

## 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 eV<sup>1</sup> for the Ce 4f orbital and dispersion corrections by DFT-D2 scheme of Grimme<sup>2</sup> (PBE+U+D) to do the spin-polarized density functional theory (DFT) calculations as implemented in the Vienna ab initio Simulation Package (VASP)<sup>3</sup>. The required dispersion parameters C<sub>6</sub> and R<sub>0</sub> for O, V, C, H and Ce were taken from refs 2 and 4. The project-augmented wave method (PAW)<sup>5</sup> 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 CeO<sub>2</sub>(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) method<sup>6</sup>.

Some selected results were also calculated by using the Hyd-Scuseria-Ernzerhof (HSE) hybrid functional<sup>7</sup> (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:

$$E_{ad}[H] = E[VO_x/CeO_2] + \frac{1}{2}E[H_2] - E[H/VO_x/CeO_2],$$

$$E_{ad}[MeOH] = E[VO_x/CeO_2] + E[MeOH] - E[MeOH/VO_x/CeO_2],$$

$$E_{ov} = E[VO_{x-1}/CeO_2] + \frac{1}{2}E[O_2] - E[VO_x/CeO_2],$$

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 CeO<sub>2</sub>(111) supported VO<sub>x</sub> (VO<sub>x</sub>/CeO<sub>2</sub>(111)), VO<sub>x</sub>/CeO<sub>2</sub>(111) with adsorbed H, VO<sub>x</sub>/CeO<sub>2</sub>(111) with adsorbed methanol, defective VO<sub>x</sub>/CeO<sub>2</sub>(111), gas-phase H<sub>2</sub>, methanol and O<sub>2</sub>, respectively.

Thermodynamic analyses of various VO<sub>x</sub> species were performed by using the formalism described in detail in our earlier study<sup>8</sup>, which is also similar with several other studies<sup>9</sup> 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 ( $T$ ):

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

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

where A is the area of the surface cell.  $E[CeO_2]$  and  $E_{bulk}[V]$  are the DFT total energies of clean CeO<sub>2</sub>(111) and metallic bcc bulk vanadium, respectively.  $K_B$  is the Boltzmann constant.

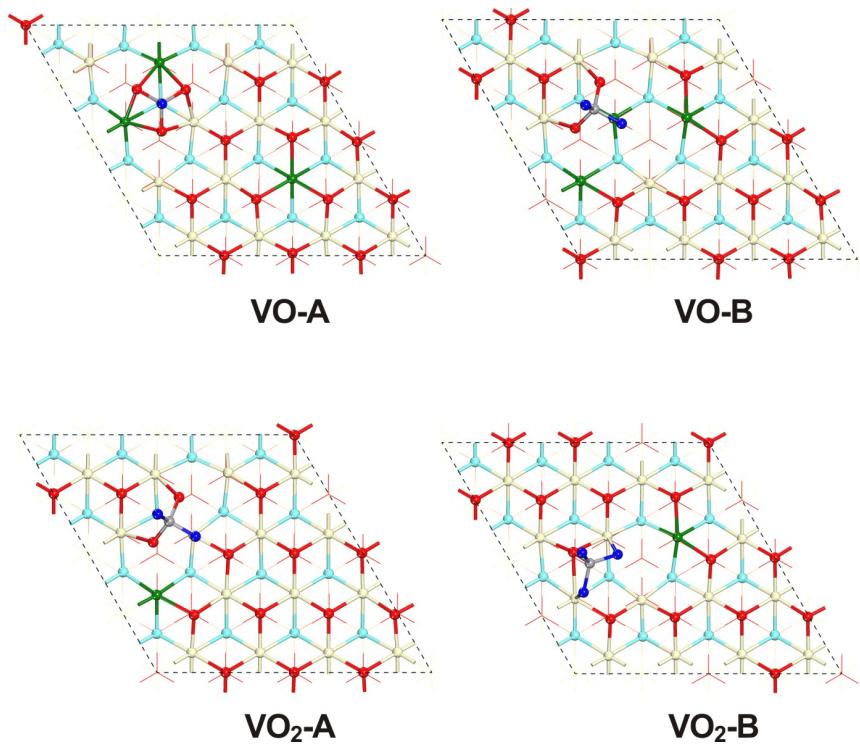
$p^0$  is the reference state of pressure that equals to 1 atm. Enthalpy ( $H$ ) and entropy ( $S$ ) at temperature  $T$  were calculated according to the formulas on the Web site of NIST<sup>10</sup>.

