_xCeO₂ catalyst do not sinter during high temperature aging in the presence of oxidative environment [9-12].

Furthermore, oxidation process plays a very important role in DOC systems (e.g. HC conversion: $\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) and so, an understanding of the interaction of the metal/metal oxide system with O₂ is imperative. To date, there are numerous researches on the adsorption and dissociation of O₂ molecules on the organic systems and the bimetallic surfaces [13-15] but very few have been done on noble metal clusters or noble metal cluster/metal oxide, for instance, Pt cluster on CeO₂. Yoon et al. [16] investigated the molecular and dissociative adsorption of O₂ on Au clusters *without* the presence of metal oxide support using density functional theory (DFT). Halachev et al. [17] studied the dissociative adsorption of O₂ on the transition metal clusters in the presence of general subsurface oxygen using Extended Huckel Method, leaving the effect of subsurface on the electronic structure of the metal clusters unexplored. This lack of understanding of reactivity of metal clusters with the support motivates

this work to tackle the reactivity of Pt cluster supported on ceria in relation to its wide application in DOC systems as described above as well as the supported cluster's geometry and electronic features. Specifically, in the reactivity, the energetics of the adsorption and dissociation of O₂ on Pt₄/CeO₂(111)p3x3 surface is studied. We chose CeO₂(111) because of its stability over other surfaces like (110) or (100) [18-20]. It is an important factor for stabilizing the metal cluster on the support surface and hence, preventing the small cluster from sintering effect. Furthermore, we draw the effects of CeO₂ support. In terms of the geometry/electronic properties of the catalyst, the adsorption of Pt cluster on CeO₂ support is investigated to verify the cluster's stabilization as observed in experiment [21]. In this work, the tetrahedron structure of the Pt₄ cluster was chosen because of its relative stability over the planar rhombus cluster [22,23]. This characteristic is also retained when the cluster is placed on the ceria support. Our calculations show that, the tetrahedral cluster is about 0.68eV more stable on the CeO₂(111) surface as compared to the planar rhombus one. In addition, the Pt₄ cluster size is used since it is large enough to capture both the "contact" and "non-contact" parts with the CeO₂ surface and, at the same time, is small enough for reasonable computational cost. Indeed, Pozdnyakova et al. [24] prepared Pt-ceria catalysts containing 0.5-0.6 nm small Pt particles by using impregnation (IMP) method; making it possible for fabricating such a small clusters on surface.

2. Computational Methods

First-principles calculations are performed using the spin-polarized version of the Vienna ab initio Simulation Package (VASP) [25,26]. The Perdew-Burke-Ernzerhof (PBE) version of the Generalized Gradient Approximation (GGA) is used to describe the exchange-correlation [27]. The interaction between the core and valence electrons is treated by the Projector Augmented Wave (PAW) method [28,29]. The valence electron configurations of cerium, oxygen, and platinum are represented in a plane wave basis set with a kinetic energy cutoff of 500 eV. The Brillouin zone is sampled using a (11x11x11) Monkhorst-Pack [30] grid for bulk ceria and the Gamma-point for the large surface model. The structures are optimized until the Hellman-Feynman force exerted on an atom is less than 0.02 eV/Å. For the systems with highly localized electrons, for instance, CeO₂ (the localized electrons belong to 4f states), we included the on-site Coulomb interaction via the Hubbard-like term U (DFT+U) as introduced by Dudarev

