

Supporting Information

Theoretical studies on the monomeric vanadium oxides supported at ceria: the atomic structures and oxidative dehydrogenation activities

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Computational details

We used the PBE functional with a Hubbard U of 5.0 eV¹ for the Ce 4*f* orbital and dispersion corrections by DFT-D2 scheme of Grimme² (PBE+U+D) to do the spin-polarized density functional theory (DFT) calculations as implemented in the Vienna ab initio Simulation Package (VASP)³. The required dispersion parameters C_6 and R_0 for O, V, C, H and Ce were taken from refs 2 and 4. The project-augmented wave method (PAW)⁵ at a kinetic energy cutoff of 400 eV was used to describe the electron-core interaction. The Ce (5s, 5p, 6s, 5d, 4f), O (2s, 2p), V (3p, 3d, 4s), C (2s, 2p), and H (1s) electrons were treated as valence states. The calculated lattice parameter of bulk ceria using PBE+U+D is 5.440 Å.

The CeO₂(111) support was modeled by a 9-atomic-layer slab which extended at a (4×4) surface unit cell. A large vacuum gap (>10 Å) was used to avoid the slab-slab interaction. The bottom three layers were fixed at all calculations to estimate bulk properties. In consideration of the big surface cell used, a (1×1×1) k-mesh was used for the Brillouin-zone integration. For all calculations, we used a force stopping-criterion of 0.02 eV/Å on each relaxed ion. Transition states were searched by using the climbing-image nudged elastic band (CI-NEB) method⁶.

Some selected results were also calculated by using the Hyied-Scuseria-Ernzerhof (HSE) hybrid functional⁷ (screening length: 0.2).

H-adsorption energies ($E_{ad}[H]$), methanol adsorption energies ($E_{ad}[MeOH]$) and O-vacancy formation energies (E_{ov}) were calculated as follows:

$$\begin{aligned} E_{ad}[H] &= E[VO_x/CeO_2] + \frac{1}{2}E[H_2] - E[H/VO_x/CeO_2], \\ E_{ad}[MeOH] &= E[VO_x/CeO_2] + E[MeOH] - E[MeOH/VO_x/CeO_2], \\ E_{ov} &= E[VO_{x-1}/CeO_2] + \frac{1}{2}E[O_2] - E[VO_x/CeO_2], \end{aligned}$$

where $E[VO_x/CeO_2]$, $E[H/VO_x/CeO_2]$, $E[MeOH/VO_x/CeO_2]$, $E[VO_{x-1}/CeO_2]$, $E[H_2]$, $E[MeOH]$ and $E[O_2]$ are the DFT total energies of CeO₂(111) supported VO_x (VO_x/CeO₂(111)), VO_x/CeO₂(111) with adsorbed H, VO_x/CeO₂(111) with adsorbed methanol, defective VO_x/CeO₂(111), gas-phase H₂, methanol and O₂, respectively.

Thermodynamic analyses of various VO_x species were performed by using the formalism described in detail in our earlier study⁸, which is also similar with several other studies⁹ as well. Briefly, we used the following thermodynamic formalism to calculate the surface free energy change per unit area ($\Delta\gamma$) at given oxygen partial pressure (p) and temperature (T):

$$\Delta\gamma(p, T) =$$

$$\frac{1}{A} \left\{ E[VO_x/CeO_2] - E[CeO_2] - E_{bulk}[V] - \frac{x}{2}E[O_2] - \frac{x}{2} \left\{ H[O_2](p^0, T) - H[O_2](p^0, 0K) - TS[O_2](p^0, T) + K_B T \ln \frac{p}{p^0} \right\} \right\} \quad (\text{note: the vibration contributions and the } pV \text{ term of solid components were neglected})$$

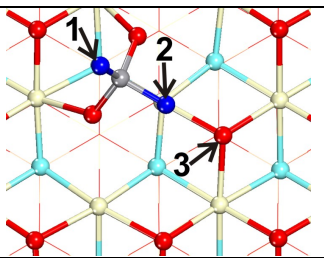
where A is the area of the surface cell. $E[CeO_2]$ and $E_{bulk}[V]$ are the DFT total energies of clean CeO₂(111) and metallic bcc bulk vanadium, respectively. K_B is the Boltzmann constant.

p^0 is the reference state of pressure that equals to 1 atm. Enthalpy (H) and entropy (S) at temperature T were calculated according to the formulas on the Web site of NIST¹⁰.