**Table S1** Calculated energies (eV) of various  $\text{VO}_x$  species. All energies are relative to the most stable species of a given composition. The corresponding structures are shown in Figure S2.

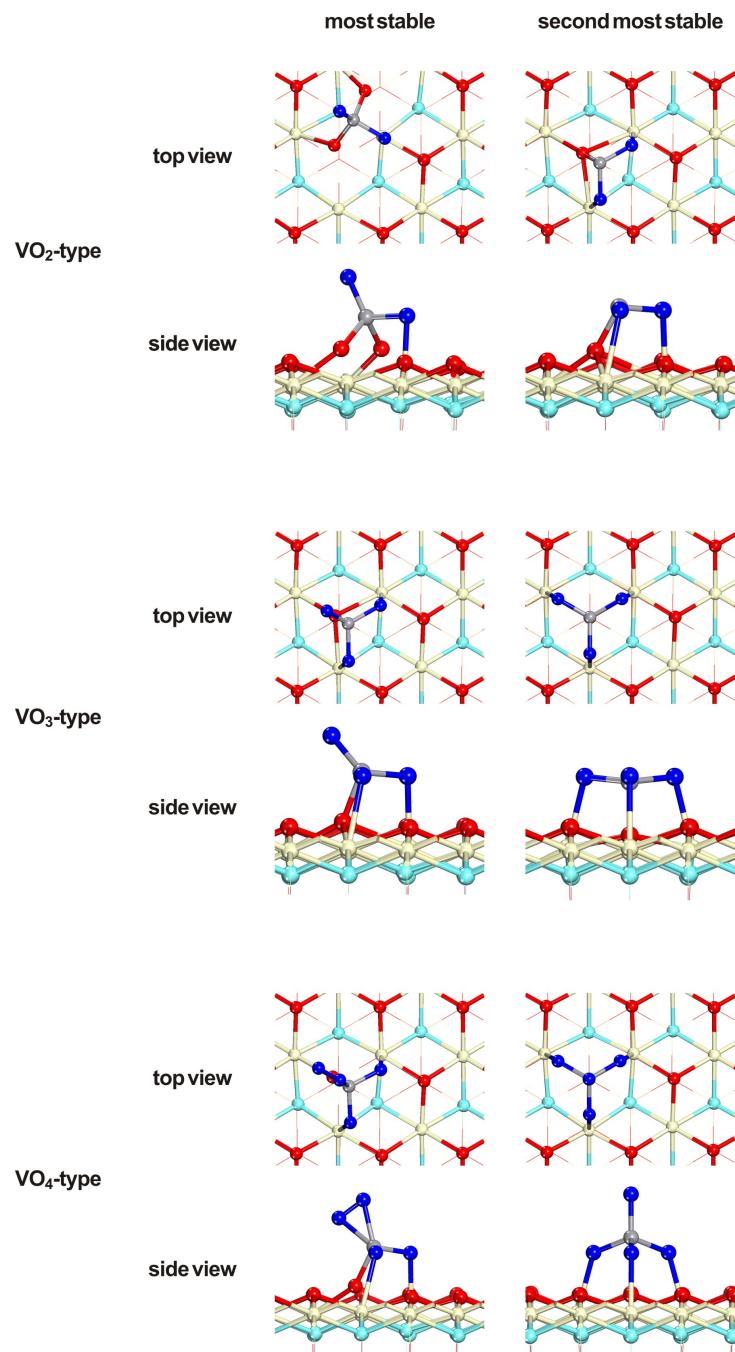
	most stable	second most stable
$\text{VO}_2$ -type	0	1.02
$\text{VO}_3$ -type	0	0.11
$\text{VO}_4$ -type	0	2.56

