Understanding the Curvature Effect on Structure and Bonding of MoC_y Nanoparticles on Carbon Supports

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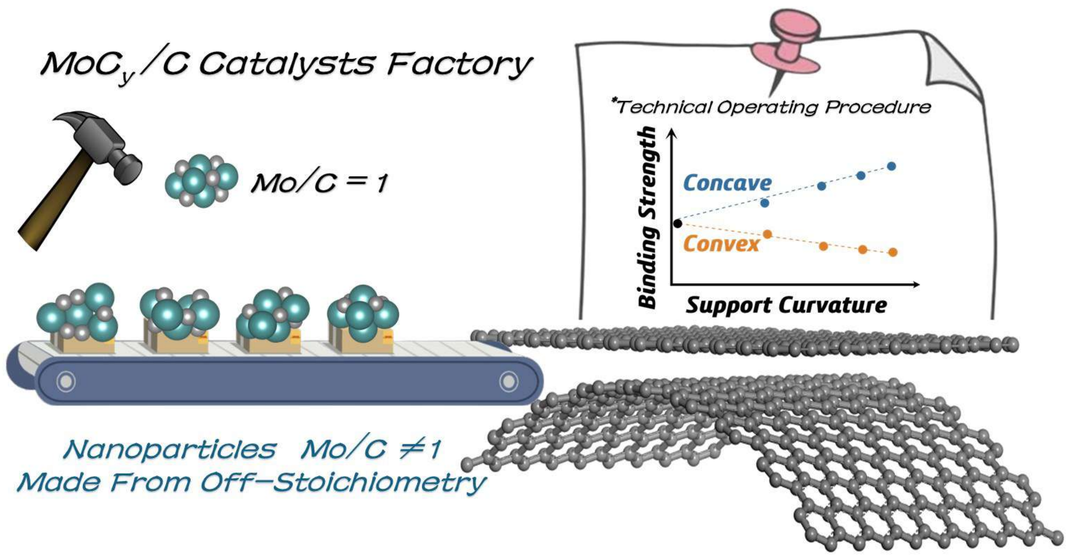
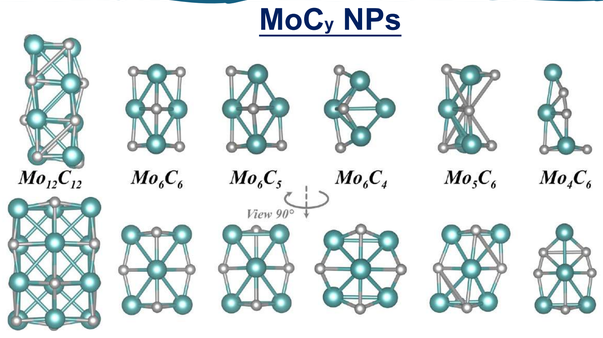


Motivation

- Molybdenum Carbide Nanoparticles (MoC_y NPs) possess distinctive features for catalysis,[1] such as low-coordinated sites and varying metal/carbon ratios, being quite useful for activating key molecules like CH_4, CO_2 and H_2.
- Graphene and carbon nanotubes (CNTs) have served as emerging supports for MoC_y NPs, enhancing the reactivity and selectivity.[2] However, the underlying mechanism remains unclear.
- A systematic study of the interaction mechanism between MoC_y NPs of varying stoichiometry and size and carbon supports with different curvatures, enhances the rational design of MoC_y/C-based catalysts.

MoC_y NPs

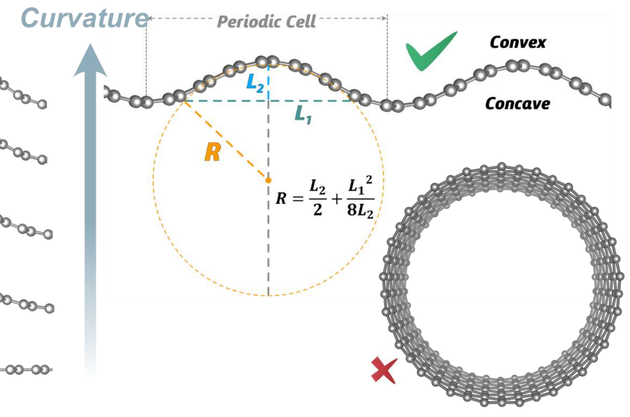


Methods

- **VASP** code, **DFT with PBE** *xc* functional, **Grimme's D3** correction.
- Compressing flat graphene to obtain curved graphene (**CG**) with varying curvatures is an effective modeling approach. Since **CGs capture the essential curvature features of CNT walls**, they enable efficient and cost-effective studies of large CNT structures.
- CNTs of several nanometers are computationally demanding, even being unfeasible.

