

1 **Effects of Electron Transfer in Model Catalysts Composed of Pt**
2 **Nanoparticles on CeO₂(111) Surface**

3 Sergey M. Kozlov,^{a,*,†} Konstantin M. Neyman^{a,b,*}

4 ^a *Departament de Ciència de Materials i Química Física and Institut de Química Teòrica i*
5 *Computacional, Universitat de Barcelona, c/ Martí i Franquès 1, 08028 Barcelona, Spain*

6 ^b *ICREA (Institució Catalana de Recerca i Estudis Avançats), Pg. Lluís Companys 23, 08010*
7 *Barcelona, Spain*

8 **Highlights:**

- 9 • ~1.5 nm particles forming Pt₁₂₂{111}||CeO₂(111) and Pt₉₅{100}||CeO₂(111) interfaces
10 • Simulation approach enabling full control of electron transfer in model catalysts
11 • Interaction of Pt particles with CeO₂(111) shifts d-states of Pt to lower energies
12 • Pt-ceria interaction increases average Pt-Pt distances in the supported particles
13 • Geometry and DOS of the Pt particles are slightly altered by the electron transfer

14
15 **Abstract.** Interactions between transition metal nanoparticles and reducible oxide supports
16 are thought to significantly affect the performance of many catalysts. Usually, several metal-
17 support effects act together and cannot be separated from each other. Herein, by means of
18 density-functional calculations we succeeded to single-out and quantify effects of the metal-
19 support electron transfer on the structure and electronic properties of important model Pt-ceria
20 catalysts. Namely, we considered ~1.5 nm large Pt₉₅ and Pt₁₂₂ particles supported on
21 CeO₂(111). We show that Pt-ceria interactions notably reconstruct Pt nanofacets forming the
22 interface and shift valence d-states of the Pt particles. These effects are rather insensitive to
23 the Pt-ceria electron transfer, at variance with the electronic structure of oxygen anions at the
24 interface, which is significantly affected by the electron transfer. The findings of this work
25 and the special modelling approach applied pave the way for deeper analysis of electronic
26 metal-support interactions in catalysis.

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28 **Keywords:** DFT, Pt, ceria, electronic metal-support interaction, electron transfer, electronic
29 structure

* Corresponding authors. *E-mail addresses:*
sergey.kozlov@kaust.edu.sa (S.M. Kozlov), konstantin.neyman@icrea.cat (K.M. Neyman)

† Present address: KAUST Catalysis Research Center, Physical Sciences and Engineering Division,
King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

1. Introduction

Transition metal nanoparticles (NPs) supported on oxides are the foundation of many indispensable catalysts, such as (de-)hydrogenation catalysts [1,2], catalysts for treatment of exhaust gases [3,4] and for environmentally friendly energy technologies [5,6]. Performance of such catalysts depends equally strongly on the active material and its support, their nature and their structure [7,8]. Presently, there is an increasing understanding of how the catalytic activity is shaped by low-coordinated atoms on metal NPs [9,10], the modification of the latter by the reaction environment [11,12] and the chemical ordering in alloy NPs [13,14]. The effects of nanostructuring of the oxide support on the catalyst properties have also been investigated [15,16]. Yet, relatively little is known regarding atomic and electronic mechanism of electronic metal-support interactions [17–19]. In particular, it is largely unexplored how metal-support electron transfer may affect the catalyst [20,21]. Partially, this is because the magnitude of the electron transfer is hard to measure and control both in experiments and simulations.

Fortunately, it is possible to quite accurately measure the electron transfer for one of the technologically important oxide supports, CeO_x [3,22,23]. The ability of cerium oxide supports to increase the activity of catalysts [15,24] is often related to their reducibility [22,25,26], i.e. the ease of reduction of particular Ce^{4+} cations to localized Ce^{3+} [27,28] and the related ability to easily store/release lattice O [29,30]. These virtues also allow one to measure the charge transferred to cerium oxide by counting Ce^{3+} cations with a highly sensitive technique called resonant photoemission spectroscopy [31,32]. In turn, in electronic structure simulations Ce^{3+} cations are easily distinguished from Ce^{4+} ones by their well-defined magnetic moment. From the amount of Ce^{3+} cations in the system one can unequivocally quantify the magnitude of metal-support electron transfer both in experiments [23,33] and simulations [26]. Moreover, in simulations one could also tune the number of transferred electrons from the metal to the oxide by enforcing a particular magnetization (and, hence, the charge) on every Ce cation in the system [23,34]. This allows one to study the electronic metal-oxide interaction as a function of the amount of the electron transfer.

