Supporting Information

to

A Computational Study of the Mechanism of CO Oxidation by a Ceria Supported Surface Rhodium Oxide Layer

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Methods

Density functional theory (DFT) with the PBE (Perdew-Burke-Ernzerhof) functional¹ as implemented in the Vienna Ab Initio Simulation Package $(VASP)^{2-4}$ was employed. A Hubbard U term was added to the PBE functional (DFT+U) employing the rotationally invariant formalism by Dudarev et al.,⁵ in which only the difference $(U_{eff} = U - J)$ between the Coulomb U and exchange J parameters enters. The spin-polarized calculations were performed. The projector augmented wave method (PAW)⁶⁻⁸ was used to describe the interaction between the ions and the electrons with the frozen-core approximation.⁷ The Ce (4f, 5s, 5p, 5d, 6s), O (2s, 2p), and Rh (4p, 4d, 5s) electrons were treated as valence states using a plane-wave basis set with a kinetic energy cut off of 400 eV. For Ce, a value of $U_{eff}=4.5$ eV was used, which was calculated self-consistently by Fabris et al.⁹ using the linear response approach of Cococcioniandde Gironcoli.¹⁰ This value is within the 3.0 - 5.5 eV range reported to provide localization of the electrons left upon oxygen removal from CeO₂.¹¹ For all the surface calculations, the model was a periodic slab with a (3×3) surface unit cell and, for the Brillouin zone integration, a Monckhorst Pack $2 \times 2 \times 1$ mesh was used. The CeO₂ (111) model includes three cerium layers and six oxygen layers, i.e. three stoichiometric O-Ce-O trilayers with a cell composition (CeO₂)₂₇, and a vacuum space of 13 Å. The bulk equilibrium lattice constant (5.49 Å) previously calculated by PBE+U ($U_{eff} = 4.5 \text{ eV}$) was used.¹² The Rh_nO_mclusters and the six top atomic layers of the ceria slab were allowed to

relax, while the three bottom layers were kept fixed to their bulk position. Atoms were relaxed until forces were smaller than 0.05 $eV \cdot Å^{-1}$. The location and energy of transition states were calculated with the climbing-image nudged elastic band method.¹³

It can be shown from first principles that an exact description of the kinetics is given by the master equation¹⁴

$$\frac{dP_{\alpha}}{dt} = \sum_{\beta} \left[W_{\alpha\beta} P_{\alpha} - W_{\beta\alpha} P_{\beta} \right]$$

Here α and β are all possible configurations of the system, the P's are their probabilities, and the W's are rate constants. We have solved this equation using kinetic Monte Carlo (kMC).¹⁵ Usually the number of configurations for surface reactions is huge, but here there are only limited configurations for a single rhodium oxide cluster plus adsorbates and a small part of the ceria support. This means that it is also possible to solve the master equation with a numerical solver for the ordinary differential equations. As the rate constants differ by many orders of magnitude, there are many reaction conditions at which numerical problems are encountered. We have therefore used kMC as it is more robust. For the calculation of the prefactors, we followed the method described by Jansen.¹⁵ For surface reactions, the similarity between the initial and transition state implies that the partition functions of these two states are very similar. This implies that the preexponential fator can be written as $k_BT/h.(Q^{TS}/Q) \approx k_BT/h \approx 10^{13} \text{ s}^{-1}$. This value has been verified for several elementary steps in our model and the correspondence was very good. For desorption, the transition state is the state with the molecule in a more mobile configuration so that typically pre-exponential factors of $\sim 10^{18}$ s⁻¹ are used. This is mainly due to translational and rotational degrees of freedom in the transition state for desorption. For adsorption, we have employed the Herz-Knudsen equation¹⁵ and also assumed that the sticking coefficient for O₂ adsorption will be very low.

