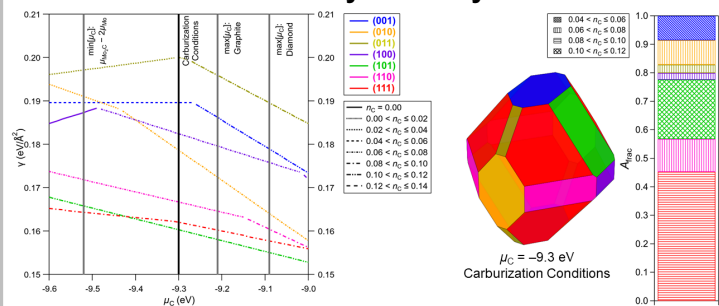


Introduction

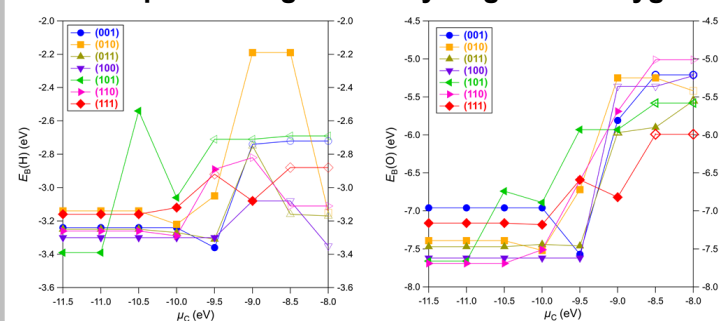
- Lower-cost Mo_xC catalysts show high activities (e.g., hydrogenation,² water-gas shift,³ and hydrodeoxygenation⁴) comparable to transition-metal catalysts.
- Atomic-scale structure/composition of catalytically active sites on Mo_xC catalysts not well-understood.
- For β - Mo_2C , the (100) surface has been traditionally studied,⁵ but previous surface-stability analyses indicate the (111) and (101) surfaces may be preferentially exposed.⁶
- C is present in catalyst and reacting species and may deposit on, diffuse across, or desorb from the surface during reaction, leading to non-stoichiometric and/or non-bulk-terminated surfaces preferentially exposed to the reaction environment.
- C on the surface could change the electronic properties and/or block catalytic active sites, thereby changing the activity/selectivity of the β - Mo_2C catalyst.

Surface stability under synthesis



- Under carburization conditions, the (111) and (101) surfaces are most stable.
- Wulff construction primarily exposes the (111) and (101) surfaces (45% and 21%, respectively).
- Even though it is traditionally studied when modeling β - Mo_2C catalysis,⁵ the (100) surface is one of the least stable surfaces and contributes only 2% to the particle surface area.

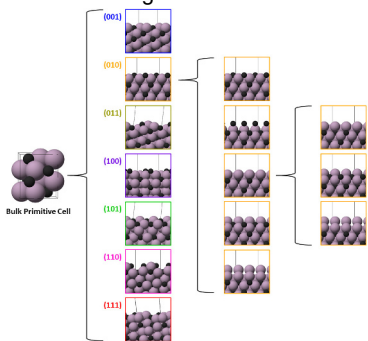
Adsorption energetics of hydrogen and oxygen



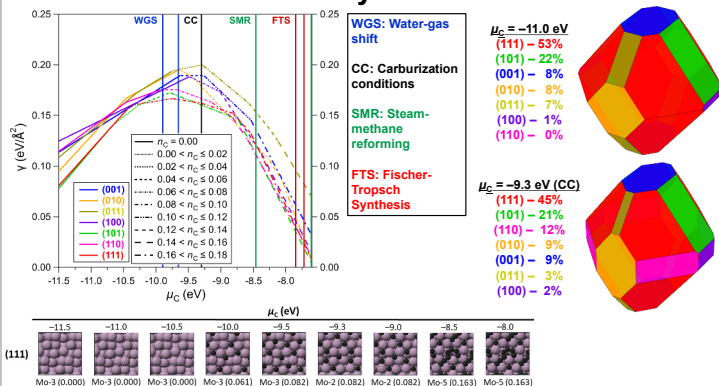
- As surface-carbon coverage increases, adsorption of atomic H generally weakens, but not systematically ($R^2 = 0.12$), while that of atomic O weakens systematically ($R^2 = 0.82$).
- Changes in adsorption strength of both species as surface-carbon coverage increases suggest that surface carbon can play a key role in catalyst activity/selectivity through either by inducing changes in electronic structure or by blocking catalytically active Mo sites.

Computational details

- VASP7.8
- PBE exchange-correlation functional⁹
- Plane-wave basis, energy cutoff of 400 eV
- Developed systematic workflow to generate all possible Mo-terminated surfaces for each low Miller index facet of β - Mo_2C , as well as all possible surface-carbon configurations for studied coverages⁵



Surface stability under reaction



- Across studied μ_C range, (111) and (101) surfaces are most stable.
- At high μ_C , the (010), (100), and (110) surfaces also become stable.
- As μ_C increases, the surfaces go from carbon-free to reaching the maximum studied surface-carbon coverage.
- Accumulation of surface carbon does not affect particle shape but does affect the contribution of each facet to the particle surface area.

Conclusions

- Density functional theory calculations indicate that the (111) and (101) surfaces are either most stable or among the most stable across the studied range of μ_C .
- Wulff particle under carburization conditions supports these findings; the (111) and (101) surfaces dominate the surface area (66%), and particle shape does not change as surface-carbon accumulates.
- Traditionally studied (100) surface contributes very little to the Wulff particle surface area.
- Facet identity and surface-carbon coverage affect the adsorption energy of atomic H and atomic O; future studies should investigate these effects on reaction pathways.

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