Herein, we have studied the electron transfer and the electronic metal-support interaction in a particularly important catalytic system, Pt nanoparticles deposited on ceria [35–38]. Although Pt-ceria interaction is very complex and may include hydrogen spillover [25,39] and reverse oxygen spillover [34,40], besides the electron transfer [23,41], we deliberately focus on the latter. In particular, we have considered the electron transfer from Pt nanoparticles to

1 the idealized $\text{CeO}_2(111)$ support without O vacancies, because the presence of the latter was
2 shown to decrease the number of transferred electrons [23]. Note that an even higher
3 magnitude of the electron transfer may be expected between Pt nanoparticles and the
4 nanostructured ceria support due to the increased reducibility of the latter [26,30].

5 In the following, we investigate ceria-supported Pt NPs of ~ 100 atoms and ~ 1.5 nm in
6 size, which is qualitatively larger than those in previous computational investigations [17,42]
7 and approaches common NP sizes in applications of Pt [43,44]. In fact, metal NPs of this size
8 usually belong to the scalable with size regime, so their properties can be extrapolated to
9 those of larger particles [45,46]. To the best of our knowledge, the shape of Pt nanoparticles
10 on the $\text{CeO}_2(111)$ support and the structure of the formed metal-oxide interface are yet to be
11 characterized with the sufficiently high resolution that would allow one to design
12 computational models based on the experimental results [47]. Despite of some understanding
13 of the interface structure between the extended $\text{Pt}(111)$ and $\text{CeO}_2(111)$ surfaces from the
14 experimental [48,49] and computational [50,51] points of view, it is not possible to apply this
15 knowledge to precisely design the interface between the considered Pt NPs and the ceria
16 support. In the absence of sufficiently accurate atomic structures of Pt NPs on $\text{CeO}_2(111)$
17 derived from observations, models of ceria-supported Pt nanoparticles in the present work
18 were designed following the shapes of Pt NPs supported on $\text{MgO}(100)$ [52–54]. The
19 considered nanoparticles featured fully relaxed *fcc* structure and a shape in line with the
20 Wulff-Kaishev construction. The present work focuses on the investigation of Pt_{95} and Pt_{122}
21 nanoparticles forming $\text{Pt}\{100\}||\text{CeO}_2(111)$ and $\text{Pt}\{111\}||\text{CeO}_2(111)$ interfaces with the
22 support, respectively (Fig. 1). The latter NP structure was found to be highly energetically
23 stable when supported on $\text{MgO}(100)$ [54]. The Pt_{95} NP was constructed from the energetically
24 stable $\text{MgO}(100)$ -supported Pt_{111} NP by removing 4 Pt atoms from each of the side $\{100\}$
25 nanofacets to decrease its lateral dimensions.

26 In the present touchstone study we explore in detail the alteration of structural and
27 electronic properties of Pt NPs by the $\text{CeO}_2(111)$ support. We take full advantage of the
28 computational possibility to control the number of transferred electrons to characterize the
29 effects of Pt-ceria interaction depending on the amount of charge transfer. Briefly, we
30 obtained multiple configurations with the transfer of up to 6 electrons from Pt_{95} and Pt_{122}
31 nanoparticles to $\text{CeO}_2(111)$ support as detailed in the next section. The number of transferred
32 electrons was counted by the number of Ce^{4+} ions reduced to Ce^{3+} in each system. For the
33 sake of brevity, the the effect of charge transfer on properties of Pt-ceria system is discussed
34 only for configurations with the transfer of 0 and 6 electrons.

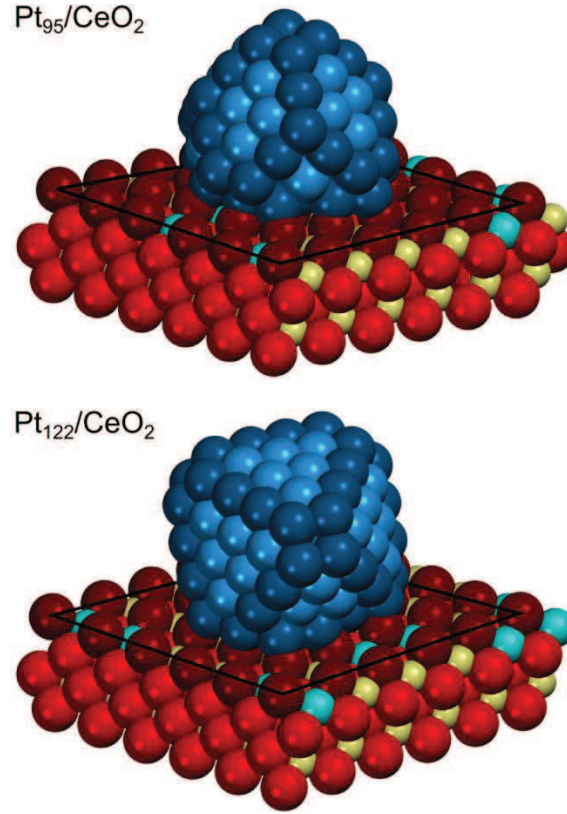


Fig. 1. Structure of the considered Pt_{95} and Pt_{122} nanoparticles forming $\text{Pt}_{95}\{100\}||\text{CeO}_2(111)$ and $\text{Pt}_{122}\{111\}||\text{CeO}_2(111)$ interfaces, respectively, with the $\text{CeO}_2(111)$ support. (Edge) Pt atoms are (dark) blue, (surface) O atoms are (dark) red, Ce^{4+} cations are beige and Ce^{3+} cations – cyan. Dimensions of the employed $\text{CeO}_2(111)$ supercells are marked by black lines.