Table S1 Calculated energies (eV) of various VO_x species. All energies are relative to the most stable species of a given composition. The corresponding structures are shown in Figure S2.

	most stable	second most stable
VO ₂ -type	0	1.02
VO ₃ -type	0	0.11
VO ₄ -type	0	2.56

Table S2 Calculated H adsorption energies ($E_{ad}[H]$) at different O sites, H diffusion barriers (E_b), and O-vacancy formation energies (E_{ov}) of VO₂-A. Energies are in eV.

Structure		
$E_{ad}[H]$	O-1	1.52
	O-2	1.45
	O-3	1.51
E_b	O-1→O-2	1.73
	O-2→O-1	1.65
	O-2→O-3	0.24
	O-3→O-2	0.31
E_{ov}		0.79

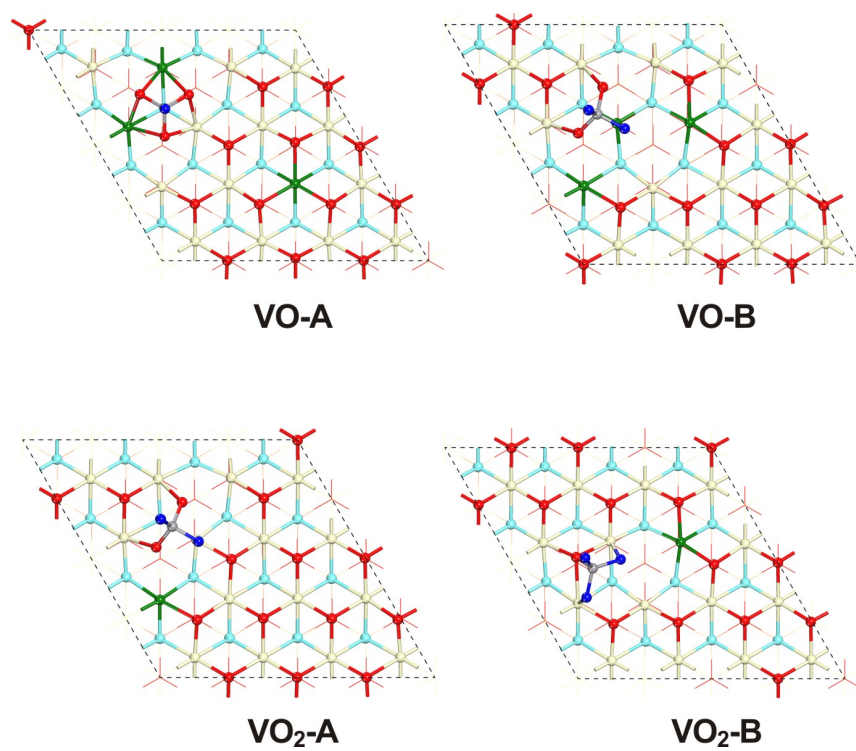


Fig. S1 Ce^{3+} distributions of VO-A, VO-B, VO₂-A and VO₂-B (top view). Ce^{3+} are in green.

