

Highly Active Cu/ β -Mo₂C and Cu/ δ -MoC Catalysts for the Conversion of CO₂: The Metal/C Ratio as a Key Factor Defining Activity, Selectivity, and Stability

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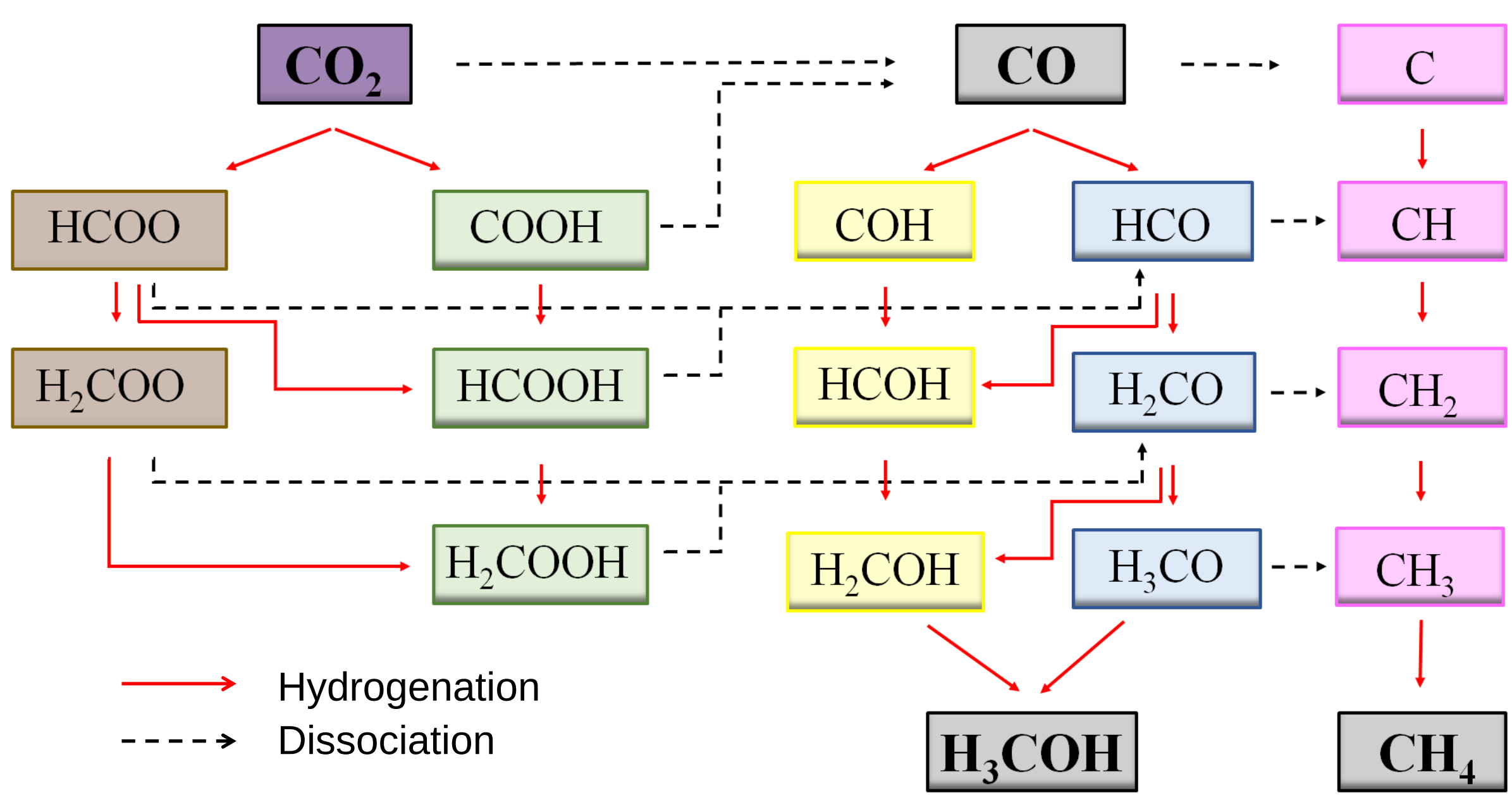
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Introduction