2. Computational details

VASP software [55] was used to perform spin-polarized calculations with the PW91 exchange-correlation functional [56] augmented with Hubbard [57] $U = 4$ eV corrections on the f-states of all Ce atoms, adopted in line with previous studies [26,58]. Valence electrons were described using a plane-wave basis set with the cut-off energy of 415 eV, whereas core electrons were treated using projected augmented wave technique (PAW) [59]. The calculations were performed at the Γ -point in the reciprocal space and with 0.1 eV smearing applied to the electronic occupancies. All Pt atoms as well as atoms of the top O-Ce-O tri-layer of the $\text{CeO}_2(111)$ slabs were relaxed during geometry optimization until the forces acting on atoms decreased to 0.2 eV/nm. Atoms in the bottom tri-layer of two tri-layer thick $p(5\times 5)$ $\text{CeO}_2(111)$ slab with dimensions 1.909×1.909 nm² were fixed in the positions derived from the experimental bulk geometry. The sensitivity of the presented results to the chosen computational parameters has been examined elsewhere [23]. In particular, the number of transferred electrons was found to be essentially independent on the slab thickness and the choice of particular lattice parameter for the ceria surface, despite possible strain

accumulation in the support [60] and previous reports for Au atoms on CeO₂(111) [61]. The separation between adjacent supported NPs was ~0.55 nm. At these distances there is an attraction between each pair of adjacent Pt₉₅ and Pt₁₂₂ species with the strength calculated to be 0.02 and 0.05 eV, respectively. Such weak interactions should not affect the conclusions of the present study.

To obtain configurations with varying number of transferred electrons we took advantage of the availability of pseudopotential for Ce³⁺ cations in VASP. In this case one occupied f-state is introduced into the fixed pseudopotential core. Calculations where a part of Ce cations had been represented by Ce³⁺ pseudopotentials were performed to pre-optimize geometries with appropriately distorted ceria substrate for calculations employing only regular Ce pseudopotentials. The discussion in this work is based only on results of the latter fully self-consistent calculations yielding locally optimized geometries.

Namely, for each nanoparticle we started the calculations by forcing the reduction of all 25 surface Ce cations to Ce³⁺ through the use of Ce³⁺ pseudopotentials. For both supported Pt₉₅ and Pt₁₂₂ nanoparticles such configurations were highly unstable and converged to configurations with 6 electrons transferred from Pt to ceria when Ce³⁺ pseudopotentials were substituted by regular Ce pseudopotentials without fixed f-electrons in the core. To obtain a configuration with one less transferred electron we enforced the oxidation state of 4+ on the Ce³⁺ cation with the lowest magnetization [62] in the previous configuration by setting its magnetization to zero in the beginning of the calculation. By repeating this procedure we obtained configurations with the transfer of zero to five electrons (Figure S1).

As a result, Ce³⁺ cations are located in similar positions for all obtained configurations of the supported Pt₉₅ or Pt₁₂₂ particles. This way of calculation minimized oscillations of the relative energies depending on the location of Ce³⁺ on the surface [60,62,63]. Note that in all considered structures Ce³⁺ cations were located exclusively on the slab surface. Whereas on pristine CeO₂(111) surfaces subsurface Ce³⁺ cations do not appear at low coverage $\theta(\text{Ce}^{3+}) < 0.5$ ML [64,65], more complex ceria-based systems may be more prone to develop subsurface Ce³⁺ cations [62,66]. Another important remark is that the electron transfer from Pt particles to the support was shown not to facilitate the formation of O vacancies in ceria [23].

