Adsorption and Oxidation of CO on Ceria Nanoparticles Exposing Single-Atom Pd and Ag: A DFT Modelling

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Abstract: Various COx species formed upon the adsorption and oxidation of CO on palladium and silver single atoms supported on a model ceria nanoparticle (NP) have been studied using density functional calculations. For both metals M, the ceria-supported MCOx moieties are found to be stabilised in the order MCO < MCO2 < MCO3, similar to the trend for COx species adsorbed on M-free ceria NP. Nevertheless, the characteristics of the palladium and silver intermediates are different. Very weak CO adsorption and the small exothermicity of the CO to CO2 transformation are found for O1Pd site of the Pd/CeO2 model featuring a square-planar coordination of the Pd2+ cation. The removal of one O atom and formation of the O3Pd site resulted in a notable strengthening of CO adsorption and increased the exothermicity of the CO to CO2 reaction. For the analogous ceria models with atomic Ag instead of atomic Pd, these two energies became twice as small in magnitude and basically independent of the presence of an O vacancy near the Ag atom. CO2-species are strongly bound in palladium carboxylate complexes, whereas the CO3− species anchored to M-containing and bare ceria particles based solely on vibrational spectroscopy seems problematic. This computational modelling study provides guidance for the knowledge-driven design of more efficient ceria-based single-atom catalysts for the environmentally important CO oxidation reaction.

Keywords: CeO2-based nanomaterials; density functional calculations; single-atom catalysts; structure; reactivity

1. Introduction

Ceria, as a component of catalysts containing transition metals (M) Pd or Ag, is used in numerous applications ranging from the abatement of soot, volatile organic compounds, and CO [1–10] to the production of syngas [11] and CO2 activation [12,13]. As an active reducible support, ceria facilitates the dispersion of metals and MOx phases on the surface [7,14–17] and provides lattice O atoms to oxidise reactants [2,9,17–20]. For instance, the interactions within Pd- ceria interfaces allow the synergistic oxidation/reduction of both subsystems [21], promote the oxidation of CO by lattice O atoms, and the oxidation of the reduced ceria by O atoms of CO2 [22]. Supported transition metals can also enhance
the redox performance and oxygen storage capacity of ceria [23]. Often, high catalytic efficiency is achieved using a nanostructured ceria support via enhanced metal–support interaction, which improves the dispersion of metal particles and suppresses their sintering at elevated temperatures [3,4,7–9,11,19,24–27].

The M-containing surface phases of the aforementioned systems are represented by M$_{m}$ [6,7,16,24,28,29] and MO$_{x}$ [6,25,26,30] nanoparticles (NPs), charged metal clusters [7,24,31], solid M$_{x}$Ce$_{1-x}$O$_{2-\delta}$ solutions [25–27,32–35], and dispersed M$_{1}$ or O$_{M_1}$ ad-species [3,6–9,16,36,37]. Analysis of the crystalline environment of the Pd$_{1}$ ad-species revealed that each Pd$^{2+}$ ion in Pd/CeO$_{2}$ catalysts prepared by the solution combustion method is coordinated, on average, by three O atoms [34]. This coordination mode of Pd$_{1}$ is a feature of adsorption complexes with CO such as O$_2$Pd$_1$-CO/CeO$_2$(111) [8], O$_1$Pd$_1$-CO/CeO$_2$(111) [8], and O$_1$Pd$_1$-CO/CeO$_2$(100) [9], while a Pd$_1$-CO/CeO$_2$(110) complex exhibits an O-Pd-O bridge [9]. In many cases, Pd$_{1}$ is in a square-planar environment. Pd$_{1}$ centres in Ce$_{1-x}$Pd$_{x}$O$_{2-\delta}$ crystals (x ≤ 0.15) reside on O$_{4}$ units adjacent to Ce centres [32]. The doping of ceria with Pd results in a structure with the dopant ion displaced from the initial cationic position to the centre of the O$_{4}$ unit [23]. Furthermore, Pd$_{1}$ species are attached to the O$_{4}$ unit of the Pd$_{x}$Ce$_{1-x}$O$_{2-\delta}$ lattice incorporating products of water dissociation [27]. Replacing every second upper-layer Ce$^{4+}$ cation and one adjacent to it O$^{2-}$ anion on the CeO$_2$(110) surface with Pd$^{2+}$ leads to a complex reconstruction and a low-energy surface geometry, with the dopant ion residing close to the centre of the square-planar O$_{4}$ site [6]. Stable structures with square-planar O$_{4}$Pd are also communicated on Pd-doped CeO$_2$(111) [33] and edges of ceria NPs at intersecting [111] and [100] facets [35]. Four-fold coordinated Pd adatoms are identified in the most stable O$_{4}$Pd structures on the CeO$_2$(110) surface [20] and [100] facets [37]. The surface O$_{4}$ sites are also capable of suppressing the sintering of Ag$_{1}$ species, despite the fact that the Ag atom binds to the (100)-O$_{4}$ pocket more weakly than other Group VIII–XI metal atoms [37,38].

The aforementioned thermally stable structures are relevant to the development of the single-atom catalysts [36,37,39].

To understand how the role of the ceria support varies in specific catalytic processes, it is crucial to examine the interactions of the involved reactants with various active centres of CeO$_{2}$. For the ceria-supported metal catalysts of CO oxidation or CO$_{2}$ activation, primary interest are the interactions of O$_{2}$, CO, and CO$_{2}$ molecules with the metal–support interfaces [2,8,9,18,20,33,40–43]. Thus, modelling based on density functional theory (DFT) has recently addressed a variety of sites with M$_{1}$-O$_{2}$, M$_{1}$-CO, and M$_{1}$-CO$_{2}$ entities on ceria [8,9,18,20,40]. The adsorption of CO on a single Pd atom embedded in the defect-free CeO$_{2}$(111) surface and that containing O vacancies followed by NO reduction with CO was explored [18,40]. Surface complexes of CO and CO$_{2}$ taking part in the catalytic cycle of CO oxidation on Pd$_{1}$/CeO$_{2}$(110), including Pd$_1$-CO-Pd$_1$-CO$_{2}$, O$_1$Pd$_1$-CO species on the stoichiometric CeO$_{2}$(110) surface and Pd$_1$-CO$_{2}$, O$_{1}$Pd$_1$-O$_{2}$-Pd$_1$-CO ones on the O-deficient CeO$_{2}$(110) surface, were calculated [20]. The CO oxidation routes passing via O$_{1}$Pd$_1$-CO, Pd$_{1}$-CO, Pd$_{1}$-CO$_{2}$, O$_{2}$Pd$_1$-CO, and O$_{1}$Pd$_1$-CO$_{2}$ moieties on the defect-free CeO$_{2}$(111) surface [8] as well as on regular and O-deficient CeO$_{2}$(100) surfaces [9] were also quantified. The catalytic CO oxidation according to the Mars-van-Krevelen mechanism combines the elementary steps of oxygen donation from a surface active centre to adsorbed CO and the subsequent replenishment of the support by steam oxygen; the much slower conversions of the first step are found to be rate-determining [8,9,19,20]. In addition to the M$_{1}$-CO$_{2}$ structures, surface carbonate complexes can be formed on M$_{1}$-ceria interfaces before the desorption of CO$_{2}$. To this end, the formation of tridentate Pd$_{1}$-CO$_{3}$ carboxrates upon CO$_{2}$ adsorption at the interface of Pd$_{1}$ and O-deficient CeO$_{2}$(111) surface was simulated [13] and the CO vibration frequencies of various ceria-supported Pd-CO species were calculated [8,9]. Unlike the quite extensive computational studies of Pd$_{1}$CO$_{x}$-ceria systems outlined above, no simulations of analogous Ag$_{1}$CO$_{x}$-ceria systems have been communicated so far to the best of our knowledge.
Previous studies have developed structural models of low-energy CeO2 NPs [44–47] and established that their [100] nanofacets notably stabilise single d-metal atoms [38,41,44,48–51]. In this work, we consider monoatomic Pd and Ag species located on a Ce21O42 NP [49] as models appropriately describing surface composites formed by single-atom Pd and Ag with nanostructured ceria. These two metals, which are neighbouring in the Periodic Table, interact very differently with ceria and behave as M-based species involved in CO oxidation. The quantification and in-depth understanding of such differences are still missing in the literature.

This study aims to (i) determine the structures of the lowest-energy complexes with CO, CO2, and CO32− moieties resulting from the interaction of CO with Pd and Ag single atoms anchored to the O4-pocket sites of the stoichiometric and O-deficient ceria NPs, (ii) analyse the structure and properties of these nanostructured adsorption systems versus earlier investigated analogues formed on extended ceria surface containing M1 centres, (iii) evaluate and rationalise the reactivity differences of Pd1/NP[100] and Ag2/NP[100] sites as active centres for CO oxidation (including the effect of M-atom on the formation of CO32− prior to CO2 desorption), and (iv) examine the vibrational fingerprints of the COx units accompanying the formation of various surface species. Obtained results related to all these aspects are summarised in the Conclusions section.

2. Models and Details of Calculations

Surface sites of the CeO2 substrate were represented by a putative global-minimum structure of stoichiometric NP Ce21O42 [46,47] exposing four O atoms on its top [100] nanofacet (a so-called O4-pocket [49]); see Figure 1a. M1/Ce21O42 models were created via anchoring a single M1 atom (M = Pd or Ag) to the O4-site of the NP; see Figure 1b,c. The removal of one O atom from the O4-pocket results in an O-deficient M1/Ce21O41 model with one O vacancy in ceria (not shown in Figures; see Supplementary Material for xyz-structures). CO adsorption does not change the number of O vacancies, whereas the oxidation of CO to CO2 and further transformation to CO32− require the expulsion of one or two O atoms from ceria, generating O vacancies. In the following, the number and origin of O vacancies in the NP Ce21O42 are labelled as NP[n/l], where n is a number of O vacancies present prior to CO adsorption (n = 0, 1) and l is a number of O vacancies created by the transfer of O atoms from ceria to the adsorbed CO to form CO2 or CO32− moieties (l = 0, 1, 2). For instance, the stoichiometric and O-deficient NP models M1/Ce21O42 and M1/Ce21O41 are referred to as M/NP[0/0] and M/NP[1/0], respectively.