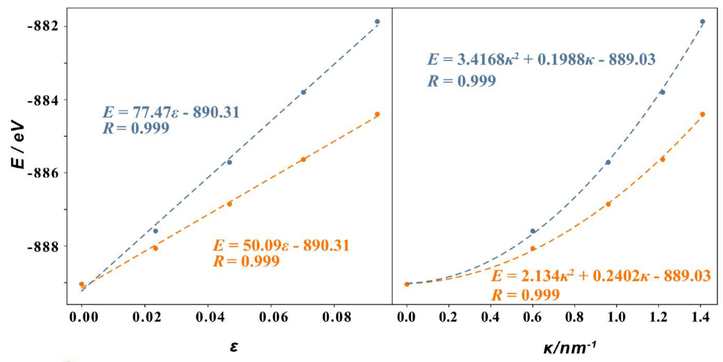
Curved Graphene as Walls of CNTs

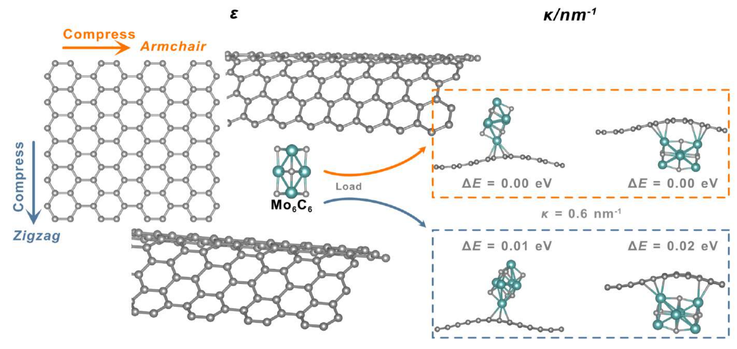
	Diameter (nm)	Curvature (nm^{-1})
①	1.42	1.41
②	1.64	1.22
③	2.08	0.96
④	3.32	0.60
⑤	∞(Graphene)	0.00