**Table S2** Calculated H adsorption energies ( $E_{ad}[\text{H}]$ ) at different O sites, H diffusion barriers ( $E_b$ ), and O-vacancy formation energies ( $E_{ov}$ ) of  $\text{VO}_2$ -A. Energies are in eV.

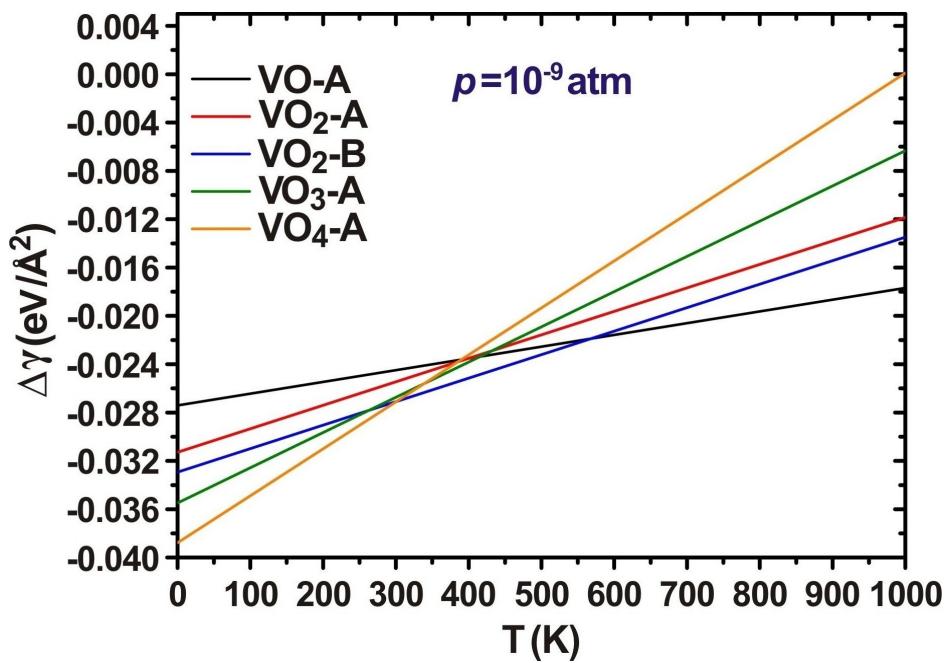
Structure	
$E_{ad}[\text{H}]$	
O-1	1.52
O-2	1.45
O-3	1.51
$E_b$	
O-1→O-2	1.73
O-2→O-1	1.65
O-2→O-3	0.24
O-3→O-2	0.31
$E_{ov}$	0.79



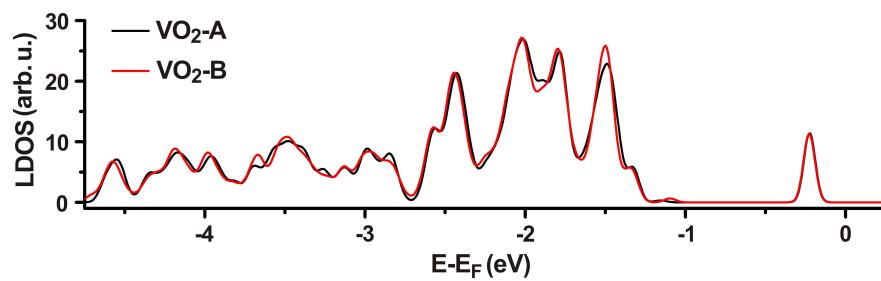
**Fig. S1** Ce<sup>3+</sup> distributions of VO-A, VO-B, VO<sub>2</sub>-A and VO<sub>2</sub>-B (top view). Ce<sup>3+</sup> are in green.