et al. [31], in calculating the lattice constant and the energy gap. The correction to self-interaction error of standard DFT by introducing Hubbard-like parameter (U) will basically modify the electronic structure of support surface and hence, change the bonding/anti-bonding energy as well as the charge transfer between the Pt_4 cluster and the $CeO_2(111)$ surface. Therefore, the energetic results such as adsorption energy or the energy barrier for dissociation of molecular oxygen on ceria supported Pt_4 are expected to change depending on the U parameter. Indeed, it is shown that the adsorption energies of atomic oxygen on $LaBO_3$ ($B = Mn, Fe, Co, Ni$) surface vary significantly with the selected value of U parameters [32]. Previous theoretical work found that, by introducing a value of $U^f = 5.0$ eV for Ce 4f, the expected geometry structure of CeO_2 can be reproduced [33]. However, other studies shown that when employing LDA/GGA to model O-derived p-type defect states in metal oxide, such as localized holes, the O 2p states correction for self-interaction error should be applied as well [34-38]. Later, Plata et al. [39] found that using a set of $U^f = 5$ eV and $U^p = 5 \div 6$ eV (for O 2p) leads to an improvement in describing the lattice parameters, band gaps, and formation and reduction energies of CeO_2 . Hence, in this work, we carefully checked different sets of (U^f, U^p) and derived that the combination of $U^f = 5$ eV and $U^p = 5.5$ eV gives a good description of some critical aspects concerning the structure, electronic properties, and thermochemistry of ceria. With these values of Hubbard-like term, the lattice constant of bulk ceria is found to be 5.476 Å. This is very close to experimental value (5.411 Å) [12], and in good agreement with other theoretical data [39,40]. The 2p-4f and 2p-5d energy gaps, ~2.33 eV and ~5.33 eV, are also close to experimental and theoretical results [39,41,42]. The lattice parameter from bulk calculation of ceria was used in all the calculations for the surface.

Next, the ceria support is modeled by constructing the $CeO_2(111)$ surface. A $p(3 \times 3)$ expansion of the (111) surface unit cell is used for Pt_4 cluster adsorption. With this model, the shortest distance from the Pt_4 cluster to the neighboring cluster is about 9.03 Å, sufficient to minimize cluster-cluster interaction. For the CeO_2 surface, each slab includes 3 atomic layers with a sandwich structure, O-Ce-O, as shown in Figure 1a. This implies that the $CeO_2(111)$ surface is terminated by oxygen atoms. We used two sandwich slabs (or six atomic layers) because, in this case, the convergence of the total energy with respect to slab thickness is achieved. A vacuum of ~18.54 Å is introduced to avoid the interactions in the z-axis (perpendicular to surface) between neighboring supercells. For geometric optimization of

Pt₄/CeO₂(111), the Pt₄ cluster and the first three atomic layers of CeO₂ (from top of the surface) are fully relaxed, while others are kept constrained to bulk positions.

For the adsorption and dissociation of O₂ molecule on Pt₄/CeO₂(111), various initial adsorption sites are considered. The adsorption energies of the O₂ molecule on Pt₄/CeO₂(111) surface were calculated using the following expression:

$$\Delta E_{\text{ads}} = (E_{\text{Pt}_4\text{CeO}_2} + E_{\text{O}_2}) - E_{\text{O}_2/\text{Pt}_4\text{CeO}_2}$$

where $E_{\text{Pt}_4\text{CeO}_2}$, E_{O_2} , and $E_{\text{O}_2/\text{Pt}_4\text{CeO}_2}$ are the total energies of the optimized Pt₄/CeO₂(111), the isolated O₂, and the Pt₄/CeO₂(111) with the adsorbed O₂, respectively. In determining the reaction pathways, the energy barriers and the transition state (TS) structure of O₂, the climbing image nudge elastic band (CI-NEB) [43,44] is used. In this method, the minimum energy path between optimized initial state (O₂ adsorption), IS and final state (dissociated), FS is obtained. Next, in the search for the TS, the initial and final states were kept fixed while other intermediate states are allowed to relax using force-based optimizers [45] along the “elastic band” until the force exerted on an atom is less than 0.05 eV/Å. The energy barrier is then obtained using the following expression:

$$\Delta E_a = E_{\text{TS}} - E_{\text{IS}}$$

where E_{IS} and E_{TS} are the total energies of the initial state (IS - molecular state) and transition state (TS) of O₂ dissociation process on Pt₄/CeO₂(111). Bader charge analysis [46-48] is used to investigate the charge transfer between Pt₄ cluster and CeO₂ surface, and between the oxygen and Pt₄/CeO₂(111).

