Supporting Information

Stable Pd-Doped Ceria Structures for CH$_4$ Activation and CO Oxidation

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1. Partition function for gaseous CH$_4$:

Rotational partition function $q_r$ can be simply described as below:

$$q_r = \frac{8\pi^2(2\pi k_B T)^2}{\hbar^2} (I_x I_y I_z)^{1/2} = \frac{8\pi^2}{\sigma} \left( \frac{2\pi k_B T}{\hbar^2} \right)^2 = \frac{8\pi^2}{\sigma} \left( \frac{T}{4\pi^2 \sigma} \right)^2 \frac{8\pi^2}{\sigma} \left( \frac{k_B T}{4\pi^2 \sigma} \right)^2$$

(1.1)

Here we roughly assume that $I_x = I_y = I_z = I$, and $I$ is the moment of inertia along one axis which is in the same line of one C-H bond. Rotational partition function for methane $\varepsilon_{CH_4} = 0.655$ meV.

Rotational character temperature $\theta_r = h^2 / 8\pi^2 k_B I_r$, and $\varepsilon_{rot}$ is rotational constant. For CH$_4$ molecules in gas phase, $\varepsilon_{CH_4} = 0.655$ meV. Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J/K, and Plank constant $\hbar = 6.63 \times 10^{-34}$ J·s.

Along one C-H bond of CH$_4$ there is a C$_3$ axis, and the symmetry number $\sigma_{C-H} = 3$. Because CH$_4$ has four C-H bonds, the total symmetry number $\sigma_{CH_4} = \frac{3}{2}$. Then rotational partition function $q_r$ can be re-written as below:

$$q_r = \frac{32\pi^2}{3} \left( \frac{k_B T}{4\pi^2 \sigma} \right)^2$$

(1.2)

Vibrational partition function $q_v$ can be closely written as below:

$$q_v = \frac{1}{1 - \exp(-\frac{\hbar}{k_B T})}$$

(1.3)

and $v$ is vibrational frequency. We can calculate the harmonic frequencies to estimate the vibrational partition function.

Translational partition function $q_t$ can be expressed as below:

$$q_t = V \left( \frac{\pi k_B T}{h^2} \right)^2 = \frac{k_B T}{P_{CH_4}/\rho^\theta} \left( \frac{2\pi k_B T}{h^2} \right)^2$$

(1.4)

The nuclear and electronic partition functions are both neglected, and the total partition function $q$ can be written as below:

$$q = q_v \cdot q_r \cdot q_t = \frac{1}{1 - \exp(-\frac{\hbar}{k_B T})} \cdot \frac{32\pi^2}{3} \left( \frac{k_B T}{4\pi^2 \sigma} \right)^2 \cdot \frac{k_B T}{P_{CH_4}/\rho^\theta} \left( \frac{2\pi k_B T}{h^2} \right)^2$$

(1.5)

Where $\hbar$ is Planck constant, $k_B$ is Boltzmann constant, $T$ is temperature, $P_{CH_4}$ is methane pressure, $P^\theta$ is standard pressure, and $m$ is the molecular mass of methane.

According to transition state theory, the rate constant $k$ of dissociative adsorption of gaseous methane can be described as

$$k = \frac{k_B T}{\hbar} \frac{q_{TS}}{q_{CH_4}} e^{(-E_a)/k_B T}$$

(1.6)

in which $q_{TS}$ and $q_{CH_4}$ are the partition functions for CH$_4$ in the transition state and the gas phase, respectively. The partition function $q_{CH_4}$ relates to CH$_4$ in the gas phase:

$$q_{CH_4} = \frac{1}{1 - \exp(-\frac{\hbar}{k_B T})} \cdot \frac{32\pi^2}{3} \left( \frac{k_B T}{4\pi^2 \sigma} \right)^2 \cdot \frac{k_B T}{P_{CH_4}/\rho^\theta} \left( \frac{2\pi k_B T}{h^2} \right)^2$$

(1.7)
Where \(q_{TS}\) refers to the immobile transition state:

\[
q_{TS} = \frac{1}{1 - \exp\left(-\frac{\Delta V}{k_B T}\right)}
\] (1.8).

Figure S1. The calculated rotational partition of methane by our formula in black line, compared with the reported values in red line.

2. Computational details

We carried out spin-polarized calculations within the DFT framework as implemented in the Vienna ab initio simulation package (VASP).