![Figure 1](image_url)  
**Figure 1.** Models of Ce21O42 NP: (a) without metal atom; (b) with Pd atom anchored at [100] facet; (c) with Ag atom anchored at [100] facet. The Ce4+, Ce3+, Pd, Ag, and O atoms are shown in yellow, light blue, dark cyan, grey, and red, respectively. The atoms under the transparent plane are omitted for clarity in the Figures 2–4.

The Vienna ab initio simulation package (VASP) [52,53] was employed to determine equilibrium structures of various isomers of the MCOx/NP[n/x − 1] complexes formed by the interaction of a CO molecule with Pd/NP[n/0] and Ag/NP[n/0] sites and transition state structures connecting selected equilibrium structures. The plane-wave basis with a 415 eV cutoff for the kinetic energy was used along with the projector-augmented wave
description of the interactions of valence electrons (2s²2p⁴ for O, 4s¹4d⁹ for Pd, 5s¹4d¹⁰ for Ag and 5s²5p⁶6s²5d¹4f¹ for Ce) with the atomic cores [54,55]. The NP models were separated by a vacuum space of ~1 nm in the three Cartesian directions (typical cell dimensions 2 × 2 × 2 nm³) sufficient to eliminate the interaction between periodically repeated NP images [56,57]. All calculations were performed at the Γ-point of the reciprocal space. A generalised-gradient corrected (GGA) exchange-correlated functional PW91 [58] was utilised with the Hubbard-type on-site corrections U [59,60] for Ce4f states providing an improved description of Ce³⁺ ion formation in redox transitions [61,62]. The value of U = 4 eV (PW91 + U = 4 setup) were used in line with previous studies [45,48,61,63,64], though the usage of even such small U values may overestimate the formation energy of carbonates [62,65]. The minimum energy reaction paths MCO/NP[n/0] → MCO₂/NP[n/1] → MCO₃/NP[n/2] were represented with the points of the string method, and the transition states were approximated with polynomial splines [66,67].

Stabilities of the studied systems were quantified based on their formation energies \( E^f \):

\[
E^f = E(MCO_x/NP[0/x - 1]) - E(CO) - E(M) - E(NP[0/0])
\]

for the MCOₓ/NP models obtained from defect-free MCO/Ce₂₁O₄₂ structure and

\[
E^f = E(MCO_x/NP[1/x - 1]) - E(CO) - E(M) - E(NP[0/0]) + 0.5 \times E(O_2)
\]

for the MCOₓ/NP models obtained from O-deficient MCO/Ce₂₁O₄₁ structure, where \( E(O_2) \) is total energy of a free \( O_2 \) molecule. The binding energies \( E_b \) of CO and CO₂ molecules in the models under scrutiny were calculated as follows:

\[
E_b(CO) = E(MCO_x/NP[n/x - 1]) - E(CO) - E(M/NP[n/0]), \ x = 1–3; \ n = 0, 1
\]

\[
E_b(CO_2) = E(MCO_x/NP[n/x - 1]) - E(CO_2) - E(M/NP[n/1]), \ x = 2, 3; \ n = 0, 1
\]

The energies (3) and (4) of the same MCO₂/NP complex were used to estimate the energy of the overall oxidation process CO(gas) + M/NP[n/0] → CO₂(gas) + M/NP[n/1]:

\[
E_{ox} = E_b(CO)(MCO_2/NP[n/1]) - E_b(CO_2)(MCO_2/NP[n/1])
\]

or

\[
E_{ox} = E_b(CO)(MCO/NP[n/0]) + E_{CO_2}^* - E_b(CO_2)(MCO_2/NP[n/1]), \ n = 0, 1
\]

where \( E_{CO_2}^* \) is the energy of CO to CO₂ oxidation at a metal site; i.e., the heat of MCO/NP[n/0] → MCO₂/NP[n/1] transformation:

\[
E_{CO_2}^* = E(MCO_2/NP[n/1]) - E(MCO/NP[n/0])
\]

where, the asterisk indicates that CO and CO₂ molecules are adsorbed.

Harmonic vibrational frequencies of COₓ groups were calculated by diagonalising the mass-weighted Hessian matrix constructed of differences of the first derivatives of total energy, obtained by displacements by ±0.015 Å in all Cartesian directions of the M, C, and Oₓ atoms as well as neighbouring ceria atoms within 3.6 Å around them.

3. Results and Discussion

Lowest-energy geometries and formation energies \( E^f \) of metal-free COₓ/NP[n/x - 1] and metal-containing MCOₓ/NP[n/x - 1] complexes are shown in Figures 2–4 (for xyz-structures see Supplementary Material). Table 1 displays the parameters used to specify attachment modes (coordination) of the COₓ groups. Along with the notations MCOₓ/NP[n/x - 1], shorter ones MₓL and MₓLV were used for complexes with \( n = 0 \) and \( n = 1 \), respectively, where L is a sequential identifier of the relative energy of a given isomer among isomers with the same \( M, x \), and \( n \) (a—the most stable, b—the second most
stable, c—the third most stable). Ce ions with magnetic moments close to 1, at a variance to 0 for most of the cations, were qualified as Ce³⁺ ions resulting from the reduction of Ce⁴⁺ by electrons of MCOₓ moieties or O vacancies.

Table 1. Calculated parameters of the surface complexes shown in Figures 2–4, created by the interaction of CO with the pristine ceria Ce₂O₂⁻ₓ and metal–ceria M/Ce₂O₂⁻ₓ sites (M = Pd, Ag; n = 0, 1): interatomic distances—r, number of the Ce³⁺ ions—N, difference between the numbers of spin-up and spin-down electrons—m, binding energies of CO—E_b(CO) (Equation (3)) and CO₂–E_b(CO₂) (Equation (4)). Negative energy values correspond to exothermic processes.

| System # | r(M-C) pm | r(M-O) pm | r(Ce-O) b pm | r(C-O) c pm | N | m | E_b(CO) eV | E_b(CO₂) eV |
|----------|-----------|-----------|--------------|-------------|---|---|-----------|-----------|
| Pd₁aV    | 193       | 237       | 114          | 2           | 2 | -0.26 | -         |
| Pd₁b     | 241       | -         | -            | -           | - | -     | -         |
| Pd₁c     | 188       | -         | -            | -           | - | -     | -         |
| Pd₁AV    | 187       | -         | -            | -           | - | -     | -         |
| Ag₁aV    | 201       | -         | -            | -           | - | -     | -         |
| Ag₁a     | 198       | -         | -            | -           | - | -     | -         |
| 1aV      | 293       | -         | -            | -           | 0 | -0.26 | -         |
| 1aV      | 297       | -         | -            | -           | 0 | -0.23 | -         |
| Complexes with CO₂ |
| Pd₂a     | 206       | 247       | 2 × 127      | 2           | 2 | -1.43 | -1.20     |
| Pd₂b     | -         | 314       | 2 × 118      | 2           | 2 | -0.41 | -0.18     |
| Pd₂aV    | 193       | 237       | 268          | 129         | 4  | -2.33 | -0.72     |
| Pd₂bV    | 330       | -         | 321          | 2 × 118     | 4  | -1.77 | -0.16     |
| Ag₂a     | 356       | -         | 316          | 2 × 118     | 3  | -1.37 | -0.16     |
| Ag₂b     | 234       | -         | 268          | 122         | 3  | -1.22 | -0.01     |
| Ag₂aV    | 207       | -         | 249          | 2 × 132     | 3  | -1.13 | -0.10     |
| Ag₂bV    | 342       | -         | 348          | 2 × 118     | 5  | -1.10 | -0.07     |
| 2aV      | -         | 300       | 2 × 118      | 2           | 2  | -1.69 | -0.25     |
| 2bV      | -         | 310       | 2 × 118      | 4           | 2  | -1.16 | -0.15     |
| 2bV      | -         | 254       | 2 × 125      | 3           | 2  | -0.42 | 0.59      |
| Complexes with CO₃²⁻ |
| Pd₃a     | 249       | 207       | 260          | 2 × 133; 125| 4  | 2   | -1.68 | -1.44     |
| Pd₃b     | 265       | 209       | 248          | 129; 135; 129| 3  | 2   | -0.99 | -0.75     |
| Pd₃c     | -         | 212       | 245          | 133; 143; 121| 2  | 2   | -0.74 | -0.50     |
| Pd₃aV    | 275       | 211       | 258          | 132; 132; 128| 4  | 2   | -2.67 | -1.06     |
| Pd₃bV    | 288       | 211       | 247          | 131; 143; 122| 4  | 0   | -2.28 | -0.67     |
| Ag₃a     | 277       | 221       | 245          | 130; 135; 127| 3  | 1   | -2.72 | -1.49     |
| Ag₃b     | 289       | 233       | 247          | 132; 141; 122| 3  | 1   | -2.09 | -0.86     |
| Ag₃aV    | 273       | 216       | 265          | 130; 132; 130| 5  | 1   | -2.36 | -1.40     |
| Ag₃bV    | 291       | 211       | 255          | 129; 146; 122| 5  | 1   | -2.09 | -1.13     |
| 3a       | -         | -         | 237          | 133; 138; 122| 2  | 2   | -2.59 | -1.15     |
| 3b       | -         | -         | 250          | 129; 132; 129| 2  | 2   | -2.28 | -0.84     |
| 3aV      | -         | -         | 262          | 130; 131; 130| 4  | 2   | -3.23 | -2.22     |
| 3bV      | -         | -         | 229          | 133; 137; 122| 4  | 2   | -2.53 | -1.52     |

* For notations, see Figures 2–4; b Average distances of the O of COₓ moiety and nearest neighbour Ce atom; c Bond lengths within COₓ moiety; d Ce-C contact.