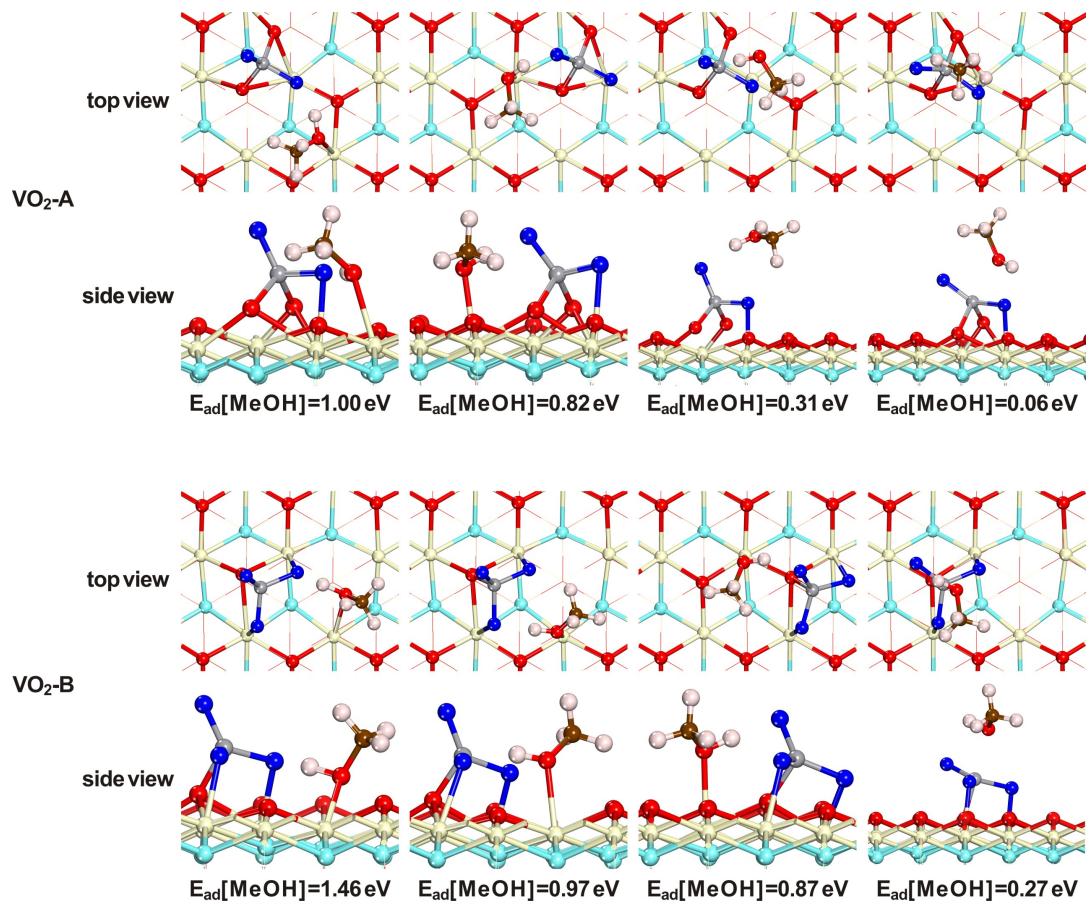
**Fig. S2** Calculated structures of the most stable and the second most stable  $\text{VO}_x$  ( $x=2-4$ ) species.



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



**Fig. S4** Calculated LDOS of the surface O and Ce atoms of  $\text{VO}_2$ -A (black) and  $\text{VO}_2$ -B (red).



**Fig. S5** Calculated structures of methanol adsorbed at VO<sub>2</sub>-A and VO<sub>2</sub>-B (top and side views) with corresponding adsorption energies.

## References

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