DOI 10.5162/EUROSENSORS2025/TP26

Vacancy-Engineered MoS_2 for Selective CO Sensing: A DFT Perspective on Intercalation

Dominik Florjan [1], *Piotr Radomski*[2] *and Maciej J. Szary*[1]
[1] Institute of Physics, Poznan University of Technology, ul. Piotrowo 3, 61-138 Poznan, Poland
[2] Institute of Materials Research and Quantum Engineering, Poznan University of Technology, ul. Piotrowo 3, 61-138 Poznan, Poland
dominik.florjan@doctorate.put.poznan.pl

Summary: Molecular intercalation holds significant implications for utilizing 2D materials in applications like gas detection and catalysis, yet it remains unexplored. Using density functional theory (DFT), this study investigates the intercalation of CO and CO_2 into MoS_2 and the role of sulfur vacancies. CO intercalation is unfavorable in pristine MoS_2, while CO_2 intercalation is marginally favorable at high coverages. Sulfur vacancies enable selective CO intercalation by incorporating CO into vacancy sites, facilitating catalytic CO-to-CO_2 conversion without affecting CO_2 intercalation. This highlights the potential of defect engineering in MoS_2 for gas detection and catalytic applications.

Keywords: Carbon monoxide conversion, CO, CO_2, Single-atom vacancy doping, Density functional theory

Introduction

The strategic manipulation of interlayer spaces in two-dimensional (2D) materials via molecular intercalation offers compelling routes for tailoring electronic, catalytic, and sensing properties [1, 2, 3]. Molybdenum disulfide (MoS_2), a prototypical transition metal dichalcogenide, stands as a prime candidate for such functionalization, particularly concerning interactions with small gas molecules relevant to environmental monitoring and catalysis, such as carbon monoxide (CO) and carbon dioxide (CO_2). However, a fundamental understanding of the thermodynamics governing intercalation and the influence of intrinsic defects remains crucial for realizing practical applications.

Methodology

This study investigates the intercalation of carbon monoxide (CO) and carbon dioxide (CO_2) into bilayer molybdenum disulfide (MoS_2) using first-principles Density Functional Theory (DFT) simulations within the QUANTUM ESPRESSO framework. The calculations employed the projector augmented-wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, incorporating Grimme's D3 van der Waals corrections (PBE+D3) to accurately describe weak interactions. Bilayer MoS_2 models were constructed using 3×3, 4×4, and 5×5 supercells to examine a range of molecular coverages (0.462 to 10.272 molecules/nm^2). Both pristine MoS_2 bilayers and systems containing single-atom sulfur vacancies were simulated to assess the impact of defects.

Results

This contribution presents a comprehensive theoretical investigation, into the intercalation behavior of CO and CO_2 within bilayer MoS_2. We systematically evaluate the energetic favorability of intercalation for both molecules in pristine MoS_2 structures and, critically, assess the impact of introducing sulfur vacancies on this process.

Our calculations reveal distinct behaviors for CO and CO_2 in pristine MoS_2. Intercalation of CO is found to be energetically unfavorable across the range of molecular coverages studied, suggesting limited interaction within the van der Waals gap of defect-free bilayers. In contrast, CO_2 intercalation demonstrates marginal thermodynamic favorability, but only becomes notable at higher molecular concentrations within the interlayer region.

The introduction of sulfur vacancies introduces a profound selectivity into the system. We demonstrate that vacancies act as potent facilitators for CO intercalation, significantly lowering the intercalation energy, rendering the process energetically favorable, as seen in Figure 1a. The mechanism involves the incorporation of a CO molecule directly into the vacancy site within one of the MoS_2 layers, which significantly lowers the system's energy and renders the overall intercalation process favorable. Furthermore, our results suggest a potential pathway for vacancy-enabled catalytic conversion of CO to CO_2 within the intercalated structure (Figure 2e). Strikingly, the presence of these same sulfur vacancies has a negligible effect on the thermodynamics of CO_2 intercalation compared to the pristine system.

These findings highlight the pivotal role of defect engineering in modulating the gas interaction properties of MoS_2. The demonstrated ability of sulfur vacancies to selectively promote CO intercalation, while remaining relatively inert towards CO_2, offers significant implications for the development of advanced MoS_2-based materials. Potential applications include enhanced sensitivity and selectivity in combustion gas sensors,