3. Results and Discussions

3.1. Pt₄ cluster adsorption on CeO₂(111)

We investigated the adsorption of Pt₄ on CeO₂(111) by setting up all possible initial adsorption sites of the cluster on the CeO₂ surface. In these sites, the Pt₄ cluster is either on top of the three-fold Ce, on top of Ce site or on top of O site. After optimizing the Pt₄/CeO₂(111) systems using the conjugate gradient method [49], we found that the Pt₄ cluster always tends to shift to the most stable position on CeO₂ surface, that is, where the center of Pt₄ stays on the

three-fold Ce atoms (or on top of sub-surface oxygen – see Figure 1b) and form three Pt-O-Ce bonds with the CeO₂(111). At this stable position, the Pt₄ structure is very symmetric. The Pt_b-O bond length (where Pt_b is the Pt atom that binds with surface) is about 2.01 Å. The Pt_b-Pt_b, Pt_t-Pt_b bond lengths (where Pt_t is the Pt atom on top of Pt₄ cluster) are 2.63 Å and 2.55 Å, respectively. This stable position is in excellent agreement with previous theoretical study of Pt₄ on CeO₂ [49]. At the most stable site, we calculated the binding energy between Pt₄ and CeO₂ surface and found to be -5.28 eV. This is much larger than of the binding energy of Pt₄ with γ -Al₂O₃(111) surface, -3.55 eV, suggesting that Pt₄ is more stable on ceria surface than on alumina surface. The Pt-O-Ce bond is composed of the Ce-O bond of bulk ceria and the strong Pt-O bond between Pt₄ cluster and the CeO₂ surface. The strong Pt-O bond can be attributed to the hybridization of 5d states of Pt_b and 2p states of O on top of the CeO₂ surface. Here, the Pt_b and O atoms share electrons to form a covalent-like bond. The shared electrons between Pt_b and surface oxygen are shown by the dark region in the charge density difference plot (see Figure 2a). Thus, the Pt-O-Ce bonds act as “anchors” between the surface and the cluster, and stabilize the cluster on the surface. This now confirms the experimental observation that the sintering effect on the Pt particles is significantly suppressed on ceria surface [21,51-52].

For the electronic property of this metal/metal oxide system, we note that an electron charge of ~0.14e is transferred to CeO₂ surface when Pt₄ adsorbs. It is also worthwhile to note that, while the adsorbed Pt₄ has positive charge, the Pt_t atom of the cluster exhibits negative charge (~0.24e). The charge density difference shown in Figure 2a verifies this. The plot shows the direction of electron charge transfer, from Pt_b atoms to CeO₂ surface and to Pt_t atom. This charge transfer from Pt cluster to CeO₂ surface confirms the trends in charge transfer in previous works [50,53,54]. Moreover, we show that due to such charge transfer to Pt_t and coupling with unpaired electrons of Pt_t, the Pt_t atom holds smaller spin moments as compared to the corresponding Pt atom of the isolated Pt₄ cluster. The total spin moments of Pt₄CeO₂ system (2.24 μ_B) is lower as compared to the isolated Pt₄ (2.83 μ_B). In addition, from Figure 2b, the spin density mainly comes from the Pt₄ and the spin density Pt_t is lower as compared to that of Pt_b atom.

