

Supporting Information

Influence of Defects on Barrier Energy Formation for OOH* Intermediate in ORR on Tetragonal-ZrO₂ with Adsorbed-Hydroxyl

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Methodology

DFT Calculations

Ab initio DFT calculations were conducted to identify the ground states of configurations involving pristine t-ZrO₂, t-ZrO_{2-x}, and t-ZrO_{2-x}N_x. Amsterdam Modeling Suite (AMS) is used for running the simulations. The surface model was constructed as 72-atoms 2 × 2 unit cell with the 2D unit dimension of 10.306 Å × 11.812 Å. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, employed within the generalized gradient approximation (GGA), is applied in all calculations. In this calculation, we employed the Double Zeta (DZ) basis set. Brillouin zone sampling was executed employing the Monkhorst and Pack scheme. Following the optimization of pristine t-ZrO₂, an oxygen atom was removed to create oxygen-deficient t-ZrO_{2-x}. Subsequently, one oxygen ion was replaced with a nitrogen ion to generate t-ZrO_{2-x}N_x. Using the same optimization parameters as for pristine t-ZrO₂, both defective structures were further optimized. Subsequently, an OH group was positioned above the surface of pristine and two defective surface at a distance of 3.3 Å, exceeding the Zr-O bond length of 2.21 Å.

Molecular dynamics (MD) Simulations

Details of the third-generation COMB (COMB3) potential

The third-generation Charge Optimized Many Body (COMB3) potential has been known as a variable charge reactive-potential formalism. It describes the processes involved in both the formation and dissociation of chemical bonds¹ while enabling dynamic adjustment of charges in response to the local environment^{2,3}.

In this potential, the total potential energy ($U^{tot}[\{q\}, \{r\}]$) of a system is composed of the short-range interaction ($U^{short}[\{q\}, \{r\}]$), van der Waals interactions ($U^{vdW}[\{q\}, \{r\}]$), electrostatic energies ($U^{es}[\{q\}, \{r\}]$), and correction terms ($U^{corr}[\{r\}]$), where $\{r\}$ and $\{q\}$ represent the coordinate array and charge array of the system, respectively. The COMB3 potential is able to describe the systems contains Zr, O, H, and N atoms³;

$$(U^{tot}[\{q\}, \{r\}]) = (U^{short}[\{q\}, \{r\}]) + (U^{vdW}[\{q\}, \{r\}]) + (U^{es}[\{q\}, \{r\}]) + (U^{corr}[\{r\}])$$

(1)

Further details of the COMB3 formulation are provided in 1, and 3. In this study, all molecular dynamics (MD) simulations utilizing the COMB3 model were executed through the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [48,49], employing the most recent Zr/O/H/N COMB3 parameters⁴.

MD simulations setup

Before the interacting O₂ molecule with OH on the surfaces, the pristine t-ZrO₂ is first relaxed by performing the canonical NVT ensemble on 5 × 5 × 4 unit cells for 300 ps. A timestep of 0.1 fs is used. The equation of motion is advanced in time by the Verlet algorithm. The canonical NVT ensemble, wherein the number (N) of atoms, volume (V), and temperature (T) remain constant, was selected. To maintain a constant temperature at 300K, the Nosé–Hoover thermostat⁵ is employed on the translational degrees of freedom of atoms, utilizing a temperature damping parameter set at 100 fs. Free boundary condition (FBC) is employed in the Z direction, and periodic boundary conditions (PBC) are imposed in X and Y directions. We obtained defective t-ZrO_{2-x} by removing one oxygen atom and t-ZrO_{2-x}N_x by substituting one oxygen atom with a nitrogen atom in the optimized pristine t-ZrO₂, respectively. Both defective structures underwent relaxation under the same conditions as the pristine t-ZrO₂. Following that, to hydroxylate the surfaces, we placed one OH on top of both the pristine and defective t-ZrO₂, allowing for the adsorption of OH on the surfaces under the same simulation

conditions. Subsequently, an O_2 molecule is strategically positioned on OH-poisoned structures using both perpendicular and oblique configurations (as shown in Fig 1Sb). we explored the minimum energy path (MEP) between the hydroxylated surfaces of pristine and defective t- ZrO_2 , serving as the initial structures, and one O_2 molecule as the final state of the transition, employing Nudged Elastic Band (NEB) calculations. The details of the NEB calculations are presented in the next section.

