Computational Details

Methods: All the plane-wave-based density functional theory (DFT) calculations were performed with the Vienna Ab intio Simulation Package (VASP) [1,2]. The electron ion interaction was described with the projector augmented wave (PAW) [3,4] potentials and the electron exchange and correlation energy was treated within the Perdew-Burke-Ernzerhof (PBE) functional [5] of generalized gradient approximations (GGA) [6]. Spin-polarization was included for iron systems to correctly account for the magnetic properties. The cut-off energy of 400eV and electron smearing via a second-order Methfessel-Paxton [7] technique with the width of 0.2eV were employed to ensure accurate energies with errors less than 1meV per atom. The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme [8]. The convergence criteria for electronic self-consistent interactions and all forces were set to 10^{-4}eV and 0.03eV/Å, respectively. To determine CO dissociation pathways with the minimum barrier, transition states were located using the climbing image nudged elastic band (CI-NEB) method [9], and stretching frequencies were analyzed to characterize a transition state with single imaginary frequency along the reaction coordinate.

To describe the thermodynamic and kinetic properties of CO dissociation, adsorption energy, reaction energy, and activation energy were calculated. The adsorption energy is defined as $E_{ads}=E(\text{adsorbates/slab})-[E(\text{slab})+E(\text{adsorbates})]$, where E(adsorbates/slab) is the total energy of the slab with adsorbates, E(slab) is the total energy of the corresponding bare slab, and E(adsorbates) is the total energy of free adsorbates. The lower (more negative) E_{ads} means the stronger adsorption. The reaction energy is defined as $E_r=E(\text{FS})-E(\text{IS})$. The activation energy is calculated by $E_a=E(\text{TS})-E(\text{IS})$. E(IS), E(FS), and E(TS) are the energies of the corresponding initial state (IS), final state (FS), and transition state (TS), respectively.

Models: By use of a 2×6×6 k-point grid, the calculated zirconium oxide unit cell has a tetragonal structure. The crystallographic parameters (a=3.602Å, b=3.602Å, c=5.164Å, **Fig. 1**) agrees reasonably with the experimental data (a=3.602Å, b=3.602Å, c=5.174Å) [10]. For studying the CO activation mechanism on the ZrO_2 catalyst, the ZrO_2(101) facet terminated by O atoms was built to simulate the catalyst surface due to the calculated lowest surface energy and the largest exposed surface area [11]. we used the p(2×3) supercells containing four oxygen layers and two zirconium layers (4O+2Zr) for the perfect (101) surface, where the top 2O+1Zr layers along

with adsorbates are relaxed and the bottom three layers are fixed in their bulk positions. To avoid significant slab interaction the vacuum gap space between slabs was set to 15Å without counting the adsorbates. According to the lattice sizes (12.61Å×10.80Å), 2×2×1 k-points grid sampling within the Brillouin zones was set.

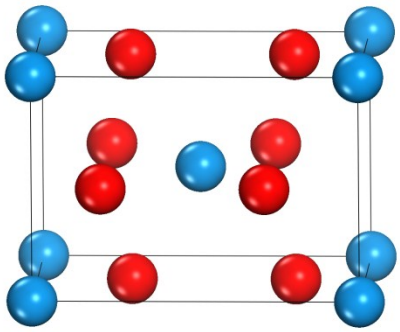

Fig. 1 The unit cell of the tetragonal zirconium oxide, the red balls represent for the O atoms and the blue balls represent for the zirconium atoms

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