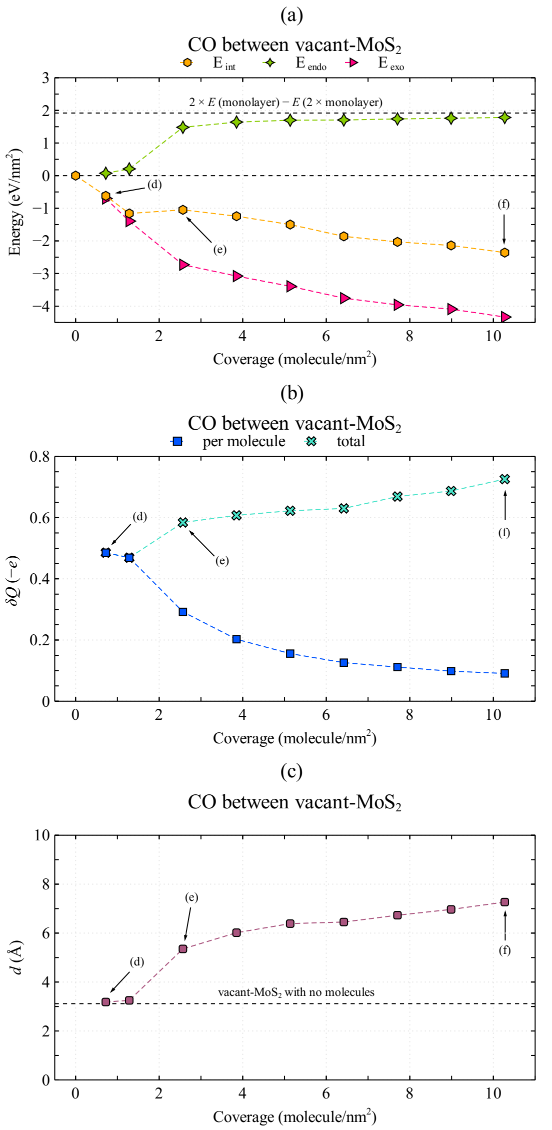

Fig. 1: Graphs characterizing CO intercalated between one pristine and one vacancy-doped MoS_2 monolayer: (a) intercalation energy with endothermic and exothermic contributions, (b) total charge transfer and charge transfer averaged per molecule, (c) distance between relaxed layers, all plotted as a function of sheet coverage.

targeted CO capture systems, and novel catalytic platforms. This work underscores the potential of leveraging intrinsic defects as a design parameter for fine-tuning the functionality of 2D materials for specific molecular interactions.

Acknowledgments

This work was funded by the Ministry of Education and Science in Poland within the project ”Perły Nauki” under Grant No. PN/01/0058/2022. Calculations reported in this work have been performed at the Interdisciplinary Center for Mathematical and Computational Modeling (ICM) of the University of Warsaw under Grant No. G96-1893.

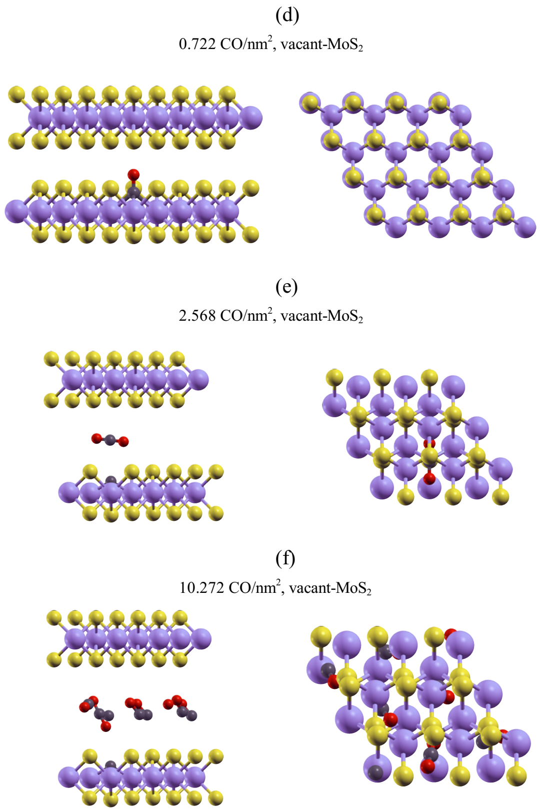

Fig. 2: Subfigures (d), (e), and (f) contain selected relaxed configurations, corresponding to the points marked with arrows in Figure 1.

References

[1] J. Wan, S. D. Lacey, J. Dai, W. Bao, M. S. Fuhrer, and L. Hu, “Tuning two-dimensional nanomaterials by intercalation: materials, properties and applications,” *Chemical Society Reviews*, vol. 45, no. 24, pp. 6742–6765, 2016.

[2] I. V. Chepkasov, M. Ghorbani-Asl, Z. I. Popov, J. H. Smet, and A. V. Krasheninnikov, “Alkali metals inside bi-layer graphene and mos2: Insights from first-principles calculations,” *Nano Energy*, vol. 75, p. 104927, 2020.

[3] A. Nijamudheen, D. Sarbapalli, J. Hui, J. Rodríguez-López, and J. L. Mendoza-Cortes, “Impact of surface modification on the lithium, sodium, and potassium intercalation efficiency and capacity of few-layer graphene electrodes,” *ACS applied materials & interfaces*, vol. 12, no. 17, pp. 19393–19401, 2020.