3. Results and discussion

3.1. Binding of Pt nanoparticles to CeO₂(111) support

The strength of Pt-ceria interaction can be evaluated by the adhesion energy $E_{\text{adh}}[\text{Pt}_N]$ defined as $E_{\text{adh}}[\text{Pt}_N] = E[\text{supported Pt}_N/\text{ceria slab}] - E[\text{unsupported Pt}_N] - E[\text{ceria slab}]$, where

E[X] is the total energy of the system X. The adhesion energies of Pt₉₅ and Pt₁₂₂ NPs to CeO₂(111) in the most stable configurations regarding the electron transfer are calculated to be ~-15.0 eV and ~-9.6 eV, respectively. That is, the binding of Pt nanoparticles to CeO₂(111) through their {100} facets is notably stronger than through their {111} facets. This finding is in line with the lower coordination number of Pt atoms on Pt(100) terraces, N_{coord} = 8, than on Pt(111) terraces, N_{coord} = 9, and with concomitantly larger number of unsaturated bonds on the former surface. Indeed, the adhesion energy of Pt₉₅{100}||CeO₂(111) interface is -0.71 eV per each of 21 Pt atoms on the interface, that is, -8.97 eV/nm², whereas the strength of the interaction on Pt₁₂₂{111}||CeO₂(111) interface is -0.38 per each of 25 Pt atoms on the interface or -5.57 eV/nm². (Adhesion energies per nm² were calculated using the areas of the corresponding bottom facets of the unsupported Pt NPs.)

As a rule, the energetic stability of bare nanoparticles increases with the particle size [67,68], and so Pt₁₂₂ particles are more stable than Pt₉₅ species. One may circumvent this well-known dependency by considering the surface excess energy [54,69,70], $\Delta_{\text{exc}}[\text{unsupported Pt}_N] = N^{1/3} \times (E[\text{unsupported Pt}_N]/N - E[\text{Pt}_{\text{bulk}}])$ or $\Delta_{\text{exc}}[\text{supported Pt}_N/\text{ceria}] = N^{1/3} \times (\{E[\text{supported Pt}_N/\text{ceria}] - E[\text{ceria}]\}/N - E[\text{Pt}_{\text{bulk}}])$. According to this metric Pt₁₂₂ is still more stable than Pt₉₅ in the unsupported state with $\Delta_{\text{exc}}[\text{unsupported Pt}_{122}] = 3.44$ eV versus $\Delta_{\text{exc}}[\text{unsupported Pt}_{95}] = 3.78$ eV. The reason for the lower stability of the Pt₉₅ NP in the unsupported state is the presence of an extended bottom {100} facet, which has higher specific surface energy than {111} facets [71,72]. Nevertheless, surface excess energies of the two nanoparticles are equal in the supported state, $\Delta_{\text{exc}}[\text{supported Pt}_{95}/\text{ceria}] = \Delta_{\text{exc}}[\text{supported Pt}_{122}/\text{ceria}] = 3.05$ eV. Thus, the intrinsic lower stability of Pt₉₅ in the unsupported state is compensated by the stronger interaction between Pt₉₅{100} and the support. As a result, the two considered NPs forming either Pt{100}||CeO₂(111) or Pt{111}||CeO₂(111) interfaces appear to be equally energetically stable in the supported state according to our calculations.

3.2. Structure of the obtained Pt||CeO₂(111) interfaces

Pt nanoparticles were put on CeO₂(111) in a way that maximizes the number of Pt-O contacts (Fig. 2), which is typical for the contacts between extended Pt and ceria surfaces [41,50] and other Pt-oxide interfaces [53,54]. Note that only local structure optimization of the considered metal-oxide interfaces was performed in view of the computational inaccessibility of the global optimization. Although the bottom Pt₁₂₂{111} facet has a hexagonal symmetry like the symmetry of CeO₂(111) and the extended Pt₉₅{100} facet has a square symmetry, both facets undergo reconstruction upon contact with the ceria support. The

reconstruction is required for a better matching between Pt and O lattices, because of the significant mismatch of the lattice parameters of the involved Pt and ceria surfaces. In the calculated systems, the distance between O atoms on CeO₂(111) surface is 382 pm, whereas the nearest Pt-Pt distances are ~280 pm.

