

The C-H bond activation triggered by subsurface Mo dopant on MgO catalyst in oxidative coupling of methane

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Computational Setup

The calculations reported here were performed by using periodic, spin-polarized density functional theory (DFT) as implemented in the form of Vienna ab initio simulation package (VASP)^{1,2}. For valence electrons, a plane-wave basis set was adopted with an energy cutoff of 400 eV and ionic cores were described with the projector augmented-wave (PAW) method^{3,4}. The Revised Perdew-Burke-Ernzerhof (RPBE) functional was used as the exchange-correlation functional approximation which shown better performance in barrier estimation⁵, and used zero damping DFT-D3 method of Grimme for van der Waals correlation correction⁶. Geometry optimization was converged with forces acting on atoms lower than 0.03 eV/Å, whereas the energy threshold defining self-consistency of electron density was set to 10⁻⁶ eV. The reaction pathways with a force tolerance of 0.05 eV/Å and energy barriers were calculated by using the climbing nudged elastic band (CI-NEB) method⁷.

The MgO(100) surface was modelled by 4x4 five-atomic-layer supercell. All the layers are relaxed. The supercell containing a vacuum space of 10 Å between the slab and its periodic images was used. The reaction barrier was calculated as difference between initial state (IS) and the highest image along pathway.

In order to analyze the methane adsorbed on catalyst, the adsorption energy (ΔE_{ads}) and the reaction energy (ΔE) were define through following equation (1):

$$\Delta E_{\text{ads}} = E_{\text{A/catalyst}} - E_{\text{A}} - E_{\text{catalyst}} \quad (1)$$

$$\Delta E = E_{\text{FS}} - E_{\text{IS}}$$

Where $E_{\text{A/catalyst}}$ is the total energies of the catalyst with the adsorbates(A) including CH₄ and O₂, E_{catalyst} and E_{A} are the clean catalyst and the free CH₄ and O₂ respectively. The E_{FS} and E_{IS} are the total energies of the final state (FS) and the initial state (IS).

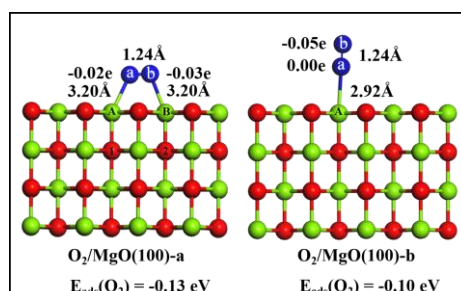


Figure S1. The adsorption energy and configuration of oxygen molecule on undoped MgO(100).

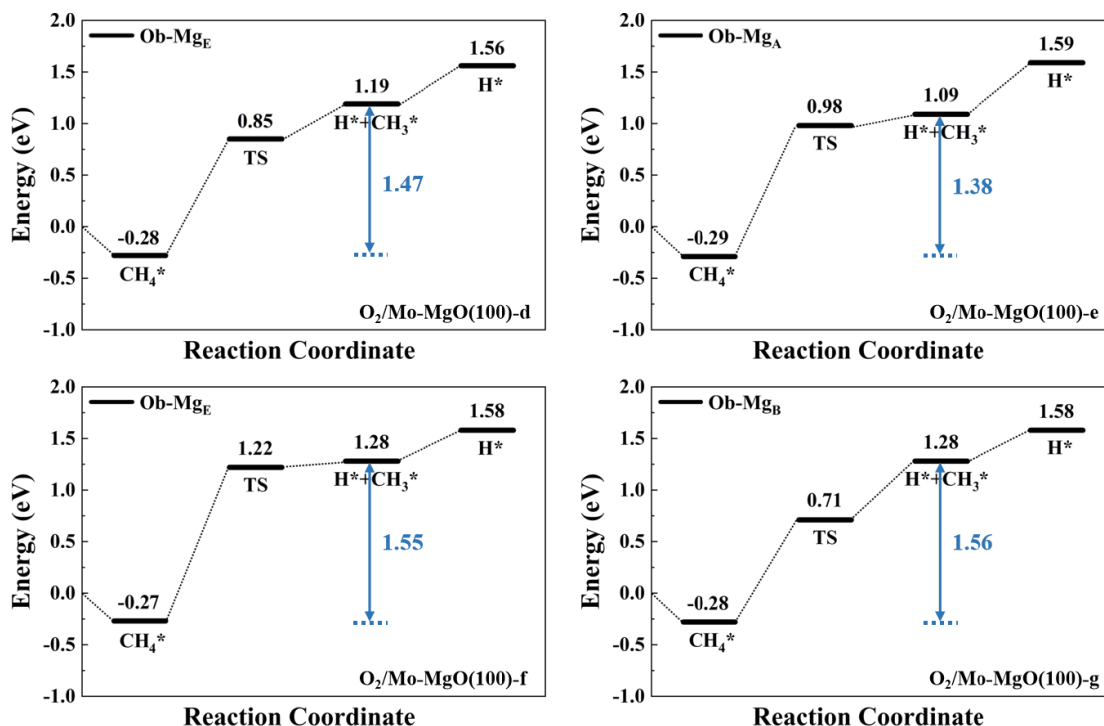


Figure S2. Reaction pathways of methane activation on Mo doped MgO(100) with adsorbed oxygen molecule.

- (1) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Physical Review B* **1993**, *47* (1), 558–561. <https://doi.org/10.1103/PhysRevB.47.558>.
- (2) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169–.
- (3) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Computational Materials Science* **1996**, *6* (1), 15–50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- (4) Blöchl, P. E. Projector Augmented-Wave Method. *Physical Review B* **1994**, *50* (24), 17953–17979. <https://doi.org/10.1103/PhysRevB.50.17953>.
- (5) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energetics within Density-Functional Theory Using Revised Perdew-Burke-Ernzerhof Functionals. *Physical Review B* **1999**, *59* (11), 7413–7421. <https://doi.org/10.1103/PhysRevB.59.7413>.
- (6) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *Journal of Computational Chemistry* **2011**, *32* (7), 1456–1465. <https://doi.org/10.1002/jcc.21759>.
- (7) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *The Journal of Chemical Physics* **2000**, *113* (22), 9901–9904. <https://doi.org/10.1063/1.1329672>.