3.2. O₂ adsorption on Pt₄/CeO₂(111)

3.2.1. Molecular adsorption

Next, for the adsorption of O_2 on $Pt_4/CeO_2(111)$, we considered all possible initial adsorption sites. The Pt_4CeO_2 system is based on the optimized structure discussed in the previous section. Initial configurations of O_2 molecule takes into account conformation via: (1) direct interaction with the CeO_2 surface; (2) interaction with the Pt_4 only and (3) interaction with both. After optimizing and examining binding energies of different adsorption sites of O_2 on Pt_4CeO_2 , four sites that have much larger adsorption energies compared to the rest are shown in Figure 3. The adsorption energies for these sites are listed in Table 1. We can see that the highest adsorption energy of O_2 on Pt_4/CeO_2 is found at site 4 (-1.39 eV), where O_2 binds with Pt_b at the vertex of the cluster. Next stable configuration is in site 2 (-0.97 eV), where the O_2 binds to the Pt_t - Pt_b edge of the cluster. The adsorption energies of sites 1, 2, and 3 range from -0.85 eV to -0.97 eV (i.e. quite close with each other), which are comparable to the other studies of O_2 adsorption on isolated Pt_3 cluster (-1.08 eV) [55] and isolated Pt_n ($n=2-5$) cluster (-0.53 to 0.83 eV) [56]. The significant large adsorption energy of site 4 as compared to other sites is attributed to the repulsion of O_2 with the oxygen of CeO_2 surface, which directly bonds with Pt_b at the vertex of the cluster. This pushes O_2 molecule far away from surface and strongly reconstructs the Pt_b -O bond of cluster with surface (Figure 3). We also checked the contribution coming from the reconstruction of the cluster and the surface (i.e. if reconstruction causes the large difference in the adsorption energies between site 4 and the rest of the sites), we perform calculations where the surface and the cluster were kept fixed while O_2 molecule is relaxed in all directions. We note that the difference in adsorption energies of sites 1, 2, 3 and 4 is within 0.10 eV. Thus, the adsorption energy of O_2 on Pt_4/CeO_2 can be affected by the reconstruction of Pt_4 cluster.

Next, upon oxygen adsorption on Pt_4CeO_2 , the bond length of O_2 molecule (d_{O-O} in Table 1) is significantly elongated. The largest elongation is obtained from site 3, which is about 1.46 Å (~19% longer as compared to the O-O bond length in gas state). The elongation of O-O bond can be explained by the electron charge transfer from Pt_4 to O_2 molecule and the possibility of intra-molecular spin transition between O_2 molecule itself [57]. Since, the anti-bonding orbitals (π^*) in O_2 are singly occupied, therefore, the charge transfer to these orbitals makes the O-O bond longer. We can see the relation between the negative charge (estimated by Bader analysis) on O_2 and the O-O bond length in Table 1. The bigger is the negative charge on O_2 , the longer is the O-O bond. To further examine the adsorption state of O_2 on Pt_4CeO_2 , we calculated the stretching frequencies of O-O bond (f_{O-O} in Table 1) and the spin density in Figure 4. For site 3,

where O₂ binds to the Pt_b-Pt_b edge of the cluster, the O-O stretching frequency is found to be 694 cm⁻¹, which is a typical value for a peroxide state of O₂ (690-700 cm⁻¹) [58,59], involving full occupation of singly occupied π^* orbitals. As a result, O₂ in this state is nonmagnetic. This can be confirmed from Figure 4 where there is no spin density found in adsorbed O₂ for this site. For sites 1, 2 and 4, the stretching frequencies are about 1047 cm⁻¹, 757 cm⁻¹, and 1035 cm⁻¹, respectively. Thus, at site 2, O₂ is in between superoxide (860-880 cm⁻¹) [60] and peroxide states; at sites 1 and 4, O₂ is in between neutral (1556 cm⁻¹) [61] and superoxide states. For these states, O₂ π^* orbitals are not fully filled and, hence, the O₂ molecule still holds a magnetic moment. Figure 4 shows a noticeable spin density in O₂ at sites 1, 2 and 4.