Raman spectra were acquired using a Jobin-Yvon T64000 triple-stage spectrograph at a spectral resolution of 2 cm⁻¹. The laser line at 325 nm of a He-Cd laser (KIMMON Electric, Japan) was used as the excitation source with an output power of 30 mW. The power of the laser on the sample was 3.0 mW. For the UV-Raman measurements the samples were placed in a home-made controlled environment in-situ Raman cell. The total gas flow rate was kept at 50 ml/min. Prior to CO oxidation, the catalyst was calcined at 450 °C in artificial air and subsequently reduced at the same temperature in 20 vol% H₂ in He. The sample was cooled to room temperature and subsequently exposed to 4 vol% CO and O₂ in He (CO/O₂ = 1) or He at increasing temperatures up to 400 °C.

References:

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Table S1: Kinetic parameters as employed in the kMC calculations (T=333k, PCO=0.045 atm,
PO_2 = 0.045 atm). The pre-factor for O_2 adsorption process adjusted using experimental obtained
activation barrier is employed.

Elementary reaction steps	Eact (kJ/mol)	μ	k
$Rh_3O_6/CeO_2 + CO \rightarrow Rh_3O_5/CeO_2 + CO_2$	44.37	4.75×10^2	5.21x10 ⁻⁵
$Rh_3O_5/CeO_2+CO \rightarrow Rh_3O_4/CeO_2+CO_2$	55.94	$6.44 ext{x} 10^2$	1.08x10 ⁻⁶
$Rh_3O_5/CeO_2+O_2 \rightarrow O_2*Rh_3O_5/CeO_2$	0.00	2.59×10^{-3}	2.59×10^{-3}
O_2 *Rh ₃ O ₅ /CeO ₂ + CO \rightarrow Rh ₃ O ₆ /CeO ₂ + CO ₂	74.27	$4.46 ext{x} 10^3$	1.00×10^{-8}
$CO*Rh_3O_4/CeO_2 \rightarrow CO_2*Rh_3O_3/CeO_2$	83.91	3.22×10^{12}	2.22×10^{-1}
$Rh_3O_4/CeO_2+CO \rightarrow CO*Rh_3O_4/CeO_2$	0.00	1.24×10^7	$1.24 \text{x} 10^7$
$Rh_3O_4/CeO_2+O_2 \rightarrow O_2*Rh_3O_4/CeO_2$	0.00	2.59×10^{-3}	2.59×10^{-3}
O_2 *Rh ₃ O_4 /CeO ₂ +CO \rightarrow Rh ₃ O_5 /CeO ₂ +CO ₂	84.88	4.21×10^3	2.05×10^{-10}
$CO_2*Rh_3O_3/CeO_2 \rightarrow CO*Rh_3O_4/CeO_2$	60.76	$1.00 \mathrm{x} 10^{12}$	2.94×10^2
$CO_2*Rh_3O_3/CeO_2 \rightarrow Rh_3O_3/CeO_2+CO_2$	46.00	$1.44 \text{x} 10^{18}$	8.80×10^{10}
$Rh_3O_3/CeO_2 \rightarrow Rh_3O_4/CeO_{2-x}$	69.44	5.99×10^{12}	$7.67 \text{x} 10^1$
$Rh_3O_4/CeO_{2-x} \rightarrow Rh_3O_3/CeO_2$	93.56	6.10×10^{13}	1.29x10 ⁻¹
$Rh_{3}O_{4}/CeO_{2-x}+CO \rightarrow CO*Rh_{3}O_{4}/CeO_{2-x}$	0.00	$1.24 \text{x} 10^7$	$1.24 \text{x} 10^7$
$CO*Rh_3O_4/CeO_{2-x} \rightarrow CO_2*Rh_3O_3/CeO_{2-x}$	80.05	1.02×10^{13}	2.83
$CO_2*Rh_3O_3/CeO_{2-x} \rightarrow CO*Rh_3O_4/CeO_{2-x}$	67.52	8.74x10 ¹¹	2.25×10^{1}