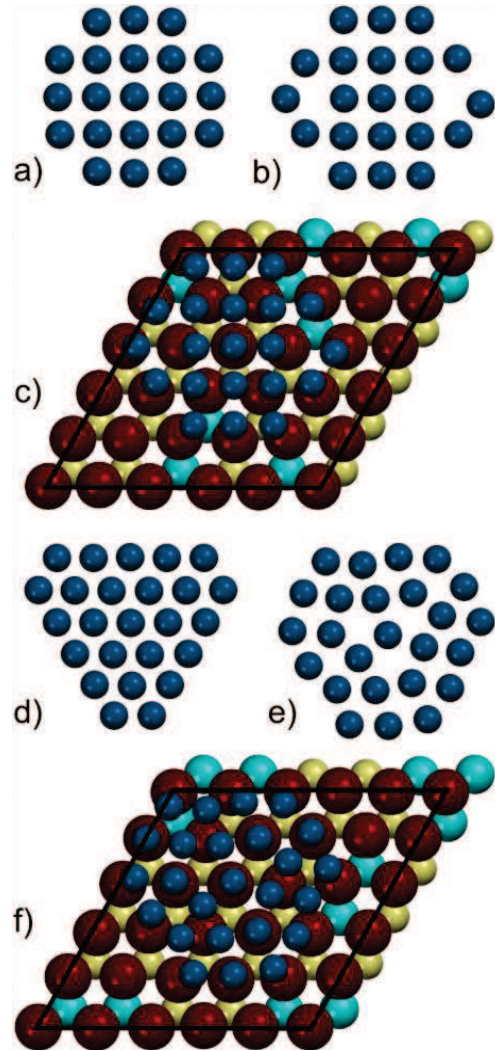


Fig. 2. Bottom facets of a), d) unsupported and b), e) supported Pt₉₅ and Pt₁₂₂ nanoparticles, respectively, as well as structures of c) Pt₉₅{100}||CeO₂(111) and f) Pt₁₂₂{111}||CeO₂(111) interfaces. Color coding as in Fig. 1.

On the Pt₉₅{100}||CeO₂{111} interface two Pt atoms on the boundary displace outward from the center of the interface in order to move from a “bridge” position between two surface O closer to an “on top” position above surface O atoms. Curiously, this reconstruction of the bottom facets is also locally stable in the unsupported Pt₉₅ NPs; however, it results in 1.25 eV higher energy than that of the unreconstructed unsupported Pt₉₅. The reconstruction of the bottom {111} facet of supported Pt₁₂₂ NPs is more complex. The shape of the bottom Pt facet changes from a hexagon with 2 and 5 atom long sides to a distorted hexagon with 3 and

4 atoms long sides and the interior area of the bottom facet adjusts accordingly. Such reconstruction is locally unstable in unsupported Pt₁₂₂ NPs, which spontaneously relax to the unreconstructed structure.

The calculated locations of Ce³⁺ ions formed upon the charge transfer seem to be somewhat different for both types of the Pt-ceria interfaces. On the Pt₉₅{100}||CeO₂(111) interface 4 out of 6 partially reduced Ce cations are located at the metal-oxide boundary, whereas only one Ce³⁺ cation resides on the Pt₁₂₂{111}||CeO₂(111) interface. The other Ce³⁺ cations are located in the substrate areas that are not covered by Pt. Thus, we do not see an obvious preference for Ce³⁺ cations to be located either under Pt NPs or away from them. A dedicated rigorous study is required to identify possible more subtle inhomogeneities in the distribution of Ce³⁺ cations. Note that the presence of Ce³⁺ cations on the ceria surface uncovered by Pt may result in an interesting alteration of the substrate's reactivity.

3.3. *Effect of CeO₂(111) support on the geometric structure of Pt nanoparticles*

Previous computational studies have found the effect of CeO₂(111) support on the overall geometric structure of small Pt clusters to be important [42,73]. However, in the case of notably larger Pt₉₅ and Pt₁₂₂ nanoparticles only atomic positions in the bottom NP facets are substantially affected by the support (Fig. 2). As a result there is an emergence of intermediate Pt-Pt distances that may or may not be considered as interatomic bonds (Fig. S2). Note that this was not the case for Pt NPs supported on MgO(100), where the strength of metal-oxide interaction was not enough to cause the reconstruction of the nanoparticle facet [54]. For example, supported Pt₉₅ particles exhibit Pt-Pt distances of ~370 pm, which are absent in unsupported Pt₉₅ species. Similarly, Pt-Pt distances of ~340 pm in supported Pt₁₂₂ particles are absent in the respective unsupported species. Thus, one cannot be certain if such Pt-Pt distances are due to the formation of interatomic bonds between adjacent Pt atoms or due to the coordination of Pt atoms by atoms in their second coordination sphere.

As a consequence, the average Pt-Pt bond-lengths in the supported nanoparticles can be quantified in different ways (Table S1). On the one hand, one could consider only Pt-Pt distances shorter than 340 pm (roughly the middle of the gap between the first and the second coordination spheres in the unsupported Pt₁₂₂) as interatomic bonds. Then, the metal-support interaction would result only in 0.3 and 0.6 pm average elongation of Pt-Pt bonds in Pt₉₅ and Pt₁₂₂ particles, respectively. On the other hand, one could assume that the overall number of Pt-Pt bonds in the nanoparticles does not change upon their interaction with CeO₂(111). Then, the average Pt-Pt bonds would appear to be 4.6 and 5.8 pm longer in the supported Pt₉₅ and

Pt₁₂₂ nanoparticles than in the respective unsupported species, because in this case numerous elongated Pt-Pt distances at the interface would be considered as bonds.