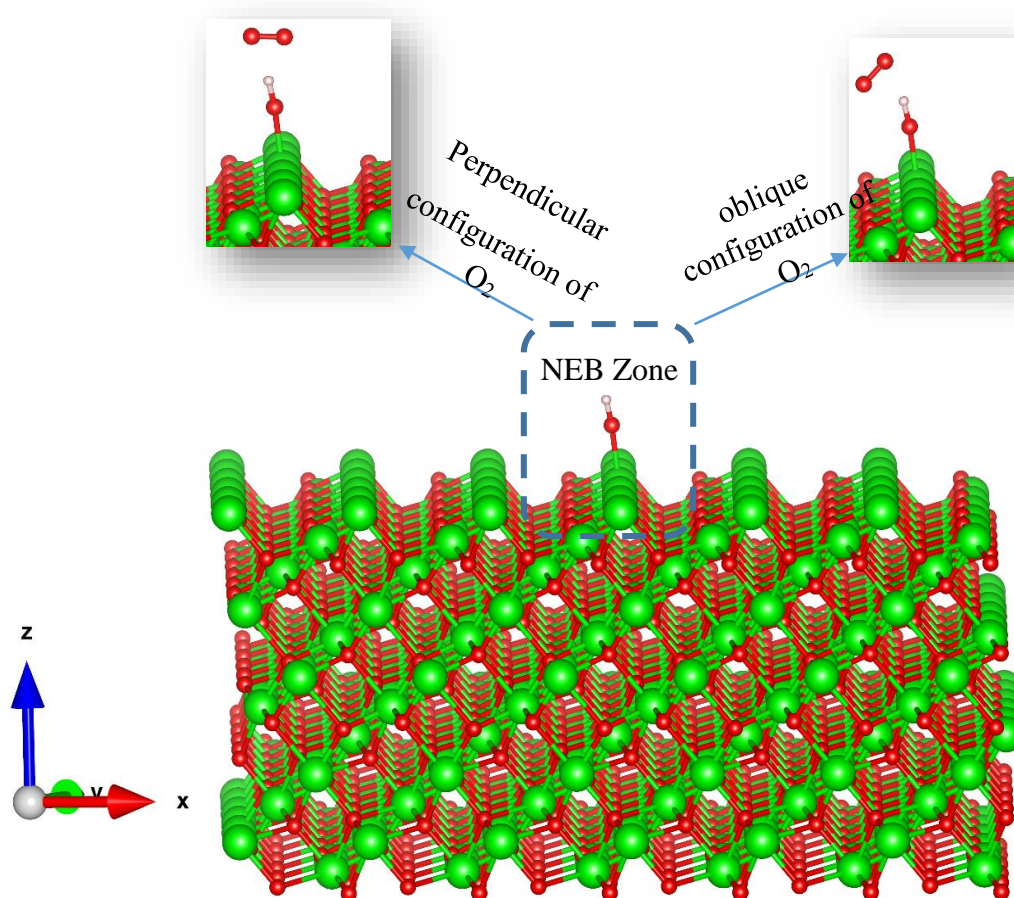


Fig 1S. The schematic of an initial structure for NEB simulation containing OH-poisoned pristine t- ZrO_2 and O_2 molecule with two perpendicular and oblique configurations, based on MD simulation.

Computational details of NEB analysis with climbing image method

To evaluate the impact of defects on the transition state of the O₂ and OH reaction on the zirconia surface, NEB computations were conducted utilizing the Climbing Image (CI) method. (NEB-CI) method efficiently identifies the minimum energy path (MEP) between a specified initial and final state of a transition. Generating a set of images (replicas) positioned along the initial and final states determines the MEP. A spring force is employed between intermediate replicas to stabilize and maintain their positions along the transition path. The schematic of the MEP calculated by NEB is shown in Fig 2S. We designated two distinct regions within our systems: NEB and non-NEB zones as shown in Fig 3S. The inter-replica springs exclusively act on atoms within the NEB zone. In principle, the non-NEB atoms establish a foundational force field for the NEB atoms, and they are allowed to move freely during the NEB minimization procedure. In the NEB zone, the image possessing the highest energy raises the potential energy surface to identify the saddle point, corresponding to the activation energy of the reaction. For each reaction, a set of 16 intermediate replicas is generated, with a uniform spring constant of 1 kcal/(mol·Å) connecting each replica.