The ion-electron interactions were represented by the projector-augmented wave (PAW) method and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The Kohn-Sham valence states were expanded in a plane-wave basis set with a cut-off energy of 400 eV. The Ce(5s,5p,6s,4f,5d), O(2s,2p), Pd(4d5s) and C(2s,2p) electrons were treated as valence states. We have used the DFT+U approach, in which \(U\) is a Hubbard-like term describing the on-site Coulombic interactions. This approach improves the description of localized states in ceria, where standard LDA and GGA functionals fail. For Ce, a value of \(U = 4.5\) eV was adopted, which was calculated self-consistently by Fabris et al. using the linear response approach of Cococcioni and de Gironcoli and which is within the 3.0-4.5 eV range that provides localization of the electrons left upon oxygen removal from ceria. For the calculations of Pd-doped CeO\(_2\)(111), we used a periodic slab with a \((4\times4)\) supercell in which one of the surface Ce atoms was substituted by Pd. The CeO\(_2\)(111) slab model is three Ce-O-Ce layers thick and the vacuum gap was set to 15 Å. The atoms in the bottom layer was frozen to their bulk position and only the top two Ce-O-Ce layers were allowed to relax. The bulk lattice constant (5.49 Å) as previously calculated using the PBE+U (\(U = 4.5\) eV) functional was used. For the Brillouin zone integration, a Monkhorst-Pack \(1\times1\times1\) mesh was used. The climbing image nudged-elastic band (CI-NEB) algorithm was used to identify the transition states for the surface reorganization induced by the Pd dopant, for relevant CH\(_4\) activation on selected models and for the CO oixdaiton.

3. Ab initio thermodynamics

We used the ab initio thermodynamics approach of Reuter and Scheffler to assess the relative stability of various Pd-doped states in ceria as a function of oxygen pressure and temperature. The free energy of Pd-doped surface states is determined as follows:

\[
\Delta G = \Delta E + \frac{n}{2} \mu_{O_2}(T, P)
\]

\[
= \left( E_{Pd-doped-nV_O} + \frac{n}{2} E_{O_2} - E_{Pd-doped} \right) + \frac{n}{2} \mu_{O_2}(T, P) \] (3.1),
where \( E_{Pd-doped} \) and \( E_{Pd-doped-nV_O} \) are the electronic ground state energies of the Pd-doped CeO\(_2\)(111) and the Pd-doped CeO\(_2\)(111) after removing \( n \) oxygen atoms, respectively, \( E_{O_2} \) the electronic ground state energy of gaseous \( O_2 \), and \( \mu_{O_2}(T,P) \) the chemical potential of gaseous \( O_2 \). The chemical potential of gaseous oxygen can be correlated to the thermodynamic state in the following manner:

\[
\mu_{O_2}(T,P) = \mu_{O_2}(T,P^\theta) + RT \ln \left( \frac{P_{O_2}}{P^\theta} \right)
\]

\[
= [H_{O_2}(T,P^\theta) - H_{O_2}(0,K,P^\theta)] - T[S_{O_2}(T,P^\theta) - S_{O_2}(0,K,P^\theta)] + RT \ln \left( \frac{P_{O_2}}{P^\theta} \right) \quad (3.2),
\]

where the enthalpy \( H_{O_2}(T,P^\theta) \) and entropy \( S_{O_2}(T,P^\theta) \) of gaseous \( O_2 \) were obtained from the standard thermodynamic tables. The entropy of the solids is neglected.

4. **Additionally structural information**

![Figure S2. Illustration of the difference between Pd-dop-I-V\(_O\) and Pd-dop-II-V\(_O\). (color code: white, Ce; grey, irrelevant O; red, relevant O; green, Pd).](image)

![Figure S3. Adsorption energy of Pd atom in Pd vacancy of PdO(101). We used PdO(101) to represent ceria-supported PdO nanoparticles. With respect to Pd bulk atom, the adsorption of Pd atom in Pd vacancy of PdO(101) is -0.59 eV and -1.68 eV, while the adsorption energy of it in Ce vacancy of CeO\(_2\)(111) is as high as -3.62 eV. It means that the Pd atom cannot segregate from Ce lattice position to surface and Ce vacancy can strongly trap single Pd atom.](image)

In order to determine the stability of metallic Pd in the phase diagram, we set up a train of thought to provide an estimate what would happen at high temperature.

a. Starting from Pd-dop-II-2Vo, removal of O atom bound to Pd dopant costs 2.86 eV; removal of the O atom neighboring the Pd dopant costs 2.46 eV; removal of other O atoms of the ceria surface cost 2.24 eV. Thus, it is easier to remove surface lattice O atoms from the ceria surface than the remaining O atoms around Pd.
b. It would require a significant number of calculations to determine which O atoms are first removed before the O atoms attached to Pd are removed. This is clearly beyond the scope of our work.