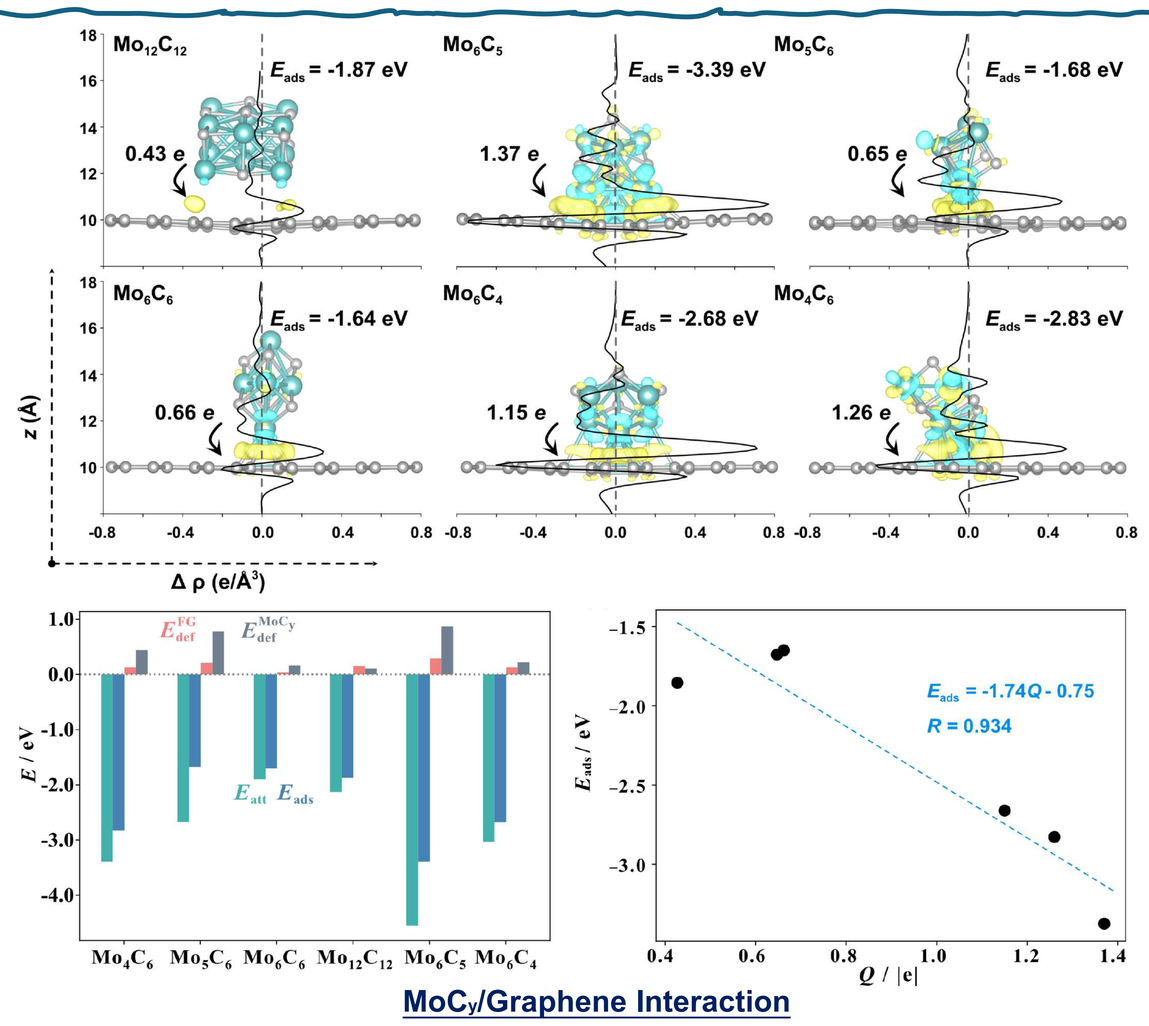


- Compression percentage $\varepsilon = (a\text{-}a_c)/a$, where a, a_c represent the lengths of the graphene ribbon before and after compression, respectively.
- Curvature κ, defined as the reciprocal of the radius, **takes the CG arc as a part of an ideal CNT**.
- Both ε and κ increase with rising total energy E of CG, following linear and quadratic functions, respectively.
- The zigzag crystallographic edge orientation is more energetically costly than armchair, while the impact on MoC_y NPs adsorption remains minimal.