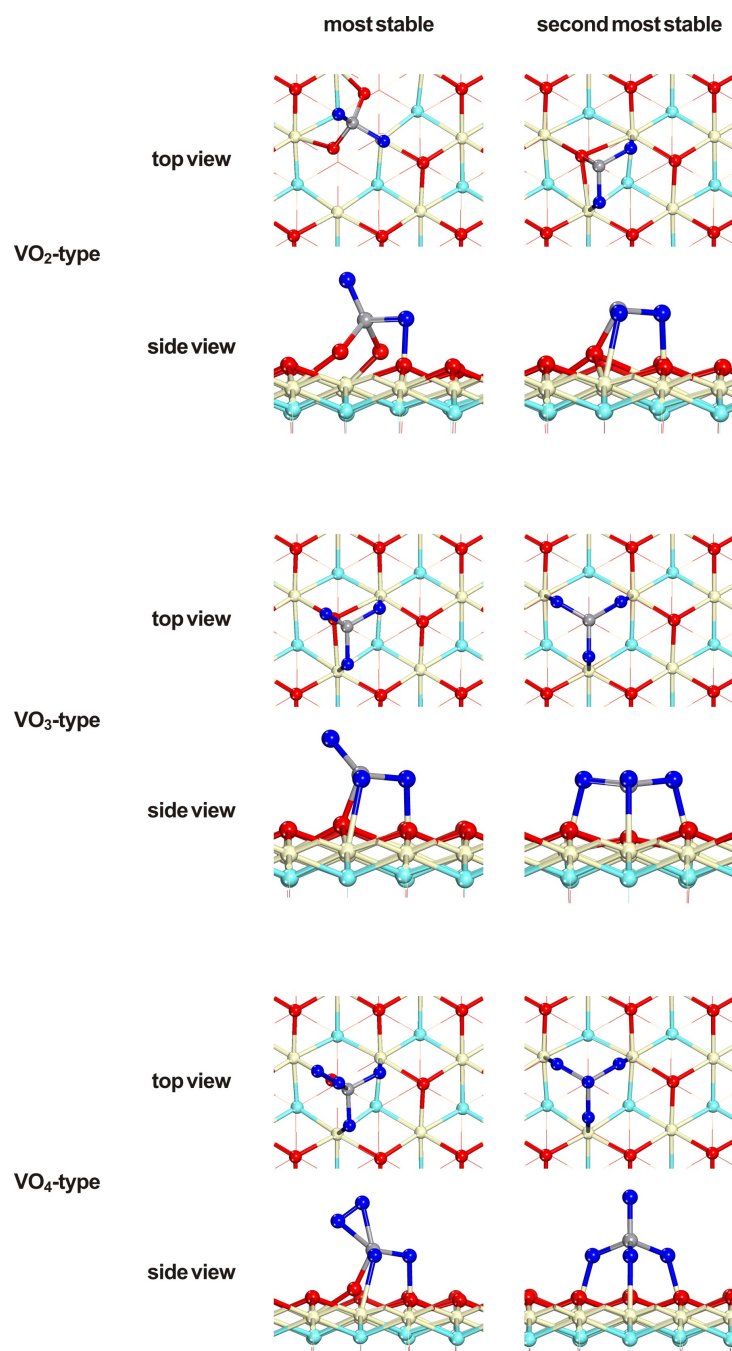


Fig. S2 Calculated structures of the most stable and the second most stable VO_x (x=2-4) species.

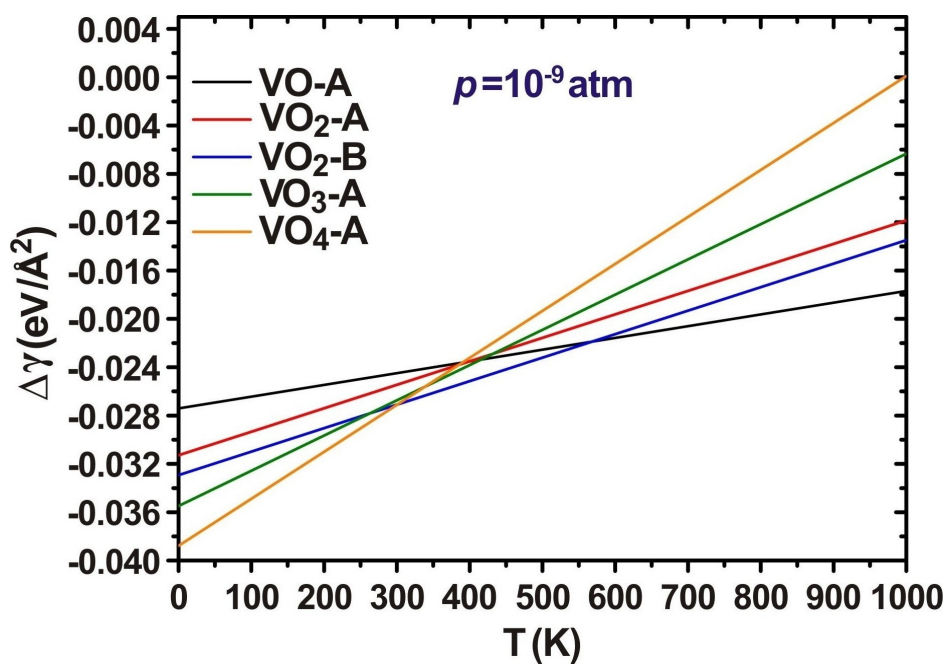


Fig. S3 Calculated diagram of surface free energy changes ($\Delta\gamma$) for the formation of various VO_x species as a function of T under $p=10^{-9}$ atm.

