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Supplementary information

First-principles study of an efficient non-noble metal single-atom catalyst $Fe_1/TiVCO_2$ for CO oxidation

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COMPUTATIONAL DETAILS

The theoretical studies were performed at the level of DFT with the Kohn-Sham spin-polarization formalism by Vienna Initio Simulation Package (VASP)[62-64] to calculate the single-point energy and spin polarization geometry, with generalized gradient approximation (GGA) of the exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) for the calculations[65]. The GGA + Hubbard U (GGA+U) functional was used to predict the electronic properties of the Fe, Ti and V atom with a Hubbard correction of about 3.8 eV, 3.8 eV and 4 eV, which was also considered in adsorption and incorporation of transition metals at the magnetite Fe_3O_4 and the work of V_2C-based MXenes [66,67]. The valence electrons are determined according to the following arrangement: $C(2s^22p^2)$, $O(2s^22p^4)$,$Ti(3d^24s^2)$, $V(3d^34s^2)$ and $Fe(3d^64s^2)$. The cutoff energy for geometric optimization and self-consistent calculations is set to 500 eV, referring to the cutoff energy of ultrasoft pseudopotentials. A (4×4) supercell of primitive cells (including 16 V atoms, 16 Ti atoms, 16 C atoms, and 32 O atoms) of MXene ($TiVCO_2$) was used to build the substrate of SAC. In addition, A 20 Å vacuum space was set to avoid the interlayer interaction between the substrate and its image. The structure with a completely geometrically optimized Fe atom and $TiVCO_2$ is shown in **Figure S1**. The

Brillouin zone was sampled by a Monkhorst−Pack special k-point mesh of Γ-center for structural relaxation and 9×9×1 for densities of states (DOS) calculations. The electron density for the ground state was considered to be converged when reaching a total energy threshold of 10-8 eV. All the ions were permitted to relax until the residual force was less than 0.01 eV/Å. In order to determine the reaction mechanism of CO oxidation, the climbing image nudged elastic band (CINEB) [70,71] and dimer method [72,73] method were used to determine the reaction path and energy barrier. All transition state (TS) geometries are confirmed and have only one imaginary vibration frequency.

In order to test the possible influence of van der Waals interaction, we use the DFT+D3 empirical correction in the Grimm scheme in **Table S1** . The calculation results listed below show that the van der Waals interaction has no significant effect on the adsorption energy of the adsorbates on the MXene surface, and it is not considered in the further calculation.

System	DFT	DFT+D3
$Fe_1/TiVCO_2$	-4.67	-4.69
E_{CO}	-1.09	-1.10
E_{O_2}	-1.48	-1.49
E_{2CO}	-2.19	-2.21
E_{CO+O_2}	-1.55	-1.56
$E_{CO_2}(C-Fe)$	1.20	1.18
$E_{CO_2}(O-Fe)$	-0.24	-0.25

Table S1 The adsorption energy of different species, which is compared with the results of DFT+D3. $E_{CO_2}(C - Fe)$ and $E_{CO_2}(O - Fe)$ means that C on CO_2 binds to Fe and O binds to Fe. All the energies are in eV.

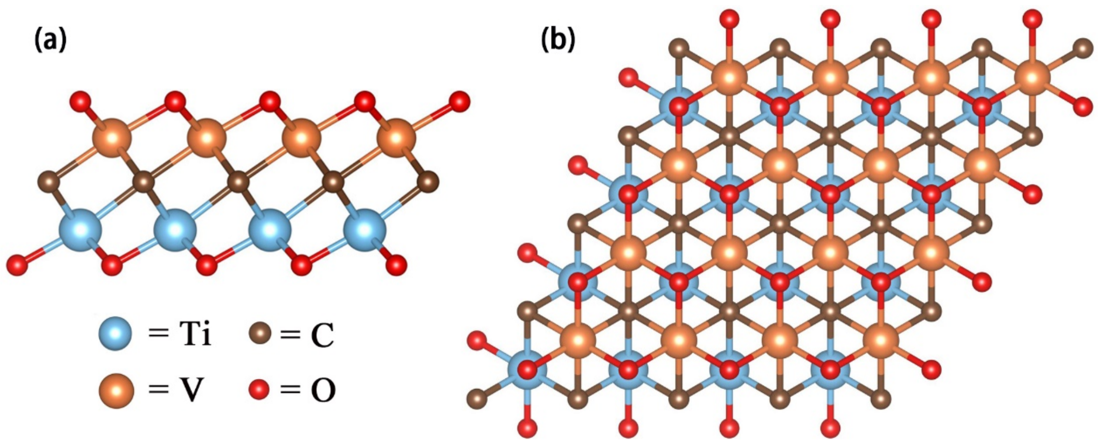

Figure S1 The side view (a) and top view (b) of $TiVCO_2$ with surface saturated oxygen functional group substrate.