To specify the coordination modes of CO₂ in MCO₂/NP[n/1] and of CO₃²⁻ in MCO₃/NP[n/2] complexes, additional three-digit indices were used [68] resulting in the notation that being invoked only when discussing the coordination modes of CO₂ species. For carbonate complexes, a notation abc (integer a, b and c range from 0 to 3) determines numbers of substrate atoms, to which each O atom in CO₃²⁻ is coordinated. The middle digit b corresponds to the O atom with the highest coordination. A dot in indices a.bc or ab.c specifies that two O atoms of CO₃²⁻ (corresponding to a and b or b and c, respectively) form a bidentate bond with one atom of the substrate. Dotless abc identifiers designate CO₃²⁻ groups with each O atom coordinated to a different substrate atom. When the three-digits notation is used to specify coordination of CO₂ in MCO₂/NP[n/1]
complexes, the first digit a gives the number of substrate atoms coordinated to C atom. For instance, in Figure 3, each of the atoms of CO$_2$ in structure 111-Pd2a contacts different ions of the Pd/Ce$_{21}$O$_{41}$ subsystem, and in complex 1.21-Pd2aV, one of the O atoms of CO$_2$ attaches to Pd and Ce atoms of Pd/Ce$_{21}$O$_{40}$, and C atom also to Pd.

3.1. Structure, Charge State, and Relative Energies of Surface Complexes with CO$_x$

3.1.1. Adsorption Sites

The particle Ce$_{21}$O$_{42}$ exposes a {100} nanofacet (Figure 1a), which can bind metal atoms much stronger than its {111} nanofacets do [38]. We anchored single Pd and Ag atoms to the {100} nanofacet composed of four nearly coplanar two-coordinated oxygen centres forming an O$_4$-pocket with diagonals of 459 and 443 pm. This arrangement is appropriate for accommodating transition metal cations with typical M-O bond lengths of 185–210 pm [37]. The distances between the O$_4$-pocket atoms and the neighboring Ce atoms, 214–215 pm, are shortened versus the Ce-O distances of three-coordinated surface O atoms and four-coordinated inner O atoms, 230–250 pm.

The Ag atom binds by 2.27 eV to the O$_4$-site (Figure 1b), making the two diagonals of the latter almost equal. The two types of Ag-O bond lengths, 236 and 242 pm, agree with Ag-O distances of 239 and 241 pm calculated at the same theory level on a larger Ce$_{40}$O$_{80}$ NP [37]. Furthermore, the present location of the Ag atom 96 pm above the O$_4$-plane is close to the elevation by 90 pm on Ce$_{40}$O$_{80}$ [37]. A slightly larger above-plane elevation, by 102 pm, was calculated for a two-fold coordinated Ag single atom adsorbed on the Fe$_3$O$_4$(001) surface with energy 2.75 eV [69]. Ag atom adsorption moves O$_4$ centres upwards, elongating the involved Ce-O distances to 218–223 pm. One Ce ion reduced to +3 state, pointing to the Ag$^+$ oxidation state.

The Pd adatom is located nearly in the O$_4$ plane (Figure 1c), with an out-of-plane displacement of 18 pm, adopting a favourable planar coordination. All four Pd-O bonds are equal to 205 pm—exactly the same as for the Pd/Ce$_{40}$O$_{80}$ model [37]. The formation of PdO$_4$ species moves O atoms closer to Pd, contracting diagonals of the O$_4$ square to 408 pm and elongating the corresponding Ce-O distances to 230 pm—the value typical for three-coordinated O centres. The high adsorption energy of the Pd atom, 4.24 eV, further increases upon interactions with the O$_4$-site of larger ceria NPs [37]. Two Ce$^{3+}$ ions appeared upon Pd adsorption, indicating the oxidation state Pd$^{2+}$.

An O-deficient site is created by the removal of the weakest bonded O atom (with \( E(O_V) = 1.87 \) eV, Table 2) from the O$_4$-pocket of the Ce$_{21}$O$_{12}$ particle (Figure 1). Two Ce$^{3+}$ centres resulting from the O removal in the second Ce layer cause the elongation of the Ce$^{3+}$-O bonds by ~0.1 Å. O vacancy formation in the Ag/Ce$_{21}$O$_{42}$ model requires 2.08 eV (Table 2), nearly the same amount as for the metal-free O$_4$-site. Thus, an extra energy cost due to breaking the Ag-O bond (in addition to two Ce-O bonds of Ce$_{21}$O$_{42}$) is estimated at ~0.2 eV. Two Ag-O bonds are contracted to 2.15 Å upon O removal, whereas the third bond is elongated from 2.36 to 2.49 Å. A similar bonding situation has been found in our previous work, where an Ag single atom was anchored to the bottom [100] nanofacet of Ce$_{21}$O$_{42}$ NP [38]. Alternatively, the creation of an O-deficient Pd/Ce$_{21}$O$_{41}$ site requires substantial energy costs of 3.08 eV (Table 2).
Table 2. Reaction and activation energies ($E^\ddagger$) on the pristine ceria Ce$_{21}$O$_{42−n}$ and metal–ceria M/Ce$_{21}$O$_{42−n}$ models (M = Pd, Ag; n = 0, 1) depicted in Figures 2–4. Oxygen vacancy formation energies $E(O_V)$ are also shown. Negative energy values correspond to exothermic processes. All energies are in eV.

| Model $^a$ | E($O_V$) | $E_{\text{ex}}$ $^b$ | $E^*_{\text{CO}_2}$ $^c$ | $E^\ddagger_{\text{CO}_2}$ | $E^*_{\text{CO}_3}$ $^d$ | $E^\ddagger_{\text{CO}_3}$ |
|------------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ce$_{21}$O$_{42}$ | 1.87 | -1.44 | -1.43 | 1.02 | -0.90 | 0.27 |
| Ce$_{21}$O$_{41}$ | 2.31 | -1.01 | -0.92 | 0.82 | -2.07 | 0.82 |
| Ag/Ce$_{21}$O$_{42}$ | 2.08 | -1.21 | -0.52 | 0.88 | -1.50 | 0.78 |
| Ag/Ce$_{21}$O$_{41}$ | 2.28 | -1.03 | -0.35 | 0.53 | -1.23 | 1.73 |
| Pd/Ce$_{21}$O$_{42}$ | 3.08 | -0.23 | -1.30 | 0.51 | -0.25 | 1.83 |
| Pd/Ce$_{21}$O$_{41}$ | 1.70 | -1.61 | -0.59 | 1.06 | -0.34 | 1.80 |

$^a$ System on which initial CO adsorption takes place; $^b$ reaction energy of the CO oxidation CO(gas) + NP[n/0] → CO$_2$(gas) + NP[n/1] or CO(gas) + M/NP[n/0] → CO$_2$(gas) + M/NP[n/1]; $^c$ reaction energy of the CO$_2$ formation CO/NP[n/0] → CO$_2$/NP[n/1] or MCO/NP[n/0] → MCO$_2$/NP[n/1]; $^d$ reaction energy of CO$_2$/NP[n/1] → CO$_3$/NP[n/2] or MCO$_2$/NP[n/1] → MCO$_3$/NP[n/2].

Figure 2. Structures and formation energies $E^\ddagger$ (in eV) of the complexes created by the interaction of CO with the Ce$_{21}$O$_{42−n}$ sites ($n = 0, 1$): CO/Ce$_{21}$O$_{42}$ (1a), CO/Ce$_{21}$O$_{41}$ (1aV), CO$_2$/Ce$_{21}$O$_{41}$ (2a), CO$_2$/Ce$_{21}$O$_{40}$ (2aV, 2bV), CO$_3$/Ce$_{21}$O$_{40}$ (3a, 3b) and CO$_3$/Ce$_{21}$O$_{39}$ (3aV, 3bV). Activation energies ($E^\ddagger$) of selected transition states are shown near the dashed arrows connecting corresponding initial reactant and product. The C atoms are shown in dark grey. O atoms numbered with “1”, “2”, and “3” enter CO, CO$_2$, and CO$_3$ moieties, respectively. For further explanations, refer to the main text and the Figure 1 caption.
Evidently, an extra energy of ~1.2 eV is needed to cleave one Pd-O bond. Note that the Pd atom remains after O removal in a virtual square-planar environment with one coordination site empty and the lengths of the remaining three Pd-O bonds unchanged, 206–209 pm, vs. the PdO₄ site of Pd/CoCe₂O₄. No reduction of Ag⁺ and Pd²⁺ ions occurs upon O vacancy creation, since the leaving O atom donates two electrons to two Ce⁴⁺ ions, increasing the number of Ce³⁺ centres by two (to three for Ag/NP and to four for Pd/NP).

3.1.2. Carbonyl Species

Let us first consider the adsorption of a CO molecule on a Ce ion of bare ceria particles (Figure 2). For both the pristine and O-deficient structures, CO adsorption energy is very small, at −0.26 and −0.23 eV, respectively (Table 1). No geometry changes are calculated upon bringing together the CO molecule and ceria species. In particular, the C-O bond is retained at 114 pm as in the free CO molecule. The C end of the CO adsorbate is 293 (1a) and 297 pm (1aV) away from the nearest Ce⁴⁺ ion of NP (Table 1). CO forms angles at 176° and 172° with the Ce site. Thus, CO is rather physisorbed than chemisorbed on the Ce site of the pristine and reduced forms of the metal-free NP. The same geometry and adsorption energy of −0.26 eV (Table 1) was calculated for the Pd-containing Pd₁a structure with the CO molecule bound to a Ce⁴⁺ ion (Figure 3), indicating that the filling of the O₄-pocket by the Pd atom mainly affects the local structure of the PdO₄ site.

An even smaller CO adsorption energy, −0.13 eV, was calculated for the coordinatively saturated Pd centre of the PdO₄ site of the unreduced model (Pd₁b, Figure 3). Here, CO binds the Pd atom at an angle of 131° and rather long Pd–C contact of 241 pm.

CO adsorption causes minor distortions in the Pd/CoCe₂O₄ structure: Pd-O bonds extend from 205 to 207 pm, and Pd moves by 27 pm above the O₄ plane. The C-O bond elongates by just 1 pm vs. gas-phase CO. No CO adsorption was reported on Pd atoms in the PdO₄ environment saturated by two O centres of the CeO₂[110] surface and two O adatoms [9]. Furthermore, $E_b$(CO) < −0.2 eV was calculated for coordinatively saturated Pd atoms in PdO(100). Thus, a very low $E_b$(CO) for Pd₁b is related to the saturation of the coordination sphere of the Pd atom in the O₄-pocket of the [110] nanofacet by O atoms; the formation of an additional Pd-C bond competes with quite strong Pd-O bonds. The exceptional stability of Pd²⁺ ions in square-planar oxygen environment in CeO₂ materials is also claimed in other experiments [6,27,32]. Note that CO adsorption on all Pd-containing models does not change the oxidation state Pd²⁺, except for Pd₁c with an endothermic mode by 0.13 eV CO adsorption (Table 1), where a Ce³⁺ → Ce⁴⁺ transition indicated a reduction to Pd⁺.

In an O-deficient structure, Pd₁aV (Figure 3), the adsorbed CO occupies one of four places around Pd. This results in Pd-C bond shortening to 187 pm (Table 1), as in Pd₁- CO/CoCe₂(110) complexes bonded with two (Pd-C = 184 pm) and three O surface atoms (Pd-C = 188 pm) [20]. The Pd-C-O angle in Pd₁aV is close to 180°. The elongation of the C-O distance from 114 to 116 pm indicates noticeable d → 2π back-donation. In Pd₁aV, CO binds at a vacant coordination site around Pd, no bonds are broken, and adsorption induced geometry changes are minor. As a result, PdCO/CoCe₂O₄ is stabilised by 1.7 eV with respect to separated Pd/CoCe₂O₄ and CO fragments (Table 1). Interestingly, similarly strong CO binding as that for Pd₁aV, 1.77 eV, and a Pd-C distance of 186 pm were calculated for the two-fold coordinated single Pd atom in Pd₁/Fe₃O₄(001) [69]. The CO bond to the isolated Pd atom is also similarly strong, at 1.8 eV [70]. The values of 1.6 eV [8] and 1.9 eV [9] were calculated for Pd₁-CO/CoCe₂(111) and O₁Pd₁-CO/CoCe₂(100) complexes, respectively, with Pd₁ coordinated to three O atoms including that of isolated O₁Pd₁ species. A CO adsorption energy of −1.5 eV was calculated for the Pd₁-CO/CoCe₂(110) complex with the Pd⁺ ion between two three-fold O atoms [20]. In the series of complexes Pd₁-CO/CoCe₂(111), O₁Pd₁-CO/CoCe₂(111), and O₂Pd₁-CO/CoCe₂(111), $E_b$(CO) decreases (by module) with the growth of the Pd₁ coordination number from 1.6 to 0.9 and to 0.6 eV [8].
An even smaller CO adsorption energy, −0.13 eV, was calculated for the unreduced model (Table 1), and essentially independent of the coordination—AgO₄ or AgO₃—of the Ag atom. This adsorption energy value fits the calculated values of −0.85 eV for CO adsorption at the two-fold coordinated Ag single atom in the Ag₃/Fe₃O₄(001) site and −0.94 eV for the two-fold coordinated Ag atom at the AgO₂(111) surface well [69]. Structures of the AgCO fragments in Ag₁ and Ag₁aV are very similar (Figure 4). The Ag-C distance of ∼200 pm (Table 1) coincides with the value computed for the Ag₁CO moiety at Fe₃O₄(001). The C-O bond, 115 pm, is 1 pm longer than that in the free CO molecule. The Ag-C-O angle of ∼170° points to slight deviation from the typically favoured linear bonding geometry. In both structures, CO adsorption triggers a further displacement of Ag atom out-of-plane of neighbouring O atoms, reaching values of 132 and 152 pm for Ag₁ and Ag₁aV, respectively (vs. 96 and 60 pm for CO-free structures). Ag-O bond lengths vary substantially, ranging from 237 to 258 pm for the AgO₄ unit and from 224 to 264 pm for the AgO₃ unit. The notable distortions at the Ag/Fe₃O₄ interface are not reflected in CO adsorption energies. This finding is in line with the quite weak Ag-O bonding estimated at 0.2 eV (see Section 3.1.1).

In summary, the modification of the ceria NP with single Pd and Ag atoms strongly affects its affinity to CO. Effects of Pd and Ag atoms are different. Due to strong Pd-O
bonds, the saturated PdO₄ site is almost inactive towards CO adsorption, whereas the PdO₃ unit with a vacant coordination place readily traps CO with a substantial energy gain. In contrast, AgO₂ and AgO₃ centres with weak Ag-O bonds and a more flexible geometry are more prone to adsorb CO molecules with equally moderate energies.

3.1.3. Carbon Dioxide Species

For the metal-free ceria, only weakly adsorbed CO₂ species were calculated: binding energies are −0.25 and −0.15 eV for 2a and 2aV models, respectively (Table 1). These energies are comparable with the values calculated for linearly-adsorbed CO at extended CeO₂(100), (110), and (111) surfaces [71–76]. In both complexes, the linear geometry of CO₂ as in the gas-phase molecule is preserved: C-O bond lengths are 118 pm and the O-C-O angle is 178°. The C atoms of CO₂ molecules are located above the O vacancy parallel to the surface of NP (Figure 2); in case of 2a, the O atom from the low-lying layer moves up and forms an O-C contact of 288 pm (vs. 390 pm in 2aV).

![Figure 4](image-url)

**Figure 4.** Structures and formation energies $E^f$ (in eV) of the complexes created by the interaction of CO with the Ag/Ce₂₁O₄₋ₙ sites ($n = 0, 1$): AgCO/Ce₂₁O₄₂ (Ag1a), AgCO/Ce₂₁O₄₁ (Ag1aV), AgCO₂/Ce₂₁O₄₁ (Ag2a, Ag2b), AgCO₂/Ce₂₁O₄₀ (Ag2aV, 2bV), AgCO₃/Ce₂₁O₄₀ (Ag3a, Ag3b) and AgCO₃/Ce₂₁O₃₉ (Ag3aV, Ag3bV). Activation energies ($E^f$) of selected transition states are shown near the dashed arrows connecting corresponding initial reagent and product. For further explanations, refer to the main text and the captions to Figures 1 and 2.
The contacts of O atoms of the CO$_2$ group with Ce atoms are ~300 pm in 2a and 304–313 pm in 2aV (Table 1). All attempts to locate more stable structures with a bent CO$_2$ moiety have led to carbonate moieties (described in detail in Section 3.1.4). No minima corresponding to bent CO$_2$ structures of carboxylate type were found. The only located structure with distorted CO$_2$ (2bV) was found to be 0.75 eV less stable relative to the linear 2aV model. It features C-O bond lengths of 125 pm and an O-C-O angle of 131°. The O atoms of CO$_2$ are at 252 and 257 pm from Ce atoms. The positive CO$_2$ binding energy in 2bV of 0.6 eV (Table 1) indicates exothermic CO$_2$ release. Since only one Ce$^{3+}$ ion is present after CO to CO$_2$ transformation, CO$_2$ in 2bV is negatively charged, forming a CO$_2^-$ anion. Thus, CO$_2$ binds weakly and easily desorbs from bare Ce$_{21}$O$_{42-\gamma}$NP.

The metal-containing Pd/NP and Ag/NP models also feature structures with “linear” and “bent” CO$_2$ (Figures 3 and 4). Similar to the bare ceria, linear CO$_2$ is weakly bound in Pd$_2$b, Pd$_2$bV, Ag$_2$a, and Ag$_2$bV, by less than 0.2 eV (Table 1). All distances between atoms of CO$_2$ molecule and ceria are longer than 300 pm. In contrast, in “bent” CO$_2$ structures Pd$_2$a, Pd$_2$aV, Ag$_2$b, and Ag$_2$aV, CO$_2$ approaches more closely to the NP surface and forms C-M and O-Ce bonds at 193–234 and 250–270 pm, respectively. Interestingly, despite the sizable changes at the metal–adsorbate interface when going from “linear” to “bent” structures, the pairs Ag$_2$aV/Ag$_2$bV and Ag$_2$a/Ag$_2$b are isoenergetic within 0.15 eV. This observation supports our earlier finding that the formation of a new Ag-ligand bond (e.g., Ag-C with CO$_2$) does not require substantial energy (limited to 0.2 eV). The bonds of CO$_2$ in Ag$_2$b are symmetrically stretched to 121 pm and the O-C-O angle is reduced to 145°, thus indicating the formation of a weakly-bound carboxylate-like complex. CO$_2$ is coordinated to Ag via the C atom at a distance of 234 pm and forms an (O)C-Ag-O angle of 175°. The Ag atom in Ag$_2$bV/Ce$_{21}$O$_{41}$ rises above the O$_x$-plane by 52 pm (vs. 132 pm in AgCO/Ce$_{21}$O$_{42}$), similar to O-deficient adsorbate-free Ag/Ce$_{21}$O$_{41}$ complex (60 pm). Thus, the surrounding of the Ag center in Ag$_2$b is nearly square-planar. The formation of the CO$_2$ moiety in Ag$_2$aV does not lead to the entire detachment of the surface O* atom by adsorbed CO (Figure 4). Rather, the Ag$_2$aV model can be viewed as a complex with CO inserted into the O*-Ag bond; as a result, the O*-Ag distance is stretched from 227 to 287 pm. Upon this insertion, Ce-O* bonds of the Ce-O*-Ce bridge are elongated from 218–233 pm in Ag$_1$aV to 249–257 pm in Ag$_2$aV (Table 1). The shortest Ce-O* distance in Ag$_2$b is 268 pm. The CO$_2$ fragment in Ag$_2$aV is more strongly distorted than in Ag$_2$b: C-O bonds are 130 pm and the O-C-O angle is quite small, at 114°. The Ag-CO$_2$ distance (207 pm) is typical for metal–CO$_2$ complexes with an η$^1$-C type of CO$_2$ coordination [77]. Energies of Ag$_2$b and Ag$_2$aV models differ by 1.9 eV, the value close to the O vacancy formation energy at the O$_4$-pocket (Table 2).

The PdCO$_2$-containing complexes, Pd$_2$a and Pd$_2$aV, with a “bent” CO$_2$ moiety (Figure 3) are characterised by substantial CO$_2$ binding energies of −1.2 and −0.7 eV, respectively (Table 1). Both models exhibit a carboxylate-like structure of CO$_2$: C-O bonds are 124–130 pm long and the O-C-O angle is 130 ± 3°. In the Pd$_2$a structure, CO$_2$ is η$^1$-coordinated to the Pd atom with the Pd-C distance, 206 pm, comparable to three Pd-O bonds around the metal center, 208–220 pm. In the Pd$_2$aV complex, the CO$_2$ molecule is η$^2$-coordinated to Pd via the short Pd-C bond, 193 pm, and long Pd-O contact of 237 pm; two other Pd-O bond lengths are 205–220 pm. The Pd atom in both Pd$_2$a and Pd$_2$aV complexes is nearly in a square-planar environment with Pd shifting from the ligand plane by 25–30 pm. Interestingly, no ceria-supported PdO$_3$ structures with calculated CO$_2$ binding energies more than −0.4 eV (by module) were found in the literature [8,9,20]. The larger values −0.82 eV [20] and −0.96 eV [8] were calculated for PdO$_2$ units at CeO$_2$(110) and CeO$_2$(111) surfaces. In part, this can be explained by a favourable square-planar geometry within the O$_3$Pd-CO$_2$ fragment formed at the [100] nanofacet of Ce$_{21}$O$_{42}$ NP. Indeed, such structures are hindered at extended CeO$_2$ surfaces by geometrical constrains.

Thus, similar to the CO case, the strongest bonding is calculated for the PdO$_2$ site with one vacant coordination place. This is followed by the PdO$_2$ unit with two vacant valences, which binds CO$_2$ in a side-on fashion. Both structures are characterised by CO$_2$ bonding.
The adsorption of CO\(_2\) in linear mode results in an energy gain less than 0.2 eV for both Pd and Ag derivatives. In contrast to the Pd derivatives, both “linear” and “bent” modes have similar small adsorption energies for the Ag systems. Thus, AgO\(_3\) and AgO\(_2\) sites again do not show differences in adsorption properties, whereas their Pd analogs do.

### 3.1.4. Carbonate Species

Carbonate species are formed upon the coordination of the CO\(_2\) molecule via the C atom to an O center of ceria NP. Thus, CO\(_3^{2-}\) formation can be considered as a form of CO\(_2\) adsorption, and CO\(_2\) binding energy can be applied to the estimation of the stability of these carbonate species.

The carbonate-like CO\(_2\) adsorption at bare ceria NPs with binding energies of 0.84–2.22 eV (Table 1) is the most exothermic of all types of CO\(_2\) coordination discussed above. The strongest binding of 2.22 eV is calculated for the tridentate 2.2.2-structure (3aV, Figure 2), with each O atom of the CO\(_3\) moiety coordinated to two Ce ions. The flat-lying carbonate fragment of 3aV fills two O vacancies with its oxygen atoms; i.e., all O atoms of the CO\(_3\) moiety are in neighbouring O-positions of the O\(_4\)-pocket. The E\(_2\)(CO\(_2\)) energy for 3aV is between –1.9 and –2.3 eV, respectively, calculated for its formal 2.2.2-CO\(_3\) analog on regular CeO\(_2\)(100) [78] and bidentate 220-CO\(_2\) on O-deficient CeO\(_2\)(110) [74]. The 2.2.2-model features three O-C bonds equally stretched to 130 pm and O-C-O angles of 118 ± 2°. Three of four Ce\(^{3+}\) ions are located in the Ce\(_4\) square just below the O\(_4\)-pocket of the [100] nanofacet. The other tridentate 1.21-structure 3b is stabilised by only 0.84 eV relative to the sum CO\(_2\) + NP (Table 1). Here, each of the two O atoms of CO\(_2\) has only one contact with Ce ions of 238 and 247 pm. As in the 3aV model, the CO\(_3\) fragment in 3b has a slightly distorted C\(_{3y}\) symmetry, with C-O bonds of 130 ± 2 pm and O-C-O angles of 117–122°. Its CO\(_3\) plane is tilted by 40° relative to the Ce\(_4\) layer. The CO\(_2\) binding energy in the 1.21-carbonate is comparable to value –0.72 eV calculated for the flat-lying 2.21-CO\(_3\) structure [71] formed upon CO adsorption at the stoichiometric CeO\(_2\)(100) surface with every second atom of the O layer removed. The deletion of an O atom from 1.21-3b to give 2.2.2-3aV costs only 0.67 eV. Thus, energy for the removal of a lattice O atom (–2.3 eV for formation of a 2nd O vacancy) is compensated by the formation of two new O-Ce contacts in 3aV with ~1.6 eV energy gain. At variance, the energy difference between two 1.20-structures 3a → 3bV, with a bidentate coordination, 1.68 eV, does not decrease with respect to E(O\(_y\)) for Ce\(_{22}\)O\(_42\) → Ce\(_{22}\)O\(_44\) transition, since both models have a similar bonding pattern of carbonate species. Thus, not surprisingly, the CO\(_2\) binding energies for 3a and 3bV models are not very different, at –1.15 and –1.52 eV, respectively (Table 1). In both 3a and 3bV models, the CO\(_3\) moiety is tied by three O-Ce bonds at 227, 238, and 245 pm. The three O-C bond lengths are different and increase from 122 to 133 and to 137 pm with the growing coordination number of O atom from 0 to 1 and to 2, respectively. Notably, at the O-deficient ceria, the flat-lying structure 3aV is preferred over the standing one 3bV by 0.7 eV. A similar difference of 0.84 eV was calculated for CO\(_3\) moieties oriented parallel and perpendicular to the O-defective CeO\(_2\) (100) facet [71]. The trend of destabilising carbonate species at ceria substrates upon surface enrichment by O atoms [71] is also supported by the present data.

Three types of carbonate structures—standing (perpendicular), tilted and flat-lying (parallel)—were also located for metal-containing ceria NPs (Figures 3 and 4). The “standing”-type carbonate species is coordinated in a bidentate way in 1.30-models Pd3c, Pd3bV, Ag3b, and Ag3bV. These structures are very similar to 1.20-carbonates 3a and 3bV at bare ceria NPs, with the difference that the CO\(_3\) moiety is additionally bound with the M center via one short M-O bond of 211 pm (233 pm in Ag3b). This extra metal–oxygen bond induces the elongation of other three O-Ce contacts by 5–15 pm as well as elongates O···CO\(_2\) contact by 4–9 pm, which probably weakens CO\(_2\) binding from –1.15–1.52 eV in metal-free models to −0.86–1.13 and −0.39–0.50 eV in Ag- and Pd-carbonates, respectively (Table 1). Thus, for Pd-systems, carbonate-like CO\(_2\) adsorption in a “standing” mode is
weaker than adsorption in carboxylate PdCO₂ form. Notably, Pd is in a zero-oxidation state in both types of complexes.

Stronger CO₂ bindings, of −1.44 and −1.40 eV, were calculated for the “flat-lying” structures 2.2.1-Pd₃a and 2.2.2.-Ag₃aV, respectively (Table 1). The CO₃ fragment is bidentately coordinated with two M-O contacts: almost equal in Pd₃a (207 and 211 pm) and asymmetric in Ag₃aV (216 and 265 pm). In the Pd₃a structure, all O atoms of the CO₃ moiety leave their lattice positions to form short Pd-O bonds (Figure 3). This leads to the creation of a CO₃²⁻ unit with a formal charge of −2 and oxidation of Pd to the +2 oxidation state. Even shorter M-O bonds are formed between metal centres and O atoms of the ceria support: 201–202 pm for Pd-O and 206 pm for Ag-O bonds. Thus, the Pd atom is four-coordinated whereas Ag is three-coordinated by O ligands. Importantly, the PdO₄ unit in Pd₃a is in a slightly distorted stable square-planar configuration. Likely, this contributes greatly to making Pd₃a the most energetically favourable among all studied ceria-supported PdCO₃ species. The Pd₃a complex is even 0.25 eV more stable than another square-planar structure: carboxylate Pd₂a complex with O₃PdCO₂ unit. The plane of the CO₃ subsystem forms a small angle of about 20° with the O₃M plane. The “lying” Ag₃aV structure is only 0.27 eV stabilised with respect to “standing” Ag₃bV, whereas the analogous stabilisation for Pd₃a → Pd₃c transition reaches 0.87 eV.

The Ag₃a 1.21-complex with the “tilted” coordination mode of CO₃ is the most favourable Ag-carbonate structure with a CO₂ adsorption energy of −1.49 eV (Table 1). Similar to the 1.30-model Ag₃b, the CO₂ moiety in the Ag₃a structure is tied in an η₁-C,O fashion with ceria support by means of two bonds. While the distance O-C,O···Ce is the same in Ag₃a and Ag₃b, the O···CO₂ contact in Ag₃a is shortened to 135 pm from 141–146 pm in Ag₃b. The shorter Ag-O contact of 221 pm (vs. 233 pm in Ag₃b) is formed with the O atom, which has no bonds with CeO₂; this is comparable to the Ag-O bond length of 218 pm with ceria. Remarkably, “tilted” 1.21-complex Ag₃a is by 0.63 eV stabilised with respect to “standing” 1.30-model Ag₃b with an E(CO₂) of −0.86 eV and reaches a CO₂ adsorption energy of −1.52 eV of the metal-free “standing” 3bV model. 1.21-Ag₃a complex has a nearly identical CO₂ adsorption energy (within 0.1 eV) to the “lying” 2.2.2.-Ag₃aV model. In both complexes, the cationic Ag⁺ center is three-coordinated. Despite the closer contact of the CO₃ unit with ceria support in the 2.2.2-model, its formation from the Ag₃a structure by the removal of O bound to the Ag atom requires a substantial energy of 2.18 eV. In contrast, O deletion from 1.21-Pd₃b to give 2.2.1-Pd₃aV is endothermic by only 1.55 eV. Both “tilted” complexes, Pd₃b and Pd₃aV, have CO₂ adsorption energies of −0.75 and −1.06 eV, respectively, bracketing the value for the “tilted” metal-free 3b complex. Note that the Pd₃b → Pd₃aV transition is associated with the reduction of the Pd centre from Pd²⁺ to Pd⁰.

In summary, carbonate CO₂²⁻ species show coordination patterns different from CO and CO₂ moieties: they tie to the ceria support or metal centres via O atoms, whereas the C atom does not participate in adsorbate–substrate interaction. From the comparison of CO₂ binding energies at the metal-free and M-containing sites, it follows that CO₂ binds slightly more strongly in MCO₃/NP[0/2] structures than in CO₃/NP[0/2]. Conversely, the creation of an extra O vacancy stronger stabilises the formation of the carbonates at metal-free NPs than that at metal-containing NPs.

3.2. Reaction Energies

In this section, we consider the energies of CO to CO₂ oxidation, Eₐ(ox), and of CO₂ to CO transformation, Eₐ(CO₂), along with the corresponding activation barriers, E̸, calculated for Pd/NP and Ag/NP models in comparison with the bare NP model. Data in Table 2 show that i) all these reactions are exothermic and ii) activation barriers for the carbonate formation are often higher than for the oxidation of CO.

Bare NPs adsorb CO very weakly, by less than 0.3 eV (Table 1, Figure 2). The extraction of lattice O and the formation of ceria-supported CO₂ yield energies of 0.9–1.4 eV and require 0.8–1.0 eV of activation (Table 2). Because of the low CO₂ desorption barriers,
0.15–0.25 eV (Table 1, $E_{\text{des}}(\text{CO}_2) = -E_{\text{d}}(\text{CO}_2)$ for 2a and 2aV), the formed CO$_2$/Ce$_{21}$O$_{42}$ and CO$_2$/Ce$_{21}$O$_{41}$ complexes can quite easily decompose. Otherwise, they are expected to exothermically transform into carbonates with activation barriers ranging from low—0.27 eV (for CO$_2$/NP[0/1])—to moderate—0.82 eV (for CO$_2$/NP[1/1])—values. The thermodynamic stability of such surface carbonate complexes makes them most probable candidates for experimental detection [68].

CO binds very weakly at the defect-free PdO$_4$ site of the Pd/NP[0/0] complex with an adsorption energy of $-0.1$ eV (Pd1b in Table 1). CO$_2$ can form via the interaction of the adsorbed CO with a lattice O atom. The process, which is exothermic by 1.3 eV, requires the overcoming of a barrier of 0.5 eV (Table 2). The formed CO$_2$ molecule is quite strongly bound, with a desorption energy of 1.2 eV (Table 1, $E_{\text{des}}(\text{CO}_2) = -E_{\text{d}}(\text{CO}_2)$ for Pd2a).

Overcoming an even higher barrier of 1.8 eV (Table 2) is needed to extract one more lattice O centre and activate the transformation of CO$_2$ to CO$_3^{2-}$, which is exothermic by only 0.25 eV. CO is strongly, by 1.7 eV, adsorbed at the O-deficient PdO$_3$ site (Pd1aV in Table 1). The formed stable O$_3$PdCO species can transform to O$_2$PdCO$_2$ with an activation barrier of 1.1 eV and moderate reaction exothermicity of 0.6 eV (Table 2). Slightly exothermic by 0.3 eV, the formation of carbonate is hindered by a high energy barrier of 1.8 eV. A much lower energy barrier of 0.7 eV ($-E_{\text{d}}(\text{CO}_2)$ for Pd2aV in Table 1) is required to desorb the CO$_2$ molecule into the gas phase. Thus, the most likely ceria-supported Pd-intermediates to be detected in reaction medium are saturated square-planar O$_2$PdCO/NP (Pd1aV) and O$_3$PdCO$_2$/NP (Pd2a) complexes whose formation proceeds with a sizable energy release (1.3–1.7 eV) and moderate activation barriers of 0.5 eV and whose decomposition is hindered by substantial barriers of about 1.1–1.2 eV.

The reactivity of Ag-containing systems is different (Table 2). CO adsorption on defect-free and O-deficient Ag/NP systems occurs with a moderate energy gain of 0.8 eV (Table 1). The formed O$_4$AgCO and O$_2$AgCO species are converted into the corresponding O$_2$AgCO$_2$ and O$_2$AgCO$_2$ species with a similar exothermicity around 0.4 eV, but the activation barrier for the more O-saturated complex O$_4$AgCO, 0.9 eV, is 0.4 eV higher than that for O$_2$AgCO (Table 2). Despite the high exothermicity of 1.2–1.5 eV, the transformation to carbonates is hindered by barriers of ~0.8–1.7 eV. Alternatively, the decomposition with CO$_2$ desorption should proceed quite readily (see $-E_{\text{d}}(\text{CO}_2)$ values for Ag2b and Ag2aV in Table 1). Thus, the carbonyl complexes O$_4$AgCO/NP (Ag1a) and O$_3$AgCO (Ag1aV), which are easily formed with notable energy gains, are expected to be detectable in a reaction medium. The detection of carboxylate AgCO$_2$/NP (Ag2b and Ag2aV) complexes seems problematic due to their instability with respect to CO$_2$ desorption.

We estimated the propensity of CO to CO$_2$ transformation by the energy of the CO(gas) + M/NP[n/0] $\rightarrow$ CO$_2$(gas) + M/NP[n/1] oxidation reaction, $E_{\text{ox}}$ (Equations (5) and (6)). It is directly connected with the ease of O release from the ceria lattice and O vacancy creation (Table 2).

Let us compare the oxidation reaction energy $E_{\text{ox}}$ calculated for the O$_4$-site of CeO$_2$ NP with the calculated energies for clean ceria surfaces [65,71,74,79,80] and the Pd$_1$–ceria interfaces [8,9,20]. This reaction was found to be slightly, by 0.4–0.6 eV, exothermic on bare CeO$_2$(111) [74,79] and notably more exothermic on CeO$_2$(110) [65,74,78,79], at 1.1–1.8 eV. The calculated reaction exothermicity further drastically increases to 3.1 eV for the CeO$_2$(100) surface with the most exposed O atoms [71]. Our calculated $E_{\text{ox}}$ energies for the stoichiometric and O-deficient NP[100] sites, $-1.44$ and $-1.01$ eV, respectively (Table 2), are considerably lower than those for the CeO$_2$(100) surface, but in a similar range to that for CeO$_2$(110) (assuming that the $E_{\text{ox}}$ value should increase by ca. 0.5 eV when the U value is increased from 4 to 5 eV [62]).

At the Pd$_1$/CeO$_2$(100) and O$_1$Pd$_1$/CeO$_2$(100) sites, the conversion of CO to CO$_2$ was characterised by energy yields of 0.6 and 1.2 eV [9], respectively—markedly lower than at the pristine CeO$_2$(100) surface. The reaction is also moderately exothermic at the Pd$_1$/CeO$_2$(110) interface, by 1.2 eV [20], and highly exothermic at the isolated O$_1$Pd$_1$ and O$_2$Pd$_1$ species on the CeO$_2$(111) surface, by 2.9 and 2.7 eV [8]—much more exothermic than
at the regular CeO$_2$(111) surface because of exposing weakly bonded O atoms. Compared to the above-mentioned transformations, that at Pd/NP[0/0] has the lowest $E_{ox}$ of $-0.23$ eV. There, the formal migration of an O-atom of the O$_2$Pd moiety to become a part of CO$_2$ molecule is difficult even in comparison with the three-coordinated O centre of the regular CeO$_2$(111) surface. For the conversion at the Pd/NP[1/0] site with $E_{ox} = -1.61$ eV, the relocation of the second O atom of the O$_2$Pd moiety is more favourable than of the O atom of the isolated O$_2$Pd$_1$ moiety on CeO$_2$(100) or Pd$_1$ at CeO$_2$(110), but less beneficial than that of O$_2$Pd$_1$ or O$_2$Pd$_3$ ad-species on CeO$_2$(111). For the reactions on Ag/NP[n/0] sites, the energy $E_{ox}$, $1.0–1.2$ eV, is slightly lower than on the Pd/NP[1/0] site, thus approaching $E_{ox}$ values for O$_2$Pd$_1$/CeO$_2$(100) and Pd$_1$/CeO$_2$(110) systems. Therefore, our model ceria particle with the Pd atom adsorbed on the O-defective [100] nanofacet appears to be more reactive in CO to CO$_2$ oxidation than its formal analogue of the Pd-doped extended CeO$_2$(100) surface.

Thus, the trend for lowering $E_{ox}$ in bare and M-containing ceria systems is Pd/NP[1/0] $>$ NP[n/0] $\approx$ Ag/NP[n/0] $>$ Pd/NP[0/0], which correlates with the growth of the O vacancy formation energy in the same row (Table 2). Note that the reactivity in CO oxidation of both Ag/NP complexes—with and without an O vacancy near the Ag atom—is similar. Conversely, the presence of an O vacancy in the vicinity of Pd atom is mandatory for CO oxidation at Pd/NP systems to proceed. This makes two consequent steps of CO oxidation at the Pd/Ce$_{27}$O$_{42}$ nanoparticle problematic. Such characteristics of the studied models as moderately strong CO adsorption, exothermic overall CO oxidation process, sufficiently low barriers of MCO to MCO$_2$ transformations, and ease of CO oxidation render CO oxidation by lattice ceria oxygen atoms more favourable at the sites with Ag than with Pd. Comparing the reaction and activation energies of CO to CO$_2$ to CO$_2$ conversions for M-containing ceria NPs, we conclude that the most probable species to be observed experimentally are AgCO and PdCO carbonyls and carboxylic PdCO$_2$ species. Unlike purely ceria nanoparticles, the formation of silver and palladium carbonates is prohibited by high activation barriers. We note, however, that for precise information on the species present in the reaction medium at equilibrium, a microkinetic modelling is required, which is out of the scope of the present study.

### 3.3. CO$_x$ Vibrational Fingerprints

Several studies reported measured [7,9,16,25,26,28,68,81] and calculated [8,9,68,82–84] vibrational frequencies of CO, CO$_2$, and CO$_2^{2-}$ groups in the complexes formed by the interaction of CO or CO$_2$ with cerium-based substrates. The calculated frequencies for selected stretching vibrations of CO$_x$ subsystems of the structures displayed in Figures 2–4 are collected in Table 3.

Our modelling revealed that the CO stretching frequency, $\nu$(CO), for the molecule attached to a cerium ion in M-free systems 1a and 1aV and Pd-containing model Pd1a shifts by 27–34 cm$^{-1}$ to the short-wave region, which agrees with the measured blue shifts of 27–32 cm$^{-1}$ (vs. 2143 cm$^{-1}$ for free molecule [85]) for CO interacting with the Ce$^{4+}$ centres of the nanostructured CeO$_2$ [19,86]. Note that the quantitatively precise reproduction of measured vibrational frequencies of CO on ceria requires going beyond the U-corrected generalised-gradient exchange-correlation functionals to hybrid-type functionals [81]. In contrast, $\nu$(CO) for the fragments with M$^{1+}$CO bonding formed on M/NP[n/0] substrates shows redshifts of 50–113 cm$^{-1}$, consistent with the C-O bond elongation by 1–2 pm. Among the models containing Pd$_1$ species, the Pd1b complex with Pd$^{2+}$ cation coordinated by four two-coordinated O anions reveals a medium redshift of 84 cm$^{-1}$, and the maximum redshifts of 109–113 cm$^{-1}$ are identified for the other two complexes, Pd1c and Pd1aV, with three-fold coordinated Pd$^{+}$ and Pd$^{2+}$ cations (Table 3). For the earlier examined systems with Pd-CO bonds, the redshifts $\Delta \nu$(CO) were calculated to increase from 6 to 96 cm$^{-1}$ in the order O$_2$Pd$_1$/CeO$_2$(111) $< O_1$Pd$_1$/CeO$_2$(100) $\approx$ O$_1$Pd$_1$/CeO$_2$(111) $< $ Pd$_1$/CeO$_2$(100) $<$ Pd$_1$/CeO$_2$(111) [8,9]. These values are comparable with those attributed to the CO molecule contacting one Pd atom in experimental studies of Pd/CeO$_2$, 13–123 cm$^{-1}$ [7,28]
and 10–69 cm\(^{-1}\) \cite{9,16,25} and PdO/CeO\(_2\), 58 cm\(^{-1}\) \cite{26}. Note that the \(\Delta \nu(\text{CO})\) redshifts for CO coordinated to the supported Pd cations are opposite to the blue shift for the free PdCO\(^+\) ion, measured at 63 cm\(^{-1}\) and calculated at 75 cm\(^{-1}\) (B3LYP), but approach a redshift for the neutral PdCO molecule, measured at 87 cm\(^{-1}\) and calculated at 99 cm\(^{-1}\) \cite{70}. The redshifts of \(\nu(\text{CO})\) for Ag1a and Ag1aV complexes, at 50 and 61 cm\(^{-1}\), respectively, are smaller than those for the Pd1-CO moieties and correspond to about one-third of the calculated redshift for the AgCO molecule, 144 cm\(^{-1}\) \cite{87}. Similarly large frequency redshifts to those obtained for CO on single Ag and Pd cations on a ceria NP were calculated for CO adsorbed on Pt\(^+\) and Pd\(^{2+}\) cations anchored to ceria \cite{83}.

**Table 3.** Calculated vibrational frequencies \(\nu(\text{CO})\), \(\nu(\text{CO}_2)\) and \(\nu(\text{CO}_3)\) for the systems depicted in Figures 2–4 along with the corresponding frequency shifts \(\Delta \nu(\text{CO})\) and \(\Delta \nu(\text{CO}_2)\) with respect to calculated vibrational frequencies of free molecules CO (\(\nu(\text{free CO}) = 2131 \text{ cm}^{-1}\)) and CO\(_2\) (\(\nu_{\text{asym}}(\text{free CO}_2) = 2363 \text{ cm}^{-1}\)).

| System \(\#\) | \(\nu(\text{CO})\) cm\(^{-1}\) | \(\Delta \nu(\text{CO})\) cm\(^{-1}\) | \(\nu(\text{CO}_2)\) cm\(^{-1}\) | \(\Delta \nu(\text{CO}_2)\) cm\(^{-1}\) | \(\nu(\text{CO}_3)\) cm\(^{-1}\) |
|---------------|------------------|-----------------|------------------|-----------------|------------------|
| **Complexes with CO** | | | | | |
| Pd1a | 2158 | 27 | - | - | - |
| Pd1b | 2047 | -84 | - | - | - |
| Pd1c | 2022 | -109 | - | - | - |
| Pd1aV | 2018 | -113 | - | - | - |
| Ag1a | 2081 | -50 | - | - | - |
| Ag1aV | 2070 | -61 | - | - | - |
| 1a | 2162 | 31 | - | - | - |
| 1aV | 2165 | 34 | - | - | - |
| **Complexes with CO\(_2\)** | | | | | |
| **Linear O-C-O** | | | | | |
| Pd2b | - | - | 2323 | -40 | - |
| Pd2bV | - | - | 2332 | -31 | - |
| Ag2a | - | - | 2348 | -15 | - |
| Ag2aV | - | - | 2350 | -13 | - |
| 2a | - | - | 2354 | -9 | - |
| 2aV | - | - | 2360 | -3 | - |
| **Bent O-C-O** | | | | | |
| Pd2a | - | - | 1535 | -828 | - |
| Pd2aV | - | - | 1628 | -735 | - |
| Ag2aV | - | - | 1332 | -1031 | - |
| Ag2b | - | - | 1950 | -413 | - |
| 2bV | - | - | 1657 | -706 | - |
| **Complexes with CO\(_3\)^2-** | | | | | |
| **Tridentate** | | | | | |
| Pd3a | - | - | - | - | 1573; 1221 |
| Pd3b | - | - | - | - | 1451; 1243 |
| Pd3aV | - | - | - | - | 1442; 1309 |
| Ag3a | - | - | - | - | 1511; 1233 |
| Ag3aV | - | - | - | - | 1434; 1337 |
| 3b | - | - | - | - | 1442; 1280 |
| 3aV | - | - | - | - | 1400; 1353 |
| **Bidentate** | | | | | |
| Pd3c | - | - | - | - | 1746; 1118 |
| Pd3bV | - | - | - | - | 1729; 1122 |
| Ag3b | - | - | - | - | 1689; 1126 |
| Ag3bV | - | - | - | - | 1752; 1169 |
| 3a | - | - | - | - | 1714; 1082 |
| 3bV | - | - | - | - | 1704; 1101 |

\(\#\) For system designations see Figures 2–4.
The highest frequencies of CO$_2$ stretching vibrations in 2a, 2aV, Ag2a, Ag2bV, Pd2b, and Pd2bV complexes with a linear CO$_2$ moiety are close to that of the IR active CO$_2$ asymmetric stretching frequency of the free molecule; the negative shift $\Delta \nu$(CO$_2$) does not exceed 40 cm$^{-1}$ (Table 3). The redshift $\Delta \nu$(CO$_2$) for a bent CO$_2$ fragment in 2bV, 706 cm$^{-1}$, is comparable to the experimental value for the free anion CO$_2^-$, 691 cm$^{-1}$ [88] (vs. measured $\nu$(CO$_2$) of free molecule 2349 cm$^{-1}$ [76]) and CO$_2^-$ species at TiO$_2$ surface, 709 cm$^{-1}$ [89]. The redshift $\Delta \nu$(CO$_2$) for the MCO$_2$/NP$[n/1]$ systems having the M-C bond from 413 to 1031 cm$^{-1}$ is associated with the bending of the CO$_2$ moiety and C-O bond elongation by 3 to 14 pm. The redshifts for PdCO$_2$/NP systems, 828 cm$^{-1}$ (Pd2a) and 735 cm$^{-1}$ (Pd2aV), are in the range of values 610–850 cm$^{-1}$ reported for coordination compounds with CO$_2$ attached to a single d-metal atom [76], while redshift $\Delta \nu$(CO$_2$) in Ag2b is smaller, at only 413 cm$^{-1}$. $\Delta \nu$(CO$_2$) for the CO$_2^{2-}$ group in Ag2aV with CO bonds elongated by 14 pm compared to those of free CO$_2$ matches the measured redshifts of 1020–1079 cm$^{-1}$ for carbonate ions at CeO$_2$ [90] and in Cs$_2$CO$_3$ [91]. Thus, the increased redshift $\Delta \nu$(CO$_2$) seems to correlate with C-O bond elongation, Ag2b < Pd2aV < Pd2a < Ag2aV (Table 1).

Differences in the length of the intramolecular C-O bonds are considered among the main factors determining the frequency splitting of CO$_2^{2-}$ stretching vibrations [68]. In tridentate CO$_2$/NP$[n/2]$ and MCO$_3$/NP$[n/2]$ complexes, the C-O bond lengths are 125–135 pm for the 1.11- and 1.21-modes, and in less symmetrical bidentate 1.20- and 1.30-structures, the C-O bonds cover a wider interval 121–146 pm. Overall, the splitting of C-O frequencies is lower for more symmetrical species. In particular, for the two highest frequencies ($\nu_1$ and $\nu_2$), it is only 47 cm$^{-1}$ for 2.2.2-structures, increasing to 97–133 cm$^{-1}$ for 2.2.1-isomers and 162–252 cm$^{-1}$ for 1.2.1- and 1.1.1-isomers (Table 3). For 1.2.0- and 1.3.0-carbonates, the splitting becomes as high as 563–632 cm$^{-1}$. According to earlier calculations, carbonate groups attached to nanostructured ceria surface by three oxygen atoms, represented by sets of 1.21-, 1.2.1- and 1.3.1-structures, are characterised by $\nu_1$ values from 1590 to 1490 cm$^{-1}$ [68]. With the inclusion of $\nu_1$ values for tridentate structures 3b and 3aV, this range extends to 1400 cm$^{-1}$. The calculated $\nu_1$ for tridentate carbonates corresponds to a broad experimental region of 1620–1450 cm$^{-1}$ attributed to the high-frequency vibrations of the carbonate groups formed on surfaces with oxygen vacancies, as well as on facet, edge, and corner sites of ceria particles [68]. The $\nu_1$ frequencies for tridentate carbonate Ag3a, Pd3a, Pd3b, Ag3aV, and Pd3aV complexes, of 1573–1434 cm$^{-1}$, fall between the limits of the clean surface of the nanostructured ceria. The $\nu_1$ values for 1.2.0-carbonate groups in 3a and 3bV systems are in a narrow range of 1718–1698 cm$^{-1}$ for bidentate carbonates [68] corresponding to the measured frequency interval of 1732–1722 cm$^{-1}$ [68]. The $\nu_1$ frequencies of the M-containing 1.30-complexes Pd3c, Pd3bV, Ag3b, and Ag3bV are in a broader range of 1752–1689 cm$^{-1}$, which includes the interval for bidentate CO$_2^{2-}$ on M-free ceria substrates.

The calculated $\nu_2$ frequency range of the complexes on the clean ceria surface is 1353–1227 cm$^{-1}$. This corresponds to the experimental frequencies of 1380 and 1280 cm$^{-1}$ [68]. The $\nu_2$ values for tridentate 1.21- and 2.2.1-carbonates P3b, Pd3aV, Ag3a, and Ag3aV for M-containing systems, at 1340–1220 cm$^{-1}$, are between these limits, and that for the 1.11-Pd3a isomer is only 6 cm$^{-1}$ below the low-end threshold. The $\nu_2$ frequencies are distributed between 1194 and 1082 cm$^{-1}$ for bidentate carbonates depicted in Figure 2 and those examined in [68]; the related experimental values are 1147–1133 cm$^{-1}$ [68].

The range of $\nu_2$ for the CO$_2$ moieties coordinated in a bidentate way at M/NP systems is 1170–1120 cm$^{-1}$. Thus, the frequency ranges are similar for the metal-free CO$_2$/NP and MCO$_3$/NP sites, making the discrimination between the metal-containing and bare ceria particles solely on the basis of the vibrational spectroscopy data problematic.

In summary, our calculations show that the C-O stretching vibrations of the ceria-supported PdCO and AgCO fragments feature redshifts up to $\sim$110 cm$^{-1}$, which is at variance with the blue shift at metal-free ceria. Redshifts of CO$_2$ asymmetric stretching frequency of the M-CO$_2$ fragments are much higher, up to $\sim$830 cm$^{-1}$ for carboxy-
late MCO₂ and further increasing by ~200 cm⁻¹ for carbonate AgCO₂. The two highest ν(CO₃) stretching frequencies of M-CO₃ structures lie in intervals 1755–1690 cm⁻¹ and 1170–1120 cm⁻¹ for the CO₃ moiety coordinated in a bidentate fashion and 1575–1430 cm⁻¹ and 1340–1220 cm⁻¹ for the CO₃ in the tridentate coordination.

4. Conclusions

CO₂ intermediates formed upon CO adsorption and oxidation on single M = Pd and Ag atoms coordinated to the O₄-site on the [100] facet of a Ce₂₁O₄₂ nanoparticle have been studied computationally. Equilibrium structures, CO₃ vibrational frequencies, and energetic parameters of various MCO₃-containing complexes have been determined. The influence of the creation of an O vacancy nearby the M atom has been also investigated. The stability of the CO₃ moieties anchored to the ceria-supported M atom is found to increase in the order MCO < MCO₂ < MCO₃, similar to the trend for CO₃ species adsorbed on M-free ceria NP.

Except for the Pd atom saturated by four O atoms of the ceria surface O₄-site, which is unable to properly adsorb CO, the doping of the ceria nanoparticle with Pd and Ag atom increases its propensity to bind the CO molecule with respect to bare ceria material. In particular, the CO adsorption energy value reaches −1.7 eV for a PdCO unit on a ceria nanoparticle with a nearby O vacancy. CO binding in AgCO complexes, regardless of the presence or absence of a nearby O vacancy, is moderately strong, at −0.8 eV. All these species are the most probable candidates to be detected experimentally, also due to the presence of moderate barriers for CO oxidation (0.5–1.0 eV). In contrast to the blue shift to CO adsorption on pristine ceria, red shifts of the C-O stretching (vs. free CO) have been calculated for MCO species anchored to ceria. The red shifts of the CO stretching frequency are higher for complexes of Pd and increase with the decreasing coordination of M from MO₄ to MO₃ for a particular metal: Ag/Ce₂₁O₄₂ (50 cm⁻¹) < Ag/Ce₂₁O₄₁ (61 cm⁻¹) < Pd/Ce₂₁O₄₂ (84 cm⁻¹) < Pd/Ce₂₁O₄₁ (113 cm⁻¹).

Carboxylate CO₂⁻ and carbonate CO₂²⁻ (for Ag-doped NP with an O vacancy) complexes featuring a bent CO₂ moiety are formed upon CO oxidation at the M/ceria interface. Contrary to AgCO₂-species, which are easily decomposed via CO₂ detachment, PdCO₂ moieties are prone to withstand decomposition due to significant CO₂ desorption energies of 0.7–1.2 eV. These PdCO₂ moieties anchored to ceria particles could be experimentally detected by the red shifts of the CO₂ asymmetric stretching frequency (vs. that of free CO₂ molecule) by 828 cm⁻¹ (one O vacancy nearby Pd) and 735 cm⁻¹ (two O vacancies nearby Pd).

Unlike pristine ceria, carbonate structures at ceria-supported Pd and Ag atoms are hardly formed before CO₂ desorption due to the high barriers of CO₂ transformation to CO₃²⁻ (up to 1.8 eV for PdCO₂ moieties) and weak CO₂ binding (below ~0.2 eV for AgCO₂ moieties). Detailed analysis of the vibrational spectra of MCO₃/NP complexes has shown that the two highest ν(CO₃) stretching frequencies lie in the well-resolved intervals 1755–1690 and 1170–1120 cm⁻¹ for the CO₃ moiety coordinated in a bidentate fashion and 1575–1430 and 1340–1220 cm⁻¹ for the carbonate groups in the tridentate coordination. These frequency ranges are similar to those for the M-free CO₃/NP sites. Thus, discrimination between the M-containing and bare ceria particles solely using vibrational spectroscopy data seems hardly possible.

In summary, such characteristics of the studied models as moderately strong CO adsorption, an exothermic CO oxidation process, sufficiently low barriers of MCO to MCO₂ transformations, and ease of CO₂ desorption render CO oxidation by lattice ceria oxygen atoms more favourable at the sites with Ag than with Pd.

Supplementary Materials: The following data are available online at https://www.mdpi.com/ article/10.3390/ma14226888/s1: Coordinates of the atomic positions of all considered Ce₂₁O₄₂−δ, CO₃/Ce₂₁O₄₂−δ, AgCO₂/Ce₂₁O₄₂−δ and PdCO₂/Ce₂₁O₄₂−δ complexes and selected transition state structures connecting these complexes along with their total energies.
Author Contributions: Conceptualisation, V.A.N., E.A.I.-S. and K.M.N.; methodology, V.A.N. and E.A.I.-S.; software, V.A.N. and S.S.L.; investigation, V.A.N. and S.S.L.; validation, V.A.N. and E.A.I.-S.; formal analysis, V.A.N., A.M.S. and E.A.I.-S.; resources, V.A.N. and E.A.I.-S.; data curation, V.A.N.; writing—original draft preparation, V.A.N., E.A.I.-S. and K.M.N.; writing—review and editing, V.A.N., E.A.I.-S., A.M.S., S.S.L. and K.M.N.; visualisation, V.A.N. and A.M.S.; supervision, V.A.N., E.A.I.-S. and K.M.N. All authors have read and agreed to the published version of the manuscript.

Funding: This work was conducted within the framework of the budget project No. 0287-2021-0012 for Institute of Chemistry and Chemistry Technology SB RAS. The work of K.M.N. was funded by the Spanish Government MCIN/AEI/10.13039/501100011033 via grants PGC2018-093863-B-C22, MDM-2017-0767 and PRX17/00348 as well as by the grant 2017SGR13 of the Generalitat de Catalunya.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article or Supplementary Material.

Acknowledgments: The authors thank the Supercomputer Center of the Institute of Computational Modeling SB RAS for providing computational resources. K.M.N. thanks the European Cooperation in Science and Technology program via the COST Action 18234.

Conflicts of Interest: The authors declare no conflict of interest.

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