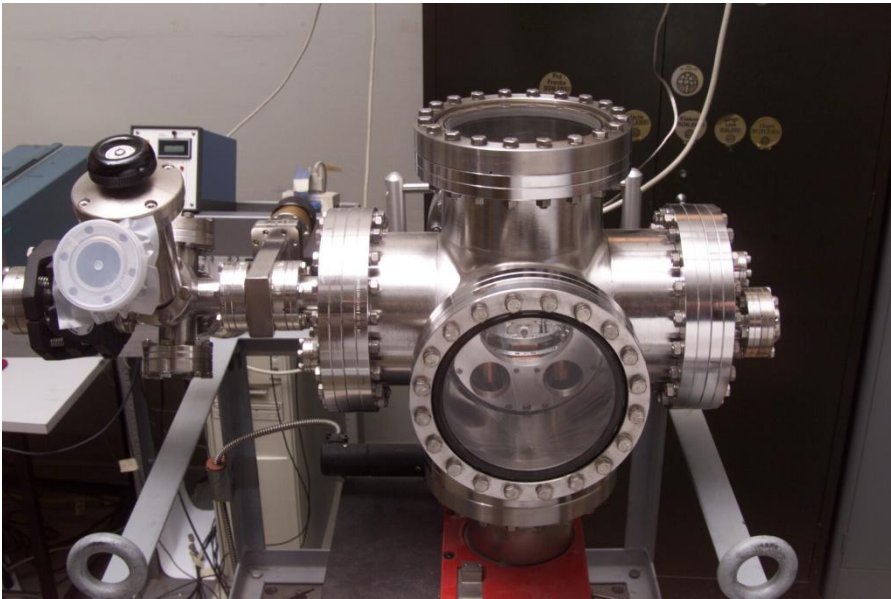
The ever growing increase of CO₂ concentration in the atmosphere is one of the main causes of global warming. Thus, CO₂ activation and conversion towards valuable added compounds is a major scientific challenge. Transition metal carbides have arise as an appealing alternative to precious metal and commercial catalyst to CO₂ conversion towards CO with some subsequent selective hydrogenation towards methanol. In this study, sophisticated experiments under controlled conditions and calculations based on density functional theory have been used to study the unique behavior of β -Mo₂C and δ -MoC catalysts provides evidence of the impact of the metal/carbon ratio in the carbide on the performance of the catalysts. The present results show that this ratio governs the chemical behavior of the carbide and the properties of the admetal, up to the point of being able to switch the rate and mechanism of the process for CO₂ conversion.^{1,2} A control of the metal/carbon ratio paves the road for an efficient reutilization of this environmental harmful greenhouse gas.

Simplified Reaction Map

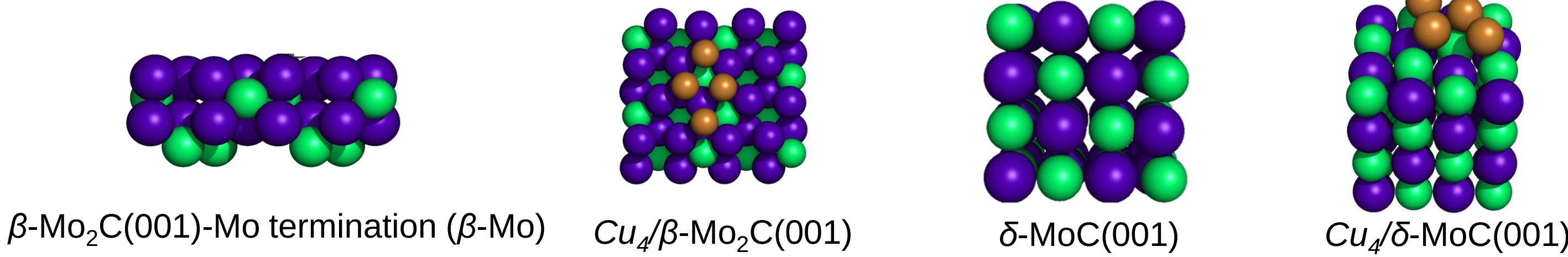


Experimental Details

- Polycrystalline δ -MoC
- Polycrystalline and single crystal β -Mo₂C
- The experimental data were collected in an ultra-high vacuum chamber equipped with instrumentation for X-ray photoelectron spectroscopy, low-energy electron diffraction, ion-scattering spectroscopy, and thermal-desorption mass spectroscopy
- Product yields were analyzed by a gas chromatograph