If the electron transfer from Pt nanoparticles to CeO₂(111) support is suppressed in the calculations, then Pt-Pt bonds become even longer on average due to the higher resulting occupancy of antibonding Pt-Pt d-states. In the case of supported Pt₉₅ particles the elongation due to the suppressed electron donation to the support amounts to ~0.5 pm. At the same time, the absence of the electron transfer leads to 0.2 or 1.3 pm longer Pt-Pt bonds in supported Pt₁₂₂ nanoparticles depending on the method used to calculate the average bond distance.

3.4. Effect of CeO₂ on the electronic structure of supported Pt nanoparticles

The contact between metallic Pt particles and ionic ceria support leads to the polarization of the electron density of the former by near-surface electric fields, described previously for the Pt(111)||CeO₂(111) interface [50]. The mutual polarization of Pt and ceria due to Pt-ceria interaction can be visualized by means of charge density difference (CDD) plots, which display isosurfaces of $\Delta\rho = \rho[\text{Pt}_N/\text{ceria}|_{6e}] - \rho[\text{Pt}_N] - \rho[\text{ceria}]$. In this formula $\rho[\text{Pt}_N]$ and $\rho[\text{ceria}]$ are electron densities of individually calculated Pt NP and ceria support with geometries from the optimized structure of supported Pt_N particle (with 6 transferred electrons), which yields electron density $\rho[\text{Pt}_N/\text{ceria}|_{6e}]$. Isosurfaces plotted at isovalue of 0.05 atomic units (a. u.) show that the electron density in supported Pt nanoparticles moves from the regions above negatively charged O anions towards regions above positively charged Ce cations (Fig. 3). However, the polarization of electron density on Pt atoms diminishes rapidly with growing distance to the ceria support (middle panels in Fig. 3). Note that the electron density of Pt nanoparticles supported on CeO₂(111) is significantly more polarized than the charge density of similar Pt nanoparticles on MgO(100) [54]. This can be explained by better charge compensation within Tasker type I MgO(100) surface compared to Tasker type II CeO₂(111) surface and by concomitantly stronger electric fields in the vicinity of the latter.

The electron density of the CeO₂(111) support also becomes polarized due to its interaction with Pt. First, there is a visible change in the electron density of Ce cations that get reduced from Ce⁴⁺ to Ce³⁺ upon Pt-ceria interaction. Second, one may notice a significant polarization of the electron density on surface O anions that are in contact with Pt NP.

To focus on the contribution of the electron transfer to the polarization of the electron density we generate CDD between two electronic states, with and without electron transfer: $\Delta\rho_e = \rho[\text{Pt}_N/\text{ceria}|_{6e}] - \rho[\text{Pt}_N/\text{ceria}|_{0e}]$. Both states are calculated on the optimized geometry with the transfer of 6 electrons. The resulting plots (right panels in Fig. 3) show that the

electron transfer leads to the polarization of reduced Ce^{3+} cations and Pt atoms on Pt-ceria interface. Importantly, by comparing CDD for overall Pt-ceria interaction and solely for the contribution of the electron transfer one concludes that the latter accounts for a mere fraction of the polarization of electrons in Pt particles.