$CO_2*Rh_3O_3/CeO_{2-x} \rightarrow Rh_3O_3/CeO_{2-x}+CO_2$	80.00	$1.44 \mathrm{x} 10^{18}$	4.09×10^5
$Rh_3O_3/CeO_{2-x}+O_2 \rightarrow Rh_3O_4/CeO_2$	0.00	2.59x10 ⁻³	2.59x10 ⁻³
$Rh_3O_4/CeO_2+O_2 \rightarrow O_2*Rh_3O_4/CeO_2$	0.00	2.59x10 ⁻³	2.59x10 ⁻³
O_2 *Rh ₃ O ₄ /CeO ₂ \rightarrow Rh ₃ O ₄ /CeO ₂ +O ₂	112.23	2.84×10^{17}	7.06×10^{-1}
$O_2*Rh_3O_4/CeO_2+CO \rightarrow CO*O_2*Rh_3O_4/CeO_2$	0.00	1.27×10^7	$1.24 \text{x} 10^7$
$CO*O_2*Rh_3O_4/CeO_2 \rightarrow CO_2*O_2*Rh_3O_3/CeO_2$	80.00	1.00×10^{13}	2.83
$CO_2*O_2*Rh_3O_3/CeO_2 \rightarrow CO*O_2*Rh_3O_4/CeO_2$	82.41	1.00×10^{13}	1.18
$CO_2*O_2*Rh_3O_3/CeO_2 \rightarrow O_2*Rh_3O_3/CeO_2+CO_2$	14.00	1.00×10^{13}	6.39x10 ¹⁰
$O_2*Rh_3O_3/CeO_2 \rightarrow O_2*Rh_3O_4/CeO_{2-x}$	103	1.00×10^{13}	6.98x10 ⁻⁴
$O_2*Rh_3O_4/CeO_{2-x} \rightarrow O_2*Rh_3O_3/CeO_2$	100	1.00×10^{13}	2.06x10 ⁻³
$O_2*Rh_3O_4/CeO_{2-x}+CO \rightarrow CO*O_2*Rh_3O_4/CeO_{2-x}$	0.00	$1.24 \text{x} 10^7$	$1.24 \text{x} 10^7$
$CO*O_2*Rh_3O_4/CeO_{2-x} \rightarrow CO_2*O_2*Rh_3O_3/CeO_{2-x}$	87.00	1.00×10^{13}	2.26×10^{-1}
$CO_2*O_2*Rh_3O_3/CeO_{2-x} \rightarrow CO*O_2*Rh_3O_4/CeO_{2-x}$	81.00	1.00×10^{13}	1.97
$CO_2*O_2*Rh_3O_3/CeO_{2-x} \rightarrow O_2*Rh_3O_3/CeO_{2-x}+CO_2$	50.00	$1.44 \mathrm{x} 10^{18}$	2.08×10^{10}
O_2 *Rh ₃ O ₃ /CeO _{2-x} \rightarrow Rh ₃ O ₄ /CeO ₂	27.00	1.00×10^{13}	5.82×10^8



Figure S1. Schematic picture of the reaction cycle between Rh_3O_6/CeO_2 , Rh_3O_5/CeO_2 and Rh_3O_4 , with structures of intermediate and transition state.



Figure S2. Adsorption structures of CO and O₂ on Rh₃O₃/CeO_{2-x}.



Figure S3. Potential energy diagram of mechanism II, with structures of intermediate and transition state.



Figure S4: In-situ Raman spectroscopy of Rh/CeO₂ catalysts. a, Raman spectra of Rh/CeO₂ catalysts containing after reduction on average 2.1 nm (top left graph, sample A) and 5.2 nm (top right graph, sample B) Rh particles during CO oxidation as a function of temperature. The dominant band around 460 cm⁻¹ is the first-order F_{2g} peak of ceria, whose shift correlates to the oxygen deficit of the ceria surface. b, The Raman shift of the F_{2g} peak is smaller for sample A than for sample B during CO oxidation in the temperature range 60-400 °C, evidencing a greater oxygen deficit of the ceria surface in the former sample. A blank experiment in He shows a much smaller variation in the concentration of oxygen vacancies in sample A, similar to that of a blank ceria support.