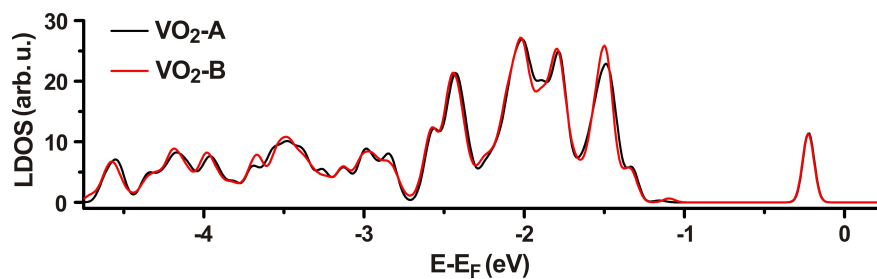


Fig. S4 Calculated LDOS of the surface O and Ce atoms of VO₂-A (black) and VO₂-B (red).

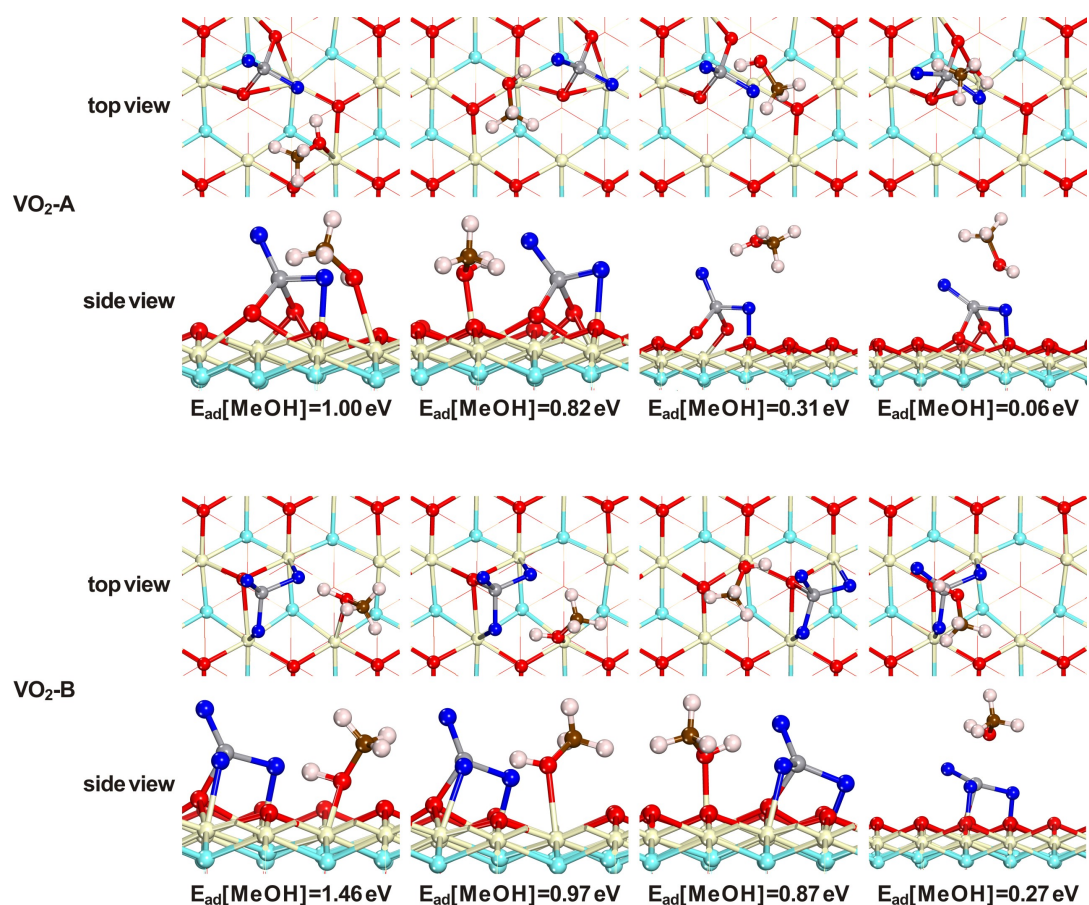


Fig. S5 Calculated structures of methanol adsorbed at VO₂-A and VO₂-B (top and side views) with corresponding adsorption energies.

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