

Methane to Methanol: Taming a Titan on Tungsten Trioxide

Computational Investigation of Selective Methane Oxidation on Modified WO_3 (001) Surfaces

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In Short

- Enable selective low-temperature CH_4 -to-methanol conversion for sustainable fuel and greenhouse gas mitigation.
- Study how surface modifications, such as metal doping, on WO_3 surfaces affect CH_4 activation.
- Different polymorphs of WO_3 will be investigated.
- DFT+ U , dispersion and dipole corrections, HSE06 hybrid functional, ci-NEB, and solvation models (VASP/VASPsol) will be used.

This project proposes a comprehensive computational investigation using Density Functional Theory (DFT) to study the selective oxidation of methane (CH_4) to methanol on chemically modified tungsten trioxide (WO_3) surfaces. Methane, the primary component of natural gas, is an abundant but underutilized energy resource that offers a sustainable alternative to crude oil-derived feedstocks.[1] However, the exceptional chemical stability of methane, due to its strong C–H bonds, poses a major challenge for selective partial oxidation.[2] This often leads to over-oxidation and the formation of undesired by-products such as carbon monoxide (CO) and carbon dioxide (CO_2), reducing the efficiency and sustainability of methane conversion. Accompanying this challenge, methane is a potent greenhouse gas with a 20-year global warming potential approximately 80 times greater than CO_2 . [3] Its atmospheric oxidation depletes hydroxyl radicals, contributing to reduced air quality and ground-level ozone formation. These factors highlight the urgent need for efficient, selective catalysts—ideally composed of earth-abundant elements—that can precisely control reaction pathways to maximize methanol yield.

Focusing on WO_3 as a catalyst, and building on insights from preliminary work on these systems, this research aims to understand how specific surface modifications—such as the substitution of terminal O atoms with chemically active groups, metal doping (the selection of the metal will be in tight collaboration with our experimental partners), and solvation effects can enhance methane activation and steer the reaction toward selective methanol formation.

The key questions this study addresses are: (1) How does the replacement of terminal O atoms of WO_3 affect methane activation? (2) What is the role of metal dopants in modifying the electronic structure and reactivity of the surface? (3) How do solvation models affect reaction energetics? The ultimate goal is to determine whether these combined effects can enable a viable low-temperature pathway for selective methane oxidation to methanol.

The project will employ advanced DFT calculations using the Vienna Ab initio Simulation Package (VASP),[4] incorporating Hubbard U correction (DFT+ U), to accurately capture the localized d -electrons of tungsten. Dispersion interactions will be included using the DFT-D3(BJ) scheme, and dipole corrections will be applied to slab models (along the z -axis) to maintain structural and electrostatic symmetry, ensuring non-polarity of the slab.

For high-accuracy single-point energy calculations and photoabsorption spectra, the computationally demanding HSE06 hybrid functional will be used to address the well-known band gap underestimation of conventional DFT. This approach will yield high-fidelity data on density of states (DOS), Bader charges, and electronic structure too. Reaction mechanisms and transition states for methane activation will be thoroughly investigated using the climbing image Nudged Elastic Band (ci-NEB) method. To simulate realistic catalytic environments, solvation effects will be modeled using both implicit solvation via VASPsol[5] and explicit solvation.

Preliminary studies on WO_3 have already demonstrated the critical role of dispersion and dipole corrections in preserving slab integrity and symmetry. In Figure 1 can be found figures of the unit cell, supercell and slab model of γ -monoclinic WO_3 of the $P2_1/c$ space group. Hydroxylation of the surface was shown to significantly lower the work function from 7.804 eV to 4.526 eV, thereby enhancing electron transfer capabilities and surface reactivity. Hydroxylation also affects key structural features such as interlayer spacing, W–O bond lengths, inversion symmetry, and adsorption energies. While computational studies on selective methane oxidation over WO_3 remain limited, this project will advance the field by systematically exploring the role of hydroxyl radicals, tailored transition metal doping, and realistic solvation environments. Additionally, high-level HSE06 photoabsorption

spectra calculations will provide insights into how surface modifications impact light absorption and charge carrier dynamics, factors directly relevant to potential photo-assisted catalytic pathways.

Developed in collaboration with leading experimental partners (including Prof. Dr. Marschall, whose catalytic work on WO_3 is detailed in [6]), our research is poised to significantly advance the understanding of methane activation on oxide surfaces. By systematically investigating the synergistic effects of surface modifications, radical chemistry, metal doping, and solvation, this study aims to identify novel reaction pathways and intermediates that could enable higher selectivity and lower energy requirements. The broader implications extend to catalytic oxidation processes vital for environmental remediation, sustainable fuel synthesis, and greenhouse gas mitigation.

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<https://www.bcp.fu-berlin.de/en/chemie/index.html>

More Information

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Project Partners

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DFG Subject Area

302-03

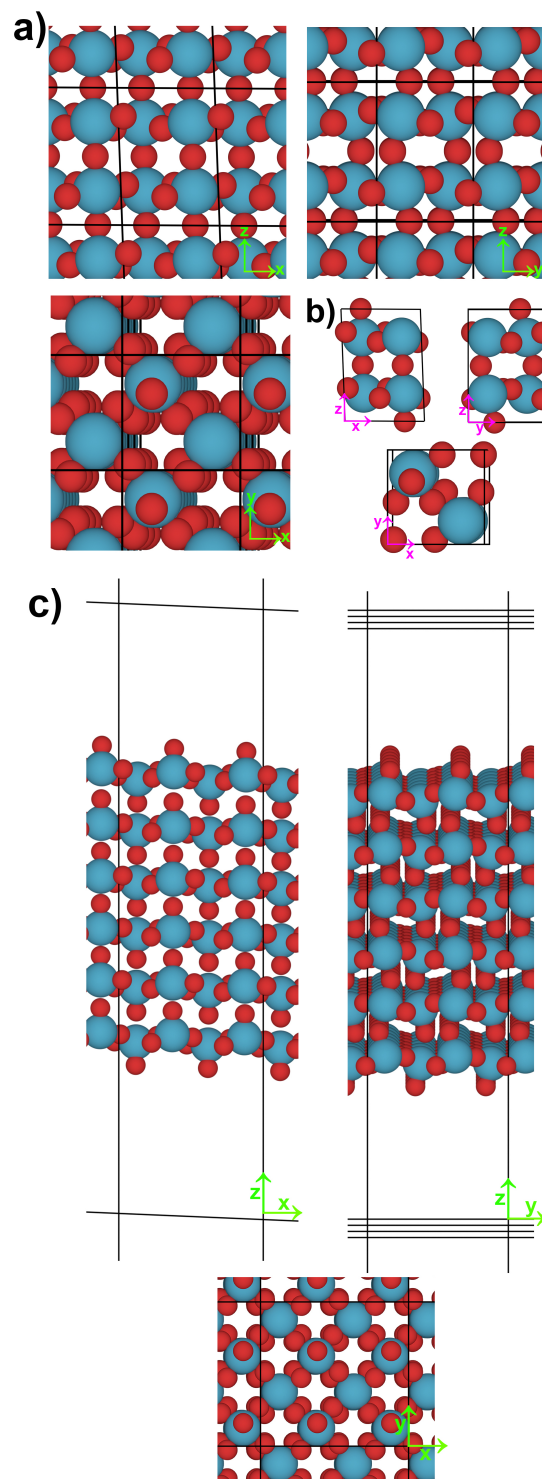


Figure 1: a) Different views on the optimized bulk structure of γ -monoclinic WO_3 , b) bulk unit cell, c) (001) slab model.