3.2.2. Dissociation of O₂

In this section, we focus on the dissociation of O₂ molecule from the molecularly adsorbed state, or the so-called molecular precursor state (MPS). Four paths are considered based on the four initial states obtained from the four molecular adsorption states of O₂ discussed in the previous section (see Figure 3). Here, we labeled the paths as path1, path 2, path 3 and path 4 (two of which start at Pt-Pt edge sites {Pt_b-Pt_b, Pt_t-Pt_b} and the other two at the Pt vertex sites {Pt_t, Pt_b} of the cluster) (see Figure 5). The final states of the dissociation process are also optimized and are shown in Figure 5. Then the energy barrier for each path of the O₂ dissociation process is obtained using CI-NEB and is shown in Table 2 and Figure 6. We note that O₂ prefers to dissociate via Pt-Pt edge sites (Path 2 and 3). The energy barriers are found to be 0.42 eV (path 2) and 0.17 eV (path 3). These values are much smaller than those of path 1 (1.50eV) and path 4 (1.93eV). Thus O₂ dissociates easiest at path 3. Looking at the charge transfer (ΔQ) from Pt₄CeO₂ to O₂ molecule and the O-O bond elongation (d_{O-O}) at the MPS in Table 1, we note that there is good correlation between charge transfer and bond elongation of O₂ molecule at the MPS states with the dissociation barriers. The higher is the charge transfer to O₂ in MPS (longer O-O bond length), the lower the energy barriers we obtain. Due to the highest charge transfer from Pt₄CeO₂ to O₂ in site 3, the barrier is lowest in the corresponding dissociation path 3. In general, the dissociation of O₂ is easier at the edge sites than at the vertex sites of Pt cluster and that the O-O bond stretching and breaking strongly depends on the initial *molecular* adsorption site of O₂.

To further understand the effect of the CeO₂ support to the *catalytic reactivity* of the Pt₄ cluster, we performed energy barrier calculation for O₂ dissociation on the edge site of the Pt₄ cluster *without the presence of CeO₂ support* (see Figure 7). Due to the symmetry of isolated Pt₄ cluster, there is only one reaction path at the edge site. This site is related to paths 2 and 3 in Pt₄/CeO₂(111). It is found that the activation barrier for O₂ dissociation at edge site of isolated Pt₄ is about 0.12eV. This is lower than when CeO₂ support is present (i.e. 0.17eV for path 3). This indicates that, dissociation occurs more easily in the isolated Pt₄ than in the Pt₄/CeO₂(111). We attribute the suppressed reactivity of Pt₄/CeO₂(111) to the support itself. To verify the electronic effect of the support, the local density of states (LDOS) plot for the isolated Pt cluster and for the Pt₄/CeO₂(111) is shown in Figure 8. **In order to compare the local density of states (LDOS) of the isolated Pt₄ cluster with the supported cluster for further use, we broadened the energy eigenvalue spectrum of the isolated cluster obtained from the Kohn-Sham energy states by using Gaussian function. The LDOS of the two clusters are directly comparable as we used the same broadening parameter for both (with the width of the smearing is set to 0.2eV).** Without the support (isolated Pt₄), a sharp spin down 5d- states at the Fermi level can be noted. This state is reactive and can hybridize with 2p states of oxygen. On the other hand, when Pt₄ is on the support, the 5d states at the Fermi level of Pt atoms (Pt_t and Pt_b) in Pt₄/CeO₂(111) have lower density and are more broadened, indicating lesser reactivity. **This mechanism for the suppression of the reactivity of the Pt₄ cluster towards O₂ dissociation might be extended for other metal oxide supports as long as the bonding conditions such as the formation of Pt-O bonds of the cluster and the support is ensured. Our previous work shows that, when Pt₄ binds to Al₂O₃ surface via Pt-Al bonds, the oxide support does not significantly alter the catalytic reactivity properties of the the Pt₄ cluster toward NO molecule [62].**

4. Conclusion

The reactivity of Pt₄/CeO₂(111) towards oxygen as well as the geometry and the electronic property of the Pt₄/CeO₂(111) system is investigated using density functional theory with inclusion of the Hubbard parameter, U (DFT+U). We found that, Pt₄ cluster strongly binds and thus can act as “anchor” to prevent sintering effect in catalyst confirming experiments. The adsorption of Pt₄ on CeO₂(111) involves a direction of electron charge transfer from Pt_b atoms to