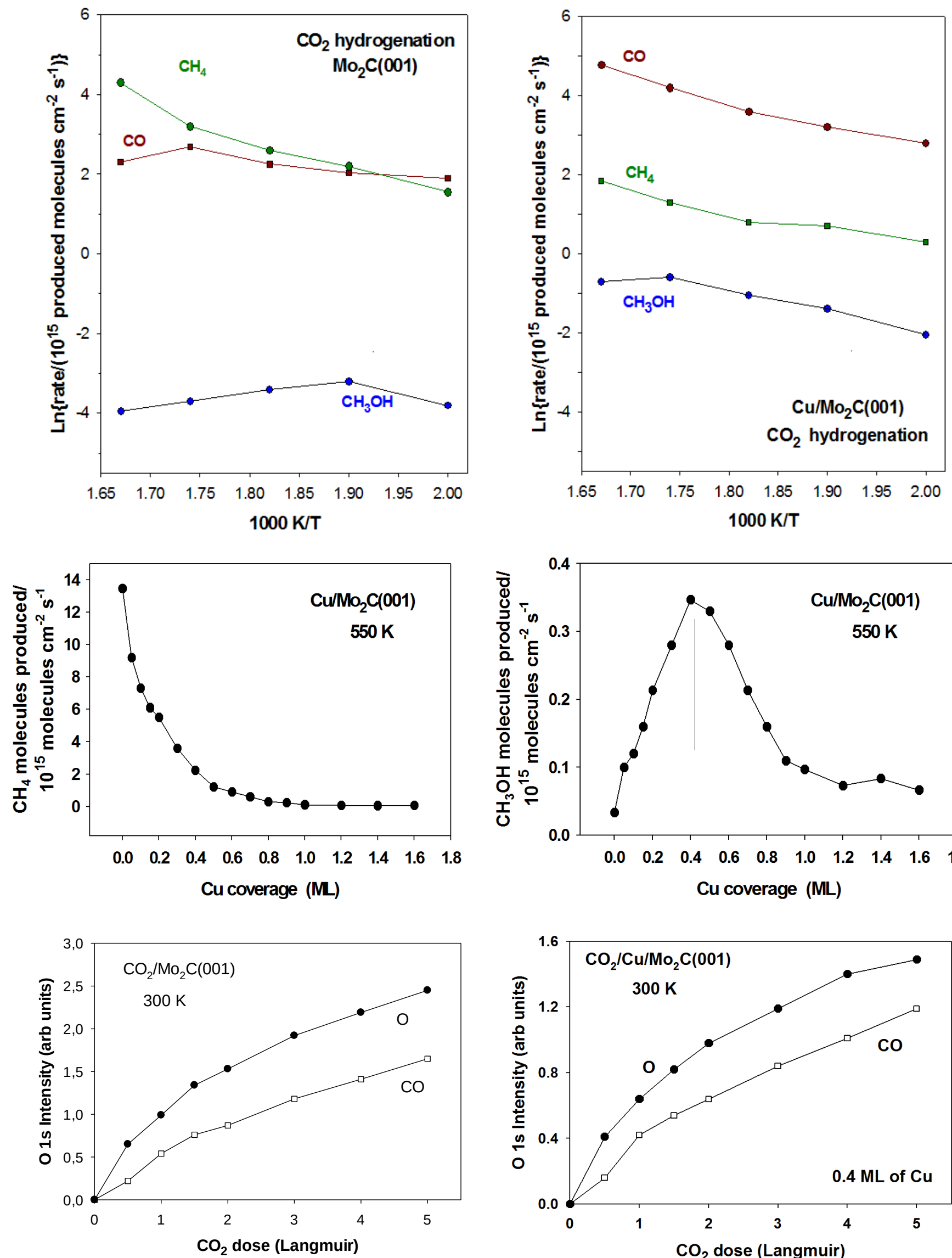


Computational models



