Surface Chemistry of an Mo_2C MXene Catalyst Under Working Conditions

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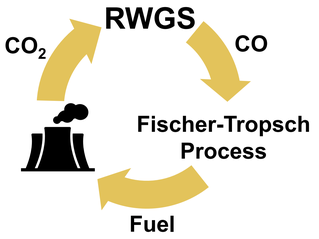
Introduction

RWGS reaction

Reverse Water Gas-Shift (RWGS) Reaction:

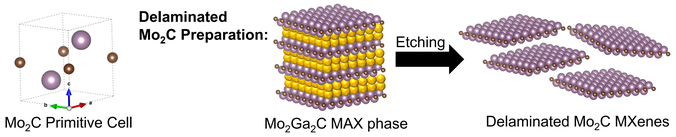
$CO_2 + H_2$ → Catalyst → $CO + H_2O$

Closed-Carbon Loop:

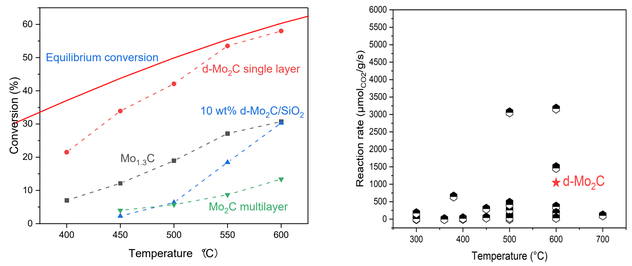


Mo_2C MXene as a catalyst for RWGS

Delaminated Mo_2C Preparation:

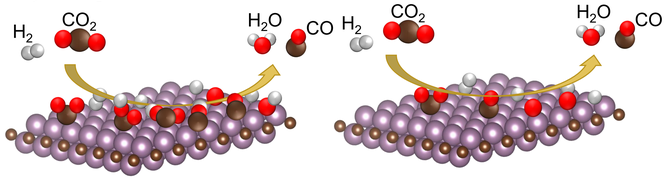


Mo_2C Primitive Cell | Mo_2Ga_2C MAX phase | Delaminated Mo_2C MXenes



Superior catalytic performance of delaminated Mo_2C MXene

Possible RWGS reaction pathways on Mo_2C surface:

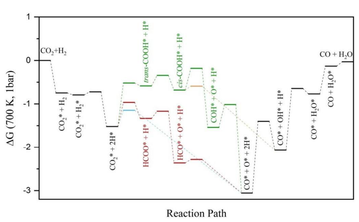


Formate Pathway

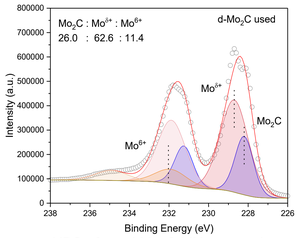
Redox Pathway

What is the reaction mechanism?

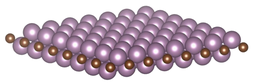
Previous work



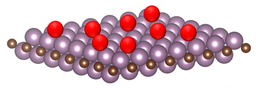
Reaction pathway calculated for bare MXene[1]



XPS of used Mo_2C MXene catalyst indicating surface oxidation



Bare MXene



Likely working state of mixed Mo_2COx

To properly investigate the reaction mechanism, we must first understand the surface chemistry during reaction working conditions

Determining the Surface Chemistry at Working Conditions

Optimal O* adsorption site

To calculate the optimal O* adsorption site, we relaxed 3x3 Mo_2C supercell structures in VASP at 0 K varying O* adsorbate site.

O* site	DFT 0 K energy (eV)
Top	-268.72
HC	-269.71
HM	-269.64
Bridge	-269.64

Ab Initio Thermodynamics

Calculating Gibbs Free Energy of Adsorption[2]:

$$\Delta G_{ads} = \frac{1}{A}[\Delta E_{ads} + N_{ads}(E_{ads}^{ZPE} - TS^{ads} - \mu_{ads}(T,P))]$$

$$\Delta E_{ads} = (E_{ads/surf} + E_{ads})$$

To find each $E_{ads/surf}$ an enumeration function from the ICET package created 18 unique structures of O* clusters on a 3x3 Mo_2C supercell surface for 1->9 O* adsorbates. 1 O being 1/9 coverage, and 9 O being 9/9 coverage.

Calculating Chemical Potential (μ_{ads}) with DFT[3,4]:

$$\mu_O(T,P) = [E_{CO2}^{DFT} - E_{CO}^{DFT}] + [\Delta\mu_{CO2}(T,P) - \Delta\mu_{CO2}(T,P) + k_bT * \ln(\frac{pCO2}{pCO})]$$

Where:

$$\Delta\mu_{CO2}(T,P) = E_{CO2}^{DFT} - G_{CO2}^{therm}(T)$$

$$\Delta\mu_{CO}(T,P) = E_{CO}^{DFT} - G_{CO}^{therm}(T)$$

Calculated using vaspkit's thermal correction of a gas in a box tool.