c. We can however try to simplify this question and assume that at least the O atom closest to Pd should be removed and we can easily see that the associated energy is at least 2.86 eV. Likely, this value becomes higher when other O atoms are removed first. Then the Pd atom will be reduced and can migrate on the surface to form metallic Pd clusters. We indicated the formation of clustered Pd in the Figure 2.

d. Notably, we considered here formation of Pd metal nanoparticles and not of PdO overlayers. The reason is as follows. Migration of embedded PdO species is very difficult. We used the PdO(101) termination to compute whether a Pd atom from ceria would migrate to a ceria-supported Pd oxide phase. To this end, we compared the energy to place a Pd atom in a Pd vacancy of PdO(101) with respect to bulk Pd. Two different Pd vacancies exist in PdO(101) with energies of -0.59 eV and -1.68 eV. Notably, Pd is much more stable in the Ce vacancy of the ceria surface (-3.62 eV). We can alternatively argue that once the O atoms bound to Pd are removed, the Pd atom will be reduced and it can move to the surface. In this case, there is a large tendency towards Pd sintering as recently shown in Chem. Mater. 2017, DOI: 10.1021/acs.chemmater.7b03555. Taken together, it implies that the Pd atom embedded in the ceria resists clustering into PdO nanoparticles on ceria top surface. If reduction occurs, this can only occur at very high temperature. In this case, we predict that Pd metal will be stable as it has been reported that above 850°C in an oxygen atmosphere Pd is present in the metallic form in Pd/CeO₂ (Science, 2012, 337, 713-717).

Figure S4. The dissociative process of CH₄ over Pd-dop-I carried out by CI-NEB algorithm. (color code: red, surface and bulk O; coral, subsurface O; white, Ce; blue, Pd). The only imaginary frequency is 699 cm⁻¹ along the reaction coordinate, indicative of the correct TS geometry. The corresponding change of bond length of C-H and O-H is also showed along the reaction coordinate.
Figure S5. The TS configurations of CH$_4$ activation by CeO$_2$(111), Pd-dop-II, Pd-dop-II-V$_\alpha$ and Pd-dop-II-2V$_\alpha$. (color code: red, surface and bulk O; coral, subsurface O; white, Ce; blue, Pd). The above and below numbers are C-H and O-H distance in TS configuration, respectively.

Figure S6. Linear scaling relationship is between activation energy of CH$_4$ dehydrogenation and formation energy of oxygen vacancy.
Figure S7. The CO oxidation cycle between Pd-dop-II and Pd-dop-II-2V_O. (color code: white, Ce; grey, irrelevant O; red, relevant O; black, C; green, Pd). The activation energy is 0.73 eV, higher than the value of 0.61 eV for the alternative combination of CO and subsurface O atom showed in Figure 4 in main text. It indicates that the CO prefers to react with subsurface O atom, not surface O atom adjacent to Pd dopant. The direct O_2 dissociation barrier is 2.02 eV here, while an alternative process can lower the barrier to 1.52 eV showed in red dashed line via the assistant of a facile O diffusion reported in our previous paper.16
Figure S8. The CO oxidation cycle between Pd-dop-II and Pd-dop-II-2V_{O,sub} which has one V_{O} in first O atomic layer and one in second O atomic layer. (color code: white, Ce; grey, irrelevant O; red, relevant O; black, C; green, Pd).
Figure S9. The CO oxidation cycle between Pd-dop-II-V\(_O\) and Pd-dop-II-3V\(_O\). (color code: white, Ce; grey, irrelevant O; red, relevant O; black, C; green, Pd).

Figure S10. Relevant configurations and energy change for Pd uplifting from the subsurface O layer to surface O layer. (color code: white, Ce; grey, irrelevant O; red, relevant O; black, C; green, Pd). After moving up of Pd dopant, it is still in square-planar coordination by two surface O and one subsurface O, and also exposes one empty site * for CO adsorption. CO can facilitate this up-shift and get the system more stable. Without CO adsorption, the up-shift is negative and is strongly endothermic by 0.95 eV at least.
5. Microkinetics simulations:

The calculated activation energies are applied to compute the forward and backward rate constants for CO oxidation. For surface reactions, the rate constants for the forward and backward elementary reaction were determined by the Eyring equation:

\[ k = \frac{k_B T Q^{TS}}{h} e^{-\frac{E_a}{k_B T}} \]  
\[ (5.1) \]

Where \( k \) is the reaction rate constant in \( s^{-1} \); \( k_B \), \( T \), \( h \) and \( E_a \) are the Boltzmann constant, temperature, Planck’s constant and the activation barrier, respectively. \( Q^{TS} \) and \( Q \) refer the partition functions of the transition and ground states, respectively. As an approximation, the pre-factor \( \frac{k_B T Q^{TS}}{h} \) is set to \( 10^{13} \, s^{-1} \) for all the elementary surface reactions.