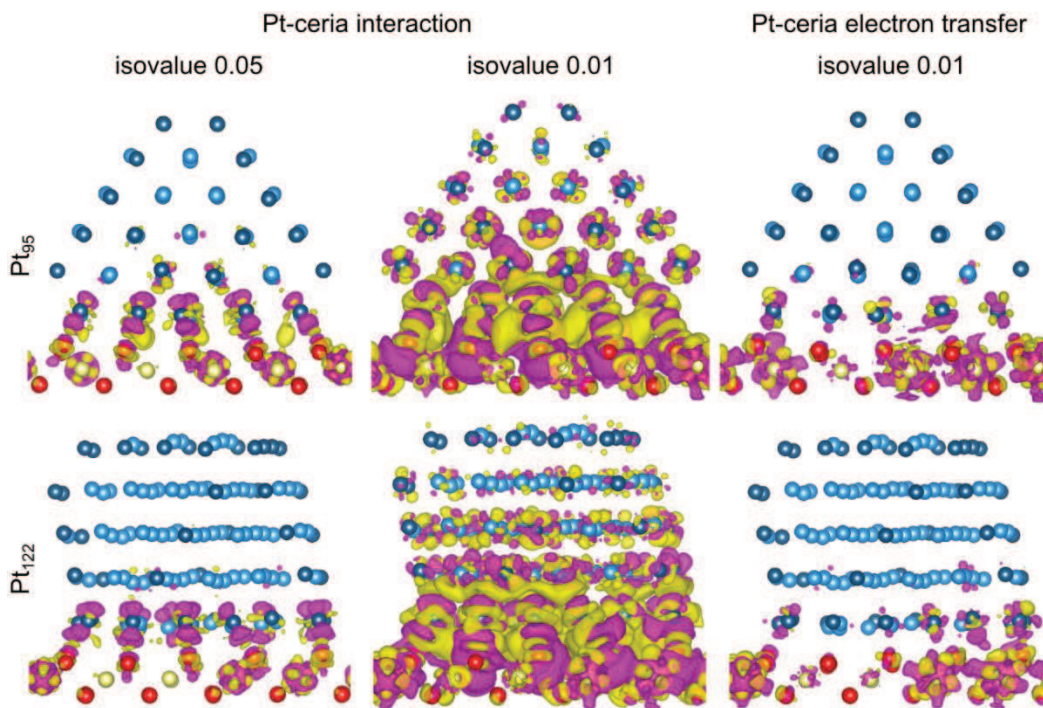


Fig. 3. Isosurfaces of charge density difference for the interaction between ceria and the considered Pt particles involving the transfer of 6 electrons plotted at different isovalues (in a.u.) as well as the distilled contribution of Pt-ceria electron transfer to the electron polarization (see discussion). Regions of electron accumulation (depletion) are colored yellow (pink). (Edge) Pt atoms are (dark) blue, O atoms are red, Ce cations are beige.

Bader charges provide another perspective on the polarization of electron density as a result of Pt-ceria interactions (Table S2). The Bader charge on the nanoparticles in the configurations without Ce^{3+} cations is 0.76 and 0.56 atomic units for Pt_{95} and Pt_{122} , respectively. However, the charge on nanoparticles increases only by ~ 1.3 a. u. when 6 Ce^{3+} cations are present in the support. This finding is in agreement with the underestimation by the Bader analysis of the difference between charges on Ce^{4+} , $\delta_{\text{Bader}}^+ = 2.4$, and Ce^{3+} , $\delta_{\text{Bader}}^+ = 2.0$, cations. In line with the CDD analysis, Bader charges indicate that most of the charge accumulated by the nanoparticle is located on the Pt atoms forming the interface with the oxide support.

A similar conclusion can be drawn from the analysis of densities of states (DOS) projected on atoms on the perimeter of the bottom facets of Pt nanoparticles, i.e. the facets

that form the interface with ceria. Indeed, there are some noticeable differences between the DOS projected on the bottom facets of the supported and unsupported nanoparticles (Fig. 4). The center of the occupied d-states projected on the bottom {111} facet of Pt₁₂₂ shifts down by 0.12 eV due to the interaction with CeO₂(111). The shift of the d-states is even more significant, 0.52 eV, for the bottom {100} facet of the Pt₉₅ NP, which interacts more strongly with CeO₂(111) than the Pt₁₂₂ species. Note that this shift is specific to CeO₂(111) support and not to all oxide supports. For example, MgO(100) support is calculated to have a negligible effect on the DOS of supported Pt particles [54].

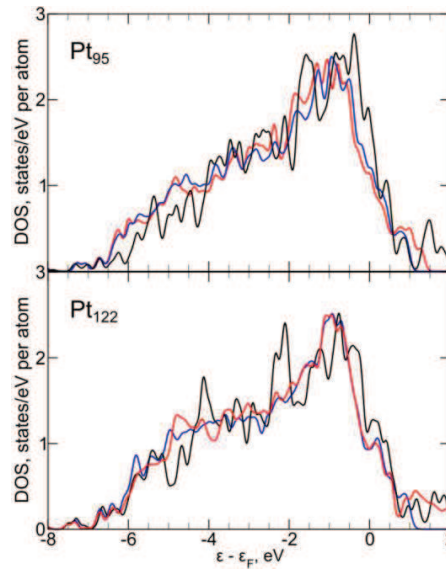


Fig. 4. Electronic densities of states projected on Pt atoms on the metal-oxide boundary. Red line – the nanoparticles supported on CeO₂(111) in the absence of the electron transfer (no Ce³⁺); blue line – the nanoparticles on CeO₂(111) in the presence of the electron transfer (6 Ce³⁺); black line – the respective atoms in unsupported nanoparticles. Electronic energies are given with respect to the Fermi level of each particular system.

At the same time, in line with results of CDD analysis, the electron transfer makes an insignificant contribution to the overall alteration of the electronic structure of Pt nanoparticles by the ceria support. The shifts of d-states due to the electron transfer were calculated to be less than 0.05 eV.

3.5. Effect of Pt nanoparticles on the electronic structure of CeO₂(111) support

Importantly, both the Pt-ceria interaction and the Pt-ceria electron transfer have a considerable effect on the electronic structure of surface O anions of the support. Fig. 5 shows that DOS projected on surface O in contact with Pt nanoparticles is qualitatively different from that of other O atoms on the same surface. Whereas DOS of the latter O atoms forms a

sharp peak between -3.5 and -1.5 eV with respect to the Fermi level, O atoms contacting with Pt exhibit a broad feature between -6.0 and -2.5 eV below the Fermi level in their DOS. The shift of O DOS to lower energies results in more significant overlap with Pt DOS extending up to -6.5 eV below the Fermi level, which strongly suggests the formation of the joint Pt-O electronic states.