Calculated vibrational frequencies of O* adsorbate

Mo_2C-O	Vibrational Frequency (cm^{-1})
ν_1	550
ν_2	353
ν_3	352

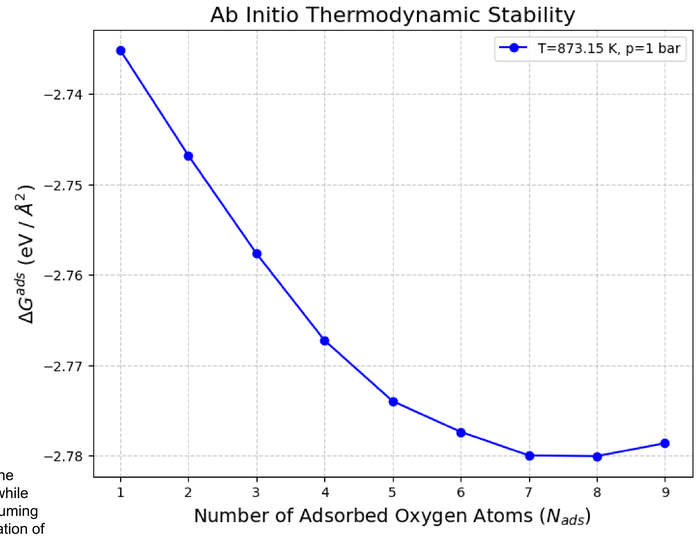
Calculated using vaspkit on a selective dynamics relaxed 3x3 Mo_2C supercell limiting the degrees of freedom to a singular O* adsorbate.

ΔG_{ads} of each minimum energy configuration

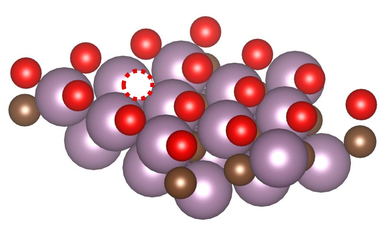
N_{ads}	$E_{ads/surf}$ (eV)	ΔG_{ads} (eV/Å)
O1	-270	-2.740000
O2	-279	-2.746899
O3	-287	-2.757568
O4	-296	-2.767251
O5	-305	-2.773924
O6	-3.13	-2.777270
O7	-3.21	-2.779820
O8	-3.29	-2.779849
O9	-3.37	-2.778359

Under the working conditions: (873 K , 3 H_2 / 1 CO_2 , 1 bar). We find the Mo_2C MXene will be 76-89% oxidized while participating in the RWGS reaction assuming equilibrium conditions with the minimization of Gibbs Free Energy at the O7 and O8 structures respectively.

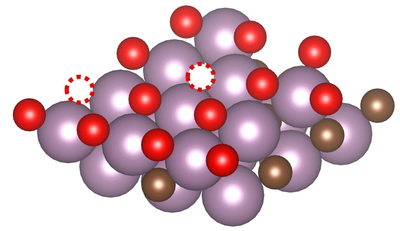
Varying ΔG_{ads} with N_{ads}



Predicted structures at working conditions



O8 Structure



O7 Structure

The O* adsorbates and their positions will greatly impact catalytic behavior. Modeling the RWGS reaction on these surfaces will provide greater accuracy to the catalytic pathway than on a bare MXene as it simulates for real-life conditions.

Conclusion

- ❑The vibrational frequencies of a singular O* adsorbate on an Mo_2C MXene have been calculated.
- ❑The optimal O* adsorption site on an Mo_2C MXene surface is the hollow-carbon site.
- ❑An Mo_2C MXene participating in the RWGS reaction at the working conditions (873 K , 3 H_2 / 1 CO_2 , 1 bar) is 76-89% oxidized on the surface.
- ❑Two relaxed minimum energy models detailing the surface chemistry during the reaction have been identified as O7 and O8, considering O* clusters on a 3x3 Mo_2C supercell.

Future Work

- ❑Conduct a computational study investigating the reaction pathway of the RWGS reaction on the Mo_2C surface using the O8 structure as the slab surface.
- ❑Investigate the relative prevalence of the O8 and O7 structures at the working conditions, considering their similar Gibbs Free Energies.

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References:

[1]Jurado, A.; Morales-García, Á.; Viñes, F.; Illas, F. Molecular Mechanism and Microkinetic Analysis of the Reverse Water Gas Shift Reaction Heterogeneously Catalyzed by the Mo_2C MXene. *ACS Catal.* **2022**, *12* (24), 15658–15667.

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