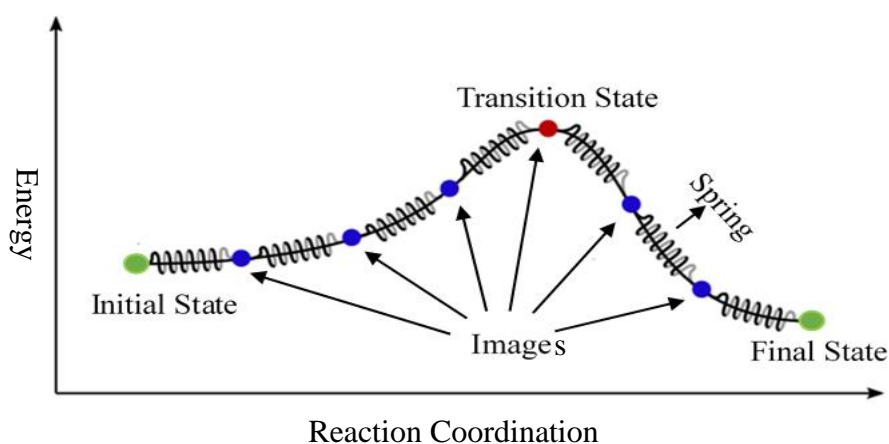


Fig 2S. The schematic of the minimum energy path (MEP) calculated by NEB

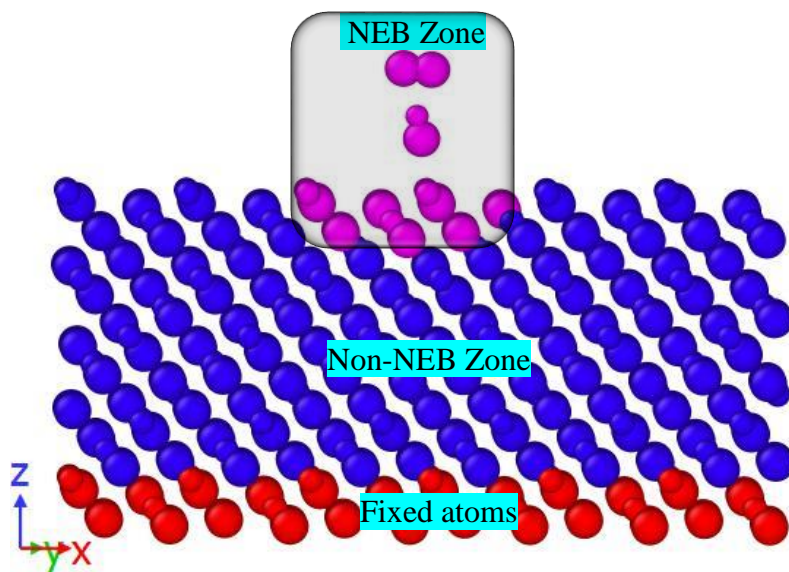


Fig 3S. NEB and Non-NEB zones

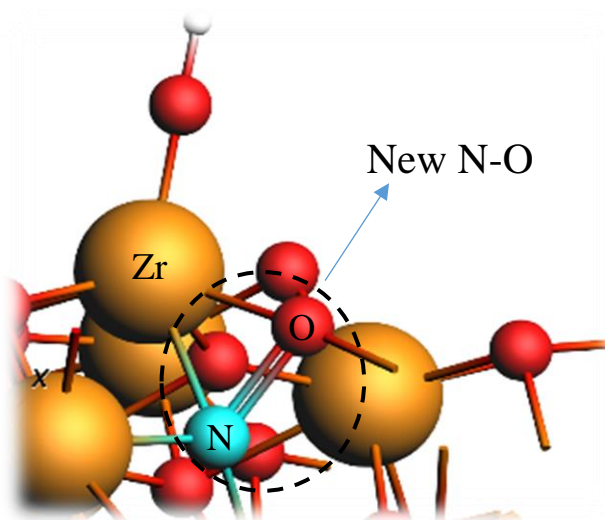


Fig 4S. The formation of the new N-O bond during the adsorption of OH on the Zr site adjacent to the N-dopant

Table 1S. The forward and backward barrier energies of OOH* creation on OH-poisoned t-ZrO₂, t-ZrO_{2-x}, and t-ZrO_{2-x}N_x with considering two oblique and perpendicular configurations of O₂.

	Forward barrier energy (eV) (oblique configurations of O ₂)	Backward barrier energy (eV) (oblique configurations of O ₂)	Forward barrier energy (eV) (perpendicular configurations of O ₂)	Backward barrier energy (eV) (perpendicular configurations of O ₂)
Pristine t-ZrO ₂	0.16	0.09	0.16	0.09
t-ZrO _{2-x}	0.26	0.25	0.23	0.22
t-ZrO _{2-x} N _x	0.11	0.10	0.08	0.06

References

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