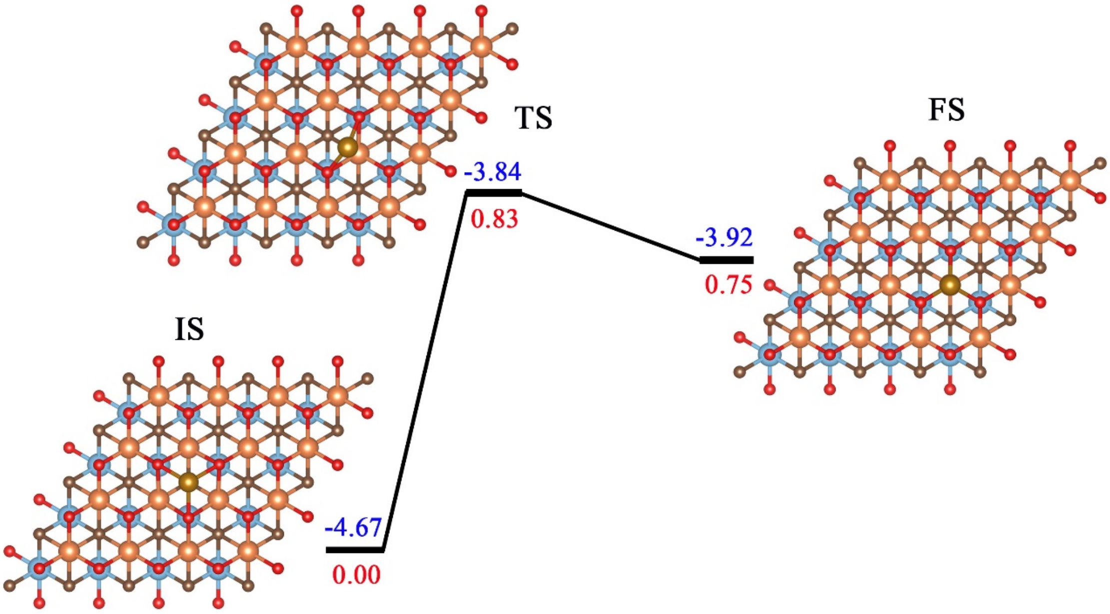

Figure S2 The schematic energy distribution of a single Fe atom moving from the most stable position on the MXene monolayer to its adjacent position. The relative energy is listed in red. All energy is expressed in eV.

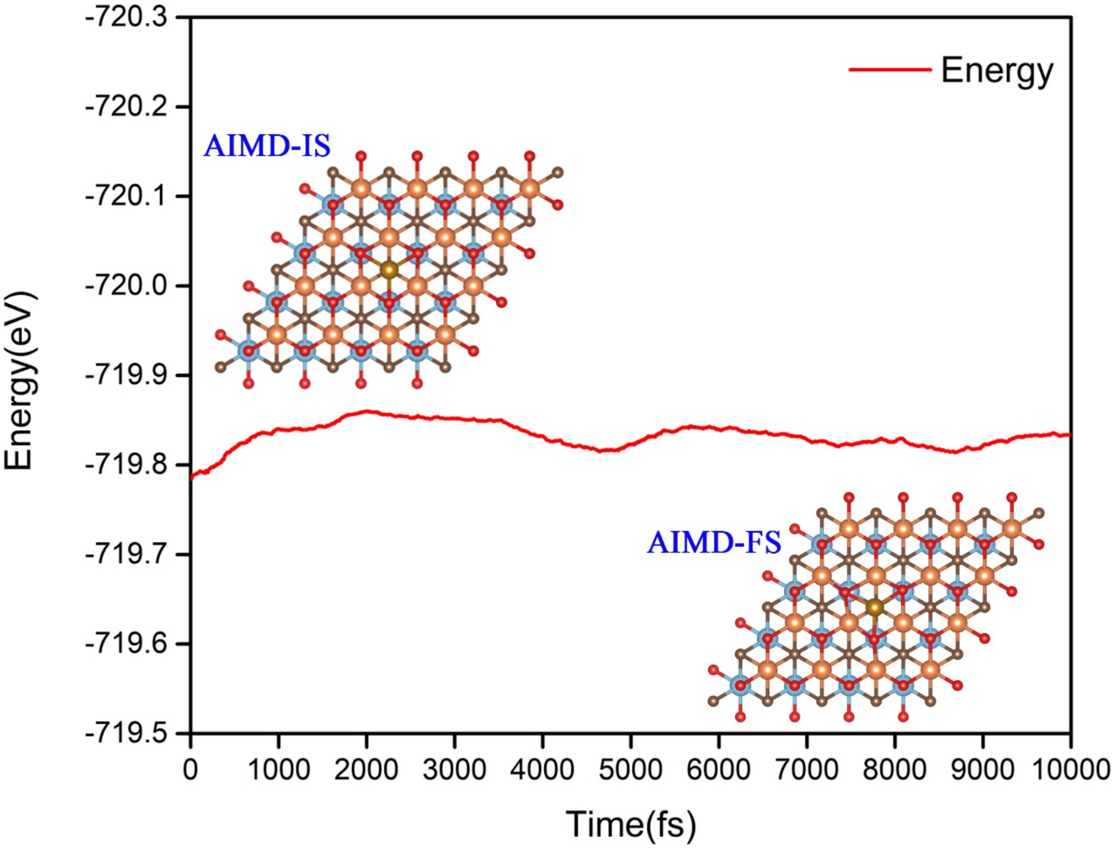

Figure S3 Energy curve within 10 ps at 300 K by AIMD(Ab initio molecular dynamics), the initial state(IS), and final state(FS) are shown in the figure.