CeO₂ surface as well as Pt_t atom. This charge transfer to Pt_t allows coupling with its unpaired electrons thereby it holds smaller spin moments as compared to the corresponding Pt atom of the isolated Pt₄ cluster. Moreover, when O₂ adsorbs on Pt₄/CeO₂(111), we found that it prefers vertex site at the bottom of Pt₄ cluster, Pt_b. However, O₂ gains a large amount of electron charge when it adsorbs at the Pt-Pt edges. As a result, the O-O bond at the edges is more elongated. At Pt_b-Pt_b edge site, where the O₂ molecule is elongated the most, is in peroxide state with no spin density, while, the magnetic properties are still evident in the other sites. Furthermore, O₂ molecule prefers to dissociate at the Pt-Pt edges of the cluster than at the vertexes. And these barriers are higher than in an isolated Pt₄. The lower activation barrier in the CeO₂ –supported Pt₄ cluster is due to the sharp spin down 5d- states at the Fermi level of the isolated cluster. When the Pt₄ adsorbs on the CeO₂ surface, the hybridization of 5d orbitals of Pt₄ with 2p orbitals of oxygen in CeO₂(111) leads to the decrease of those active 5d states. Hence, there is a suppression of the reactivity of the Pt₄ cluster due to the CeO₂ support.

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Figure Caption(s):

Figure 1. (a) Side view and (b) top view of the most stable structure of Pt₄ on CeO₂(111)p3x3 surface. Pt_t and Pt_b represent the Pt atoms, which are on top and at the bottom (binds with surface oxygen) of the cluster, respectively. The Pt, Ce and O atoms are labeled accordingly.

Figure 2. (a) Charge density redistribution and (b) spin density in Pt₄/CeO₂(111) system. For charge density redistribution (a), the dark and bright regions represent the increase and decrease of electron charge, respectively. For the spin density (b), the dark and bright regions depict spin-up and spin-down electrons, respectively. The iso-surface value is 0.005 e/Å³.

Figure 3. The four most stable adsorption configuration of O₂ on Pt₄ supported by CeO₂ surface. The legend for adsorbed O₂, Pt, Ce and O (of CeO₂) are labeled accordingly.

Figure 4. Spin density on different adsorption sites of O₂ on Pt₄/CeO₂(111). The dark and bright regions show the spin-up and spin-down electron density; respectively The iso-surface value is 0.005 e/Å.

Figure 5. The optimized final (FS) and initial (IS) states of O₂ dissociation on Pt₄/CeO₂(111).

Figure 6: Reaction energy diagram for O₂ dissociation on Pt₄/CeO₂(111) at four different pathways (Path 1, Path 2, Path 3, Path 4). The adsorbed oxygen is labeled with (x).

Figure 7: Reaction energy diagram for O₂ dissociation on isolated Pt₄ cluster at Pt-Pt edge site. Oxygen is the smaller sized atom.

Figure 8. Local density of states (LDOS) of Pt atoms in isolated Pt₄ cluster and Pt₄/CeO₂. The upper and the bottom panels correspond to spin-up and spin-down electrons, respectively. The Fermi level is shifted to zero.

Table I. The adsorption energies (ΔE_{ads}), the O-O bond lengths ($d_{\text{O-O}}$), the O-O stretching frequencies ($f_{\text{O-O}}$), and the charge transfer to the adsorbed O₂ molecule on CeO₂ supported Pt₄ cluster at Site 1, Site 2, Site 3, Site 4 (corresponding to Figure 3).

Site	ΔE_{ads} (eV)	$d_{\text{O-O}}$ (Å)	$f_{\text{O-O}}$ (cm ⁻¹)	ΔQ (e)
1	-0.91	1.36	1047	-0.53
2	-0.97	1.41	757	-0.69
3	-0.85	1.46	694	-0.88
4	-1.39	1.37	1035	-0.57

Table II. Activation barriers (ΔE_a), the O-O bond distances (d_{O-O}) for initial (IS), transition (TS) and final states (FS) for the dissociation of O_2 molecule on CeO_2 supported Pt_4 cluster at Path 1, Path 2, Path 3, Path 4 (corresponding to Figure 5)

Path	ΔE_a (eV)	d_{O-O} (Å)		
		IS	TS	FS
1	1.51	1.36	2.01	3.85
2	0.42	1.41	2.01	5.30
3	0.17	1.46	2.35	5.22
4	1.93	1.37	2.24	3.85

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8: