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Stable Pd-Doped Ceria Structures for CH₄ Activation and CO Oxidation

Ya-Qiong Su,‡ Ivo A. W. Filot,‡ Jin-Xun Liu, and Emiel J. M. Hensen*‡

Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Supporting Information

ABSTRACT: Doping CeO₂ with Pd atoms has been associated with catalytic CO oxidation, but current surface models do not allow CO adsorption. Here, we report a new structure of Pd-doped CeO₂(111), in which Pd adopts a square planar configuration instead of the previously assumed octahedral configuration. Oxygen removal from this doped structure is favorable. The resulting defective Pd-doped CeO₂ surface is active for CO oxidation and is also able to cleave the first C–H bond in methane. We show how the moderate CO adsorption energy and dynamic features of the Pd atom upon CO adsorption and CO oxidation contribute to a low-barrier catalytic cycle for CO oxidation. These structures, which are also observed for Ni and Pt, can lead to a more open coordination environment around the doped-transition-metal center. These thermally stable structures are relevant to the development of single-atom catalysts.

KEYWORDS: Pd-doped ceria, square planar PdO₄, CH₄ activation, CO oxidation, DFT

CeO₂ (CeO₂) is a key component in environmental catalysis with main applications in the treatment of exhaust gases of combustion processes. The ability to reversibly store oxygen and the propensity to stabilize transition metals in high dispersion render CeO₂ a useful support for CO oxidation.⁴⁻³ Pd is already used in three-way catalytic converter technology, because it is cheaper than Pt and Rh and its combination with CeO₂ results in excellent low-temperature CO oxidation activity.⁴⁻⁵ Pd/CeO₂ is also an effective catalyst for the combustion of methane, which is of growing interest to avoid detrimental CH₄ slip from natural-gas powered combustion processes.⁹,¹⁰

For these oxidation reactions, the importance of a close interaction between Pd and CeO₂ has been stressed.⁴⁻⁷,¹¹ The identification of the nature of the active Pd sites in Pd/CeO₂ remains a considerable challenge. Ionic Pd in the surface or the bulk of ceria and metallic and oxidized Pd atoms, clusters, and nanoparticles on the surface have all been considered in this context.⁴⁻⁷,¹¹⁻¹⁵ Although metallic Pd nanoparticles on CeO₂ are active in CO oxidation,⁶ high catalytic performance at low temperature has been linked to doping of Pd ions into the CeO₂ surface.⁴,¹¹ On the contrary, we recently showed that isolated PdO₄ species are the active sites for low-temperature CO oxidation.¹⁶ Gulyaev et al. contended that the active sites for CO oxidation are highly dispersed PdO₄ clusters supported on a Pd–CeO₂ solid solution.²

For CH₄ oxidation, the role of ionic Pd has also been discussed.⁸,¹⁷ Trovarelli and co-workers suggested that the active sites are isolated square planar PdO₄ moieties in the CeO₂ surface.⁸,¹⁷ Lu and co-workers mentioned that ionic Pd in CeO₂ is more active than PdO on CeO₂.¹⁸ Tao and co-workers reported the promise of transition-metal dopants in CeO₂ for CH₄ oxidation.¹⁹ Thus, it is important to determine the way CH₄ is activated on Pd-doped CeO₂.

Determining the location of highly dispersed Pd in or on the CeO₂ surface remains an experimental challenge.⁵,¹⁷,²⁰ Priolkar et al. used EXAFS to show that Pd in Pd/CeO₂, prepared by a one-step solution combustion method, coordinates to only three O atoms.² Watson and co-workers reported that Pd and Pt prefer a square planar coordination in the bulk of CeO₂ in which each Pd atom is coordinated by four O atoms.²¹,²² Boronin and co-workers suggested that Pd²⁺ ions retain a nearly square planar coordination in Pd₄CeₓO₂₋ₓ solid solutions.²⁰ Quantum-chemical modeling can aid in determining the catalytic role of candidate structures of Pd-doped CeO₂. The most stable structure identified for single-atom Pd-doped CeO₂ involves replacement of a surface Ce atom by Pd₄⁻²⁶ which results in octahedral Pd species. A problem of this proposed structure is that it cannot adsorb CO.¹¹

We identified by state-of-the-art density functional theory (DFT) a novel stable structure for a single Pd atom doped in the CeO₂(111) surface. This structure is different from the octahedral configuration that has been previously considered to...
be the most stable structure of Pd-doped CeO$_2$(111). We will show that removal of surface oxygen is easier from the square planar Pd-doped CeO$_2$(111) structure than from the octahedral Pd-doped CeO$_2$(111) one. This results in increased CH$_4$ activation. While octahedrally coordinated Pd in ceria cannot adsorb CO, a low-barrier catalytic cycle for CO oxidation was found for the new structure, in which the flexibility of Pd upon CO adsorption and surface O atoms feature prominently.

The initial surface model was constructed by replacing a Ce atom by a Pd atom in the (111) surface of CeO$_2$. This substitution is favorable ($\Delta E = -3.62$ eV), in line with the literature. The resulting structure corresponds to the previously identified configuration in which Pd is octahedrally coordinated (Pd-dop-I in Figure 1). The energy to create an O vacancy ($V_0$) for Pd-dop-I ($\Delta E = 0.85$ eV) is much lower than for the stoichiometric CeO$_2$(111) surface ($\Delta E = 2.24$ eV), reflecting the weaker bonding of a surface O atom to Pd in comparison to Ce. Pd adopts a square planar coordination in the resulting defective Pd-dop-I-VO structure in which two O atoms lie in top surface, and the other two in the second O layer (Figure S2).

As the EXAFS study of Priolkar et al. suggested the existence of a stable structure with a lower Pd–O coordination, we carefully explored alternative structures of the Pd-doped CeO$_2$ surface. This resulted in the identification of a stoichiometric Pd-dop-II structure shown in Figure 1, in which the Pd atom is coordinated in a square planar manner by four O atoms, i.e., one surface O atom, two subsurface O atom, and one O atom in the third atomic layer of CeO$_2$ with respective Pd–O bond lengths of 1.92, 2.01, and 1.97 Å. This square planar Pd coordination can be obtained from the octahedral Pd-dop-I structure by a surface reconstruction, which involves a small barrier of only 0.53 eV. Pd-dop-I and Pd-dop-II are equally stable.

A square planar structure has already been reported for Pd doped in the less stable CeO$_2$(100) surface and the bulk of CeO$_2$. It is important to stress that this already known structure resembles Pd-dop-I-VO. The structure of Pd-doped-II is different from these structures as highlighted in Figure S2.

Different from Pd-dop-I, the formation of an O vacancy in Pd-dop-II is exothermic ($\Delta E = -0.56$ eV). This is important, because the resulting defective structure Pd-dop-II-VO is strongly thermodynamically favored over Pd-dop-I and its defective counterpart Pd-dop-I-VO. Figure 1 also shows that Pd-dop-I-VO is metastable, as it can very easily transform into the much more stable Pd-dop-II-VO structure ($E_{\text{act}} = 0.07$ eV). The removal of a second O atom from Pd–V$_0$II to obtain Pd-dop-II-2V$_0$ is unfavorable ($\Delta E = +1.09$ eV). This energy is, however, still much lower than the energy required to create an O vacancy in the stoichiometric CeO$_2$(111) surface. By removing the second O atom, two Ce$^{3+}$ ions are formed.

In order to determine the stability of the various structures as a function of temperature and O$_2$ partial pressure, we carried out an ab initio thermodynamics analysis. The resulting phase diagram in Figure 2 shows that Pd-dop-II-V$_0$ is the most stable structure at typical temperatures and in an oxygen atmosphere. The fully oxidized Pd-doped surface (Pd-dop-II) is only stable at very high O$_2$ pressure. The removal of another O atom from Pd-dop-II-V$_0$ will occur at very high temperature (T > 715 °C at 1 atm O$_2$ pressure). Removal of more O atoms from Pd-dop-II-2V$_0$ is even less favorable, costing more than the removal of O from the stoichiometric CeO$_2$(111) surface. This suggests that a single Pd atom embedded in the CeO$_2$(111) surface is very stable. Based on the oxygen vacancy formation energies, we can estimate under which conditions the O atoms close to Pd can be removed (see the Supporting Information). This would lead to the reduction of Pd, after which Pd can easily diffuse over the ceria surface and form metallic Pd clusters or large nanoparticles (NPs).

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In order to gain an understanding of the electronic structure of Pd-doped CeO$_2$(111), we studied the partial density of states (pDOS) for Pd-dop-I, Pd-dop-II, and Pd–V$_0$II. Figure 3
presents the partial DOS for the Pd atom and the adjacent O atom. There are no Ce$^{3+}$ ions in Pd-dop-I, implying that Pd is in the +4 oxidation state. This is also reflected by the unoccupied Pd-4d state located slightly above the Fermi level. These states become occupied in the Pd-dop-II structure, corresponding to the formal reduction of Pd$^{4+}$ to Pd$^{2+}$. This reduction is related to the cleavage of two of the Pd–O bonds, which results in electron transfer from the lattice O atoms to Pd. The changes in the geometric and electronic structures are corroborated by the increasing Pd–O bond lengths for these two O atoms and the appearance of an unpaired electron in one of the 2p orbitals of the lattice O atoms. The radical character of these two O atoms is also evident from their magnetic moment of 0.534 $\mu_B$. As no Ce 4f states are filled, the Pd atom is in the +2 oxidation state. Finally, the removal of one of these two O atoms to obtain Pd-dop-II-$V_{O}$ results in the conversion of the other O$^{−}$ ion to an O$^{2−}$ ion, as follows from the disappearance of the occupied 2p state in the DOS. When the second O atom is removed, two Ce$^{4+}$ ions are reduced to the +3 state, meaning that the Pd atom maintains the +2 oxidation state. The oxidation states of the two Pd configurations are in line with crystal field theory, which predicts that Pd$^{4+}$ (d$^6$) is preferentially octahedrally coordinated by O and that Pd$^{2+}$ (d$^8$) prefers to reside in a square planar oxygen coordination environment.

We then explored the reactivity of the various Pd-doped CeO$_2$ surface models towards the first C–H bond in CH$_4$. CH$_4$ directly reacts with a surface O atom to form a methyl radical and a surface hydroxyl species. Table 1 shows that CH$_4$ only weakly interacts with the surface. Therefore, C–H bond activation will follow an Eley–Rideal mechanism. The activation energies with respect to the gas phase for Pd-dop-I, Pd-dop-II, Pd-dop-II-$V_{O}$, and the stoichiometric CeO$_2$(111) surface are 0.75, 0.12, 0.83, and 1.36 eV, respectively. The activation energy is 1.14 eV for C–H activation by the O atom bound to Pd in Pd-dop-II-$2V_{O}$, similar to the value of 1.22 eV for the PdO(100) surface. For all of the transition states, the C–H and O–H bond lengths are between 1.13 and 1.45 Å, and the C–H–O valence angle is around 170°. After CH$_4$ dissociation, the H atom binds to a surface lattice O atom and the CH$_3$ radical will diffuse to another surface O atom. The activation energy of 1.36 eV for the stoichiometric CeO$_2$(111) model agrees with the value reported in the literature. Clearly, C–H bond activation in CH$_4$ is most favorable on Pd-dop-II. The more stable Pd-dop-II-$V_{O}$ structure presents an activation barrier of 0.83 eV, still much lower than that for the stoichiometric CeO$_2$(111) surface and close to the value computed for the Pd-dop-I surface model. The reaction rates predicted for dissociative CH$_4$ adsorption are listed in Table 1. Although Pd-dop-II shows the highest intrinsic activity, its low abundance under typical reaction conditions implies that its contribution to CH$_4$ activation will be negligible. Despite the fact that Pd-dop-I and Pd-dop-II-$V_{O}$ exhibit comparable rates, the much higher abundance of Pd-dop-II-$V_{O}$ means that this state is the dominant catalytically active species for CH$_4$ activation, in line with the suggestion of Trovarelli and co-workers. A more detailed analysis shows that the activation energy of dissociative CH$_4$ adsorption strongly correlates with the oxygen vacancy formation energy (Figure S6). The more weakly an O atom is bound to the surface the lower the activation energy for CH$_4$ activation. The most reactive atom is the unstable O atom adjacent to Pd dopant in Pd-dop-II, the least a ceria surface O atom.

As it has been speculated that Pd atoms doped in CeO$_2$ play an important role in CO oxidation, we also explored possible reaction cycles for CO oxidation to CO$_2$. Figure 4 shows the free energy pathways computed at 300 K. The conventional structure cannot catalyze CO oxidation as the Pd atom does not adsorb CO. In contrast, CO can adsorb on the Pd ion in Pd-dop-II (IM1 → IM2) with an energy of −0.58 eV. The oxidation of CO by a CeO$_2$ lattice O atom is facile, and the activation energy is only 0.03 eV. CO$_2$ desorption (IM3 → IM4) is exergonic by 1.33 eV. Adsorption of a subsequent CO molecule (IM4 → IM5, $\Delta G = −0.36$ eV) results in surface reorganization, in which Pd migrates to the first atomic layer, after which Pd is surrounded by two surface O$_x$ one subsurface O$_y$ and CO. This CO molecule will react with one of the O atoms in the second O atomic layer (IM5 → IM6) involving an activation barrier of 0.61 eV. This reaction is slightly preferred over the reaction with a surface O atom (IM5 → IM6, $E_{act} = 0.73$ eV). After CO$_2$ desorption (IM6 → IM7, $\Delta G = −0.78$ eV), the preferred square planar coordination is restored with one $V_{O}$ in the first O atomic layer and one $V_{O}$ in the second O atomic layer, denoted by Pd-dop-II-$2V_{O}$-sub. Then, O$_x$ adsorption (IM7 → IM8) occurs with $\Delta G = −1.14$ eV followed by dissociation (IM8 → IM1) with $E_{act} = 1.52$ eV. Alternatively, CO adsorption (IM7 → IM9, $\Delta G = −0.13$ eV) results in surface reorganization and reaction with a surface O atom (IM9 → IM10) to form another CO$_2$ with a barrier of 0.73 eV. This process is exergonic ($\Delta G = −1.99$ eV), and CO$_2$ desorption (IM10 → IM11, $\Delta G = 0.35$ eV) leads to Pd-dop-II-

<table>
<thead>
<tr>
<th>surface sites</th>
<th>$E_{ad}$ (eV)</th>
<th>$E_{act}$ (eV)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$(111)</td>
<td>−0.18</td>
<td>1.36</td>
<td>$5.25 \times 10^{-14}$</td>
<td>-</td>
</tr>
<tr>
<td>Pd-dop-I</td>
<td>−0.17</td>
<td>0.75</td>
<td>$1.29 \times 10^{-7}$</td>
<td>0.0183</td>
</tr>
<tr>
<td>Pd-dop-II</td>
<td>−0.15</td>
<td>0.12</td>
<td>$5.25 \times 10^{-7}$</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pd-dop-II-V$_O$</td>
<td>−0.16</td>
<td>0.83</td>
<td>$2.91 \times 10^{-10}$</td>
<td>0.979</td>
</tr>
<tr>
<td>Pd-dop-II-2V$_O$</td>
<td>−0.19</td>
<td>1.14</td>
<td>$2.01 \times 10^{-12}$</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

$P_{CH4} = 0.1$ atm, $P_{O2} = 1$ atm, and $T = 700$ K.

Figure 3. Partial density of states (pDOS) of Pd-4d and O-2p orbitals (O atom adjacent to Pd) in Pd-dop-I, Pd-dop-II, and Pd-dop-II-$V_{O}$.
3VO, a structure with three O vacancies, two in the first O atomic layer and one in the second O atomic layer. Adsorption of molecular O2 (IM11 → IM12, ΔG = −1.03 eV) followed by dissociation (IM12 → IM4; E_{act} = 0.54 eV) results in healing of the two O vacancies, thereby restoring Pd-dop-II-VO. We also considered the alternative pathway: after CO desorption occurs from the IM6 state to form Pd-dop-II-2VO, O2 adsorption (IM7′ → IM8′) is slightly exergonic by −0.38 eV and involves a barrier of 1.52 eV for O2 dissociation.

Microkinetics simulations were used to identify the preferred reaction pathway under practical conditions. In this way, we found that CO is predominantly oxidized via the sequence (IM4 → IM5 → ... → IM11 → IM12), which starts from Pd−II−VO and involves the removal of two O atoms before O2 heals these two vacancies. The CO oxidation rate of this cycle at 300 K is ~10^9 and ~10^6 times higher than the two cycles starting from Pd-dop-II, i.e., IM1 → IM8 and IM1 → IM8′, respectively. The rate-controlling step for the overall process is the second CO oxidation event (IM9 → IM10). The rate of the other two cycles is mainly suppressed by the high barrier to O2 dissociation. The key aspects of the dominant catalytic cycle are the relatively weak adsorption of CO, which leads to moderate activation barriers for recombination with the lattice O atoms in the first and second O atomic layers of CeO2, and the uplifting out of the surface of the Pd atom from its initial location upon CO adsorption. This reorganization around the active Pd center facilitates the recombination of CO with an O atom. Figure S10 highlights the role of adsorbed CO in this reorganization process. This is the first reported catalytic cycle for CO oxidation of a single Pd atom doped in the CeO2(111) surface.

To verify the generality of the predicted square-planar structure, we considered similar structures with Ni and Pt, which are the other important group 10 elements used in combination with ceria for CH4 activation.39,41,42 Figure 5 shows the corresponding potential energy diagrams (cf. Figure 1). Ni, Pd, and Pt can form similar square planar structures. Their stability increases going from Pt < Pd < Ni. Only the stoichiometric square planar Pt structure is slightly less stable than the octahedral one. Yet, in all cases, it is favorable to remove an O atom from the square planar structure. These structures are always more stable than those obtained by removing an O atom from the octahedral structure. Notably, doing so for Ni-dop-I leads to an unstable structure that transforms without barrier to Ni-dop-II-VO, consistent with the high stability of this structure.
In conclusion, we have used quantum-chemical calculations to identify an alternative structure for a single Pd atom doped in the most stable surface termination of CeO2. Compared with the conventional octahedrally coordinated PdO6 moiety, the novel square planar PdO4 structure is more reactive due to the radical character of the two surface O atoms. Creating a vacancy in this square planar structure is energetically favorable, and the resulting defective surface is the most stable structure under oxidative conditions. Similar structures exist for the Ni- and Pt-doped surfaces. A surface O atom nearby the Pd dopant can easily activate the first C=H bond in CH4. In contrast to octahedrally coordinated Pd, the square planar configuration can adsorb CO. The relatively weak CO adsorption results in moderate activation barriers for recombination with the O atoms of CeO2. The novel structure identified in this study paves the way for deeper exploration and optimization of CeO2 surfaces toward single-atom catalysts with high activity and stability.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03295.

Partition function of gaseous CH4, computational details, ab initio thermodynamic analysis, additional structural information, and results of microkinetics modeling (PDF)

AUTHOR INFORMATION

E-mail: e.j.m.hensen@tue.nl

ORCID

Ivo A. W. Filot: 0000-0003-1403-8379
Jin-Xun Liu: 0000-0002-7499-4197
Emiel J. M. Hensen: 0000-0002-9754-2417

Author Contributions
‡(Y.-Q.S. and L.A.W.F.) These authors contributed equally.

Notes

The authors declare no competing financial interest.

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REFERENCES