For non-activated molecular adsorption, the rate of adsorption is determined by the rate of surface impingement of gas-phase molecules. The flux of incident molecules is given by Hertz-Knudsen equation:

\[ F = \frac{P}{\sqrt{2\pi m_k T}} \]  
\[ (5.2) \]

Therefore, the molecular adsorption rate constant can be written as:

\[ k_{ads} = \frac{PA}{\sqrt{2\pi m_k T}} S \]  
\[ (5.3) \]

Where \( P \) is the partial pressure of the adsorbate in the gas phase, \( A' \) is the surface area of the adsorption site, \( m \) is the mass of the adsorbate, and \( S \) is the sticking coefficient.

For the desorption process, it is assumed that there are three rotational degrees of freedom and two translational degrees of freedom in the transition state. Accordingly, the rate of desorption is given by

\[ k_{des} = \frac{k_B T^3 A'(2\pi k_B)^{1/2}}{h \sigma \theta} e^{-\frac{E_{des}}{k_B T}} \]  
\[ (5.4) \]

where \( \sigma \) and \( \theta \) are the symmetry number and the characteristic temperature for rotation of gaseous CO, respectively. \( E_{des} \) is the desorption energy of CO molecules.

The approach to microkinetic simulations has been presented in detail elsewhere.\textsuperscript{19-20} Differential equations for all the surface reaction intermediates were constructed using the rate constants and the set of elementary reaction steps. For each of the \( M \) components in the kinetic network, a single differential equation is obtained in the form as below:

\[ r_i = \sum_{j=1}^{N} \left( k_{ij} v_i' \prod_{k=1}^{M} c_k^{v_k'} \right) \]  
\[ (5.5) \]

In this equation, \( k_i \) is the elementary reaction rate constant (see equation 1), \( v_i' \) is the stoichiometric coefficient of component \( i \) in elementary reaction step \( k \) and \( c_k \) is the concentration of component \( k \) on the catalytic surface.

The CO oxidation rate is calculated by the in-house developed MKMCXX program.\textsuperscript{18-27} Steady-state coverages were calculated by integrating the ordinary differential equations in time until the changes in the surface coverages were very small. Because chemical systems typically give rise to stiff sets of ODEs, we have used the backward differentiation formula method for the time integration.\textsuperscript{20} The rates of the individual elementary reaction steps can be obtained based on the calculated steady-state surface coverages. In our simulations, the gas phase contained a mixture of CO and O\(_2\) in 2:1 molar ratio at a total pressure of 1 atm, and \( T = 300 \) K.

The elementary reaction steps that contribute to the rate control over the overall reaction can be determined by degree of rate control (DRC) concept introduced by Campbell et al.\textsuperscript{22-24} For elementary step \( i \), the degree of rate control \( X_{RC,i} \) can be defined as

\[ X_{RC,i} = \frac{k_i}{r} \frac{\partial r}{\partial k_i} \bigg|_{k_1, \ldots, k_M} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right) \bigg|_{k_1, \ldots, k_M} \]  
\[ (5.6) \]

where \( k_i \), \( k_1 \), \( k_M \) and \( r \) are the rate constants, the equilibrium constant for step \( i \) and the reaction rate, respectively. Furthermore, the DRC coefficients have to obey the sum rule over all steps \( i \) in the mechanism in such a way that\textsuperscript{23}:

\[ \sum_i X_{RC,i} = 1 \]  
\[ (5.7) \]
Figure S. DRC of these three CO oxidation cycles corresponding to Figure S4-S6, respectively. The results demonstrate that the rate-controlling step of these three cycles is the O₂ dissociation, the O₂ dissociation and the second CO oxidation at 300 K, respectively. The MKM-determined total rate of CO₂ production is 8.88×10⁻¹⁶, 5.09×10⁻¹³, and 2.45×10⁻⁶ s⁻¹/site, respectively.

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