System	TER-IS	TER-TS5	TER-IM	TER-TS7	TER-FS
magnetic moments	2.92	2.39	2.86	3.12	3.04

Table S2 Calculated magnetic moments (in μB) of Fe atom of IS, IM, TSs, and FS in TER reaction pathways.

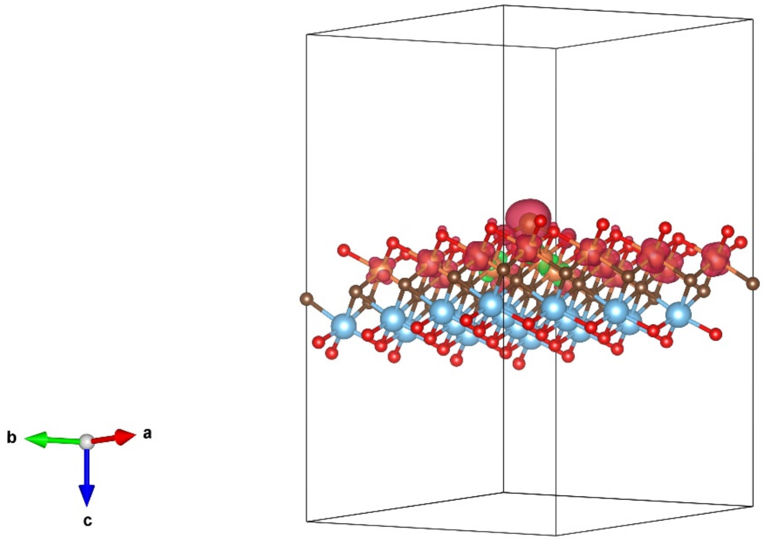

Figure S4 The spin density localization and magnetic moments of 4 unpaired electrons of Fe in $Fe_1/TiVCO_2$ with the spin density population displayed in red and green.

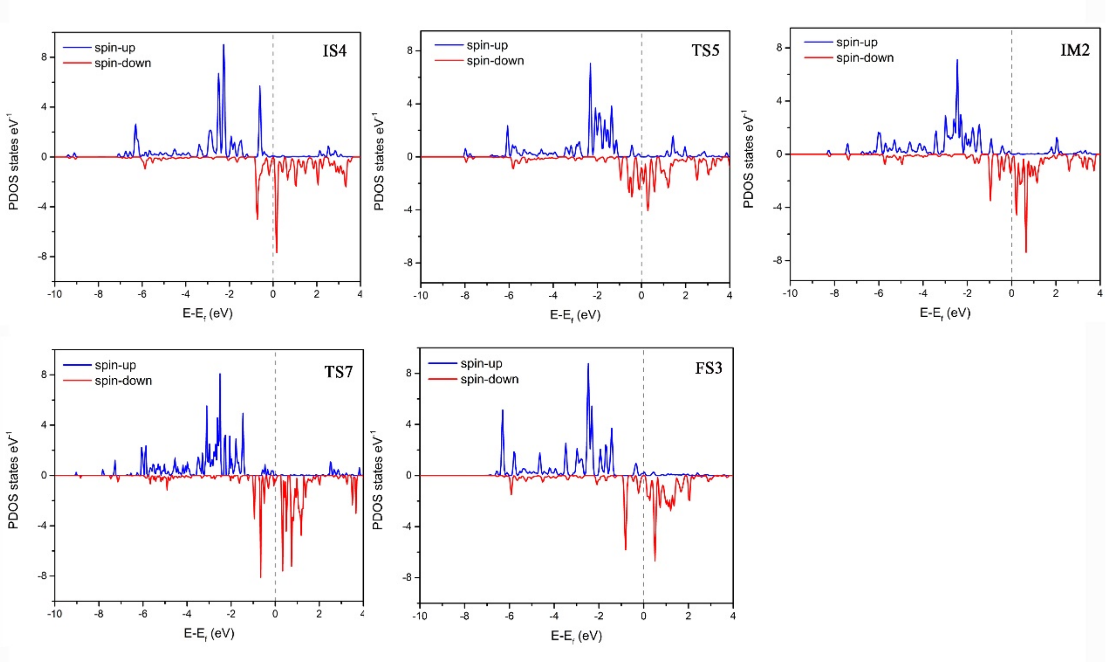

Figure S5 The spin-polarized partial density of states (PDOS) of all the elementary steps (IS, IM, TSs, and FS) along the Trimolecular Eley-Rideal (TER) mechanism involved in the CO oxidation reaction projected on Fe-3d states. The Fermi level is set to zero.