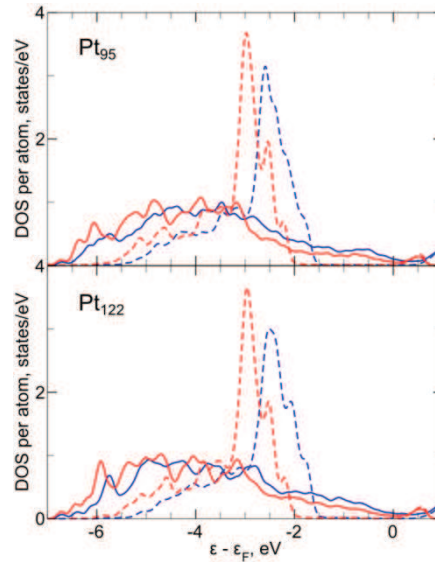


Fig. 5. Electronic densities of states projected on surface O atoms (solid line) on the metal-oxide boundary and (dashed line) not in contact with Pt. Red line – the nanoparticles supported on CeO₂(111) in the absence of the electron transfer (no Ce³⁺); blue line – the nanoparticles on CeO₂(111) in the presence of the electron transfer (6 Ce³⁺). Electronic energies are given with respect to the Fermi level.

In turn, the electron transfer affects DOS of surface O atoms, irrespective whether they form bonds with Pt or not. As a result of the transfer of 6 electrons from Pt nanoparticles to ceria support electronic states of O shift by 0.3-0.4 eV to higher energies. One can expect that the deposition-induced modifications of the electronic states of O anions at the Pt-ceria interface, including those related to the electron transfer from Pt to ceria, represent important channels for affecting the reactivity of Pt-ceria catalysts.

4. Conclusions

We investigated how interaction between Pt nanoparticles and defect-free CeO₂(111) support affects properties of the former using density-functional calculations. In particular, we considered 1.4 nm large Pt₉₅ and 1.5 nm large Pt₁₂₂ particles forming Pt{100}||CeO₂(111) and Pt{111}||CeO₂(111) interfaces. Both studied supported nanoparticles exhibit similar calculated energetic stability. This may be an indication of a similar thermodynamic stability

of both interfaces, implying that both interfaces could be observed experimentally. For both nanoparticles we investigated how Pt-ceria interaction and transfer of 0 or 6 electrons to the support affect the properties of the supported particles.

First, the metal-oxide interaction results in a certain elongation of average interatomic distances in supported Pt nanoparticles. This elongation is accompanied by a reconstruction of the Pt facet forming the interface with CeO₂(111) support due to the notable lattice mismatch between Pt and ceria surfaces. Notably, the transfer of 6 electrons from Pt to ceria leads to the contraction of Pt-Pt bonds by less than 1 pm on average. The Pt-ceria interaction also shifts the electronic density of states of Pt atoms on the metal-oxide boundary to lower energies, with the more significant shift for Pt atoms on Pt₉₅{100}||CeO₂(111) interface than on Pt₁₂₂{111}||CeO₂(111). However, the role of the electron transfer in this shift appears to be insignificant. Charge density difference analysis also indicates that Pt-ceria interaction leads to a significant polarization of the electron density of Pt nanoparticles. However, again the electron transfer does not affect the polarization as much as other components of the metal-oxide interaction. At the same time, the electronic structure of O atoms on Pt-ceria interface is profoundly affected by the metal-oxide interaction and the electron transfer. Moreover, some Ce³⁺ cations are calculated to be present on the areas of ceria surface that were not covered by Pt, which may alter the reactivity of the ceria substrate.

Note that the effects of Pt-ceria interaction on the geometric and the electronic structures of the supported particles have been somewhat different for the two considered Pt₉₅ and Pt₁₂₂ species due to the different types of formed Pt-ceria interfaces. This finding suggests that the effects of Pt-ceria interaction on the properties of Pt particles are also likely to depend on the type of ceria surface forming the interface.

In summary, the electron transfer only modestly contributes to the overall ceria-induced changes of the geometric and electronic structure of Pt particles that are large enough to be relevant for technical catalysis (Pt₉₅ and Pt₁₂₂). In variation, sub-nanometer clusters such as Pt₈ are shown to be strongly affected by the electron transfer to the ceria support [23]. Hence, it is still uncertain at what particle size the metal-support electron transfer becomes important for practical catalysis. The key requisite for a study addressing this problem is the ability to control the magnitude of the metal-support electron transfer, which was achieved in the present work for the important case of Pt-ceria model catalysts.

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Appendix A

Supplementary data associated with this article can be found in the online version.

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