Zigzag *vs.* Armchair

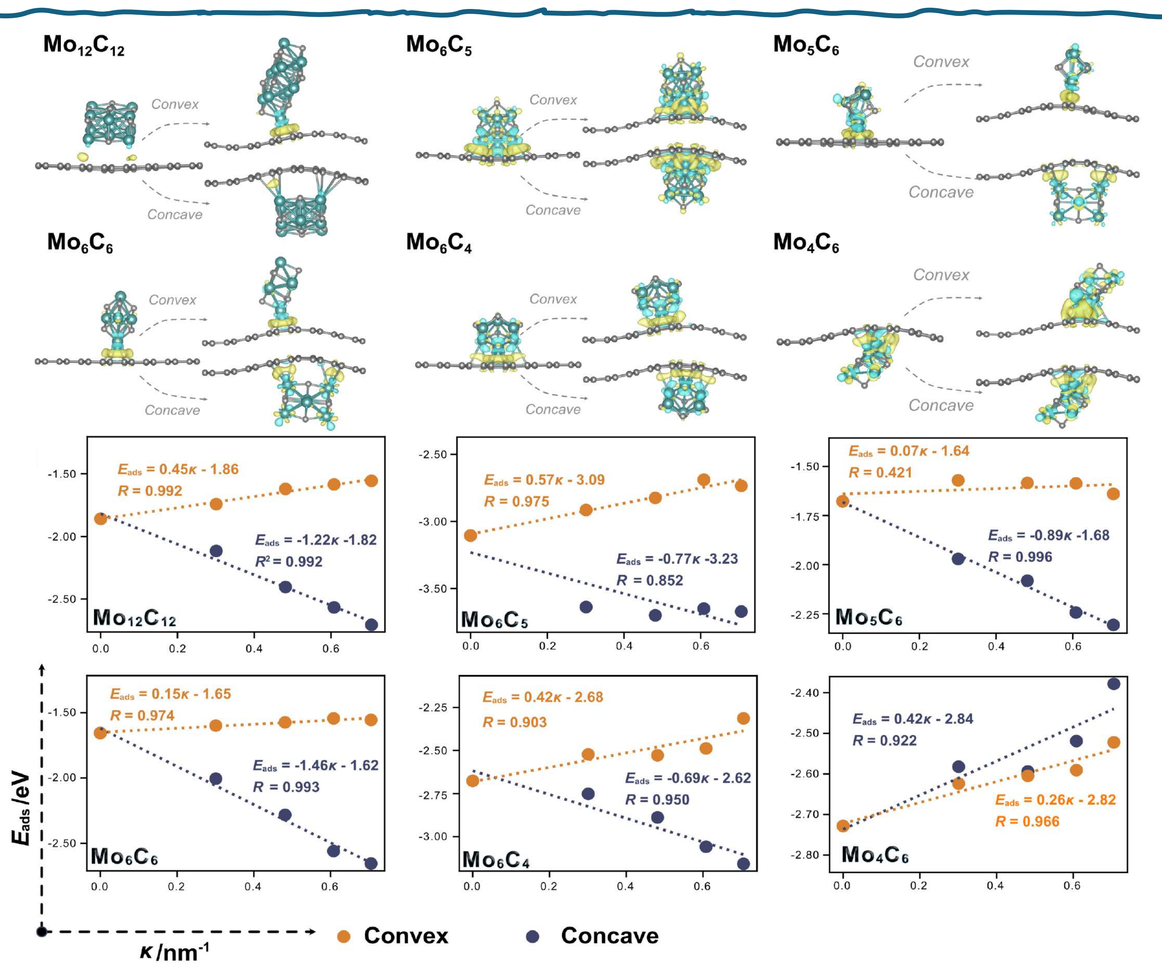






MoC_y/Graphene Interaction

- Off-stoichiometric MoC_y NPs with more low-coordinated Mo atoms, exhibit stronger adsorption.
- Electron transfer consistently occurs from MoC_y NPs to the graphene sheet, with stronger adsorption leading to increased electron transfer, showing a strong linear correlation.



MoC_y/CG Interaction

- In CNTs, the adsorption strength of MoC_y NPs increases on concave surfaces and decreases on convex surfaces, showing a strong correlation with support curvature.
- Concave/convex surfaces, with sparse/dense electron densities, respectively, enhance/weaken electron transfer from the carbide to the support, leading to more/less positively charged MoC_y NPs.

Conclusion

- Off-stoichiometric MoC_y NPs exhibit stronger interactions and increased electron transfer to the carbon supports through additional Mo-C bonds formation.
- The adsorption strength of MoC_y NPs and the extent of electron transfer both increase on concave surfaces and decrease on convex surfaces, exhibiting a strong linear correlation with support curvature.
- The present results demonstrate that the interaction strength and charge or NPs can be effectively tuned by manipulating the carbide stoichiometry, the substrate curvature, and the local concave/convex environments, providing valuable guidelines for the rational design of MoC_y/C-based catalysts.

Acknowledgements

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References

[1] Rodriguez, J. A.; Viñes, F.; Illas, F. C_1 Chemistry on Metal Carbide Nanoparticles: Boosting the Conversion of CO_2 and CH_4. *J. Phys. Chem. C* **2023**,*127*, 16764–16780

[2] Baddour, F. G.; Brutchey, R. L.; Malmstadt, N. An Exceptionally Mild and Scalable Solution-Phase Synthesis of Molybdenum Carbide Nanoparticles for Thermocatalytic CO_2 Hydrogenation. *J. Am. Chem. Soc.* **2020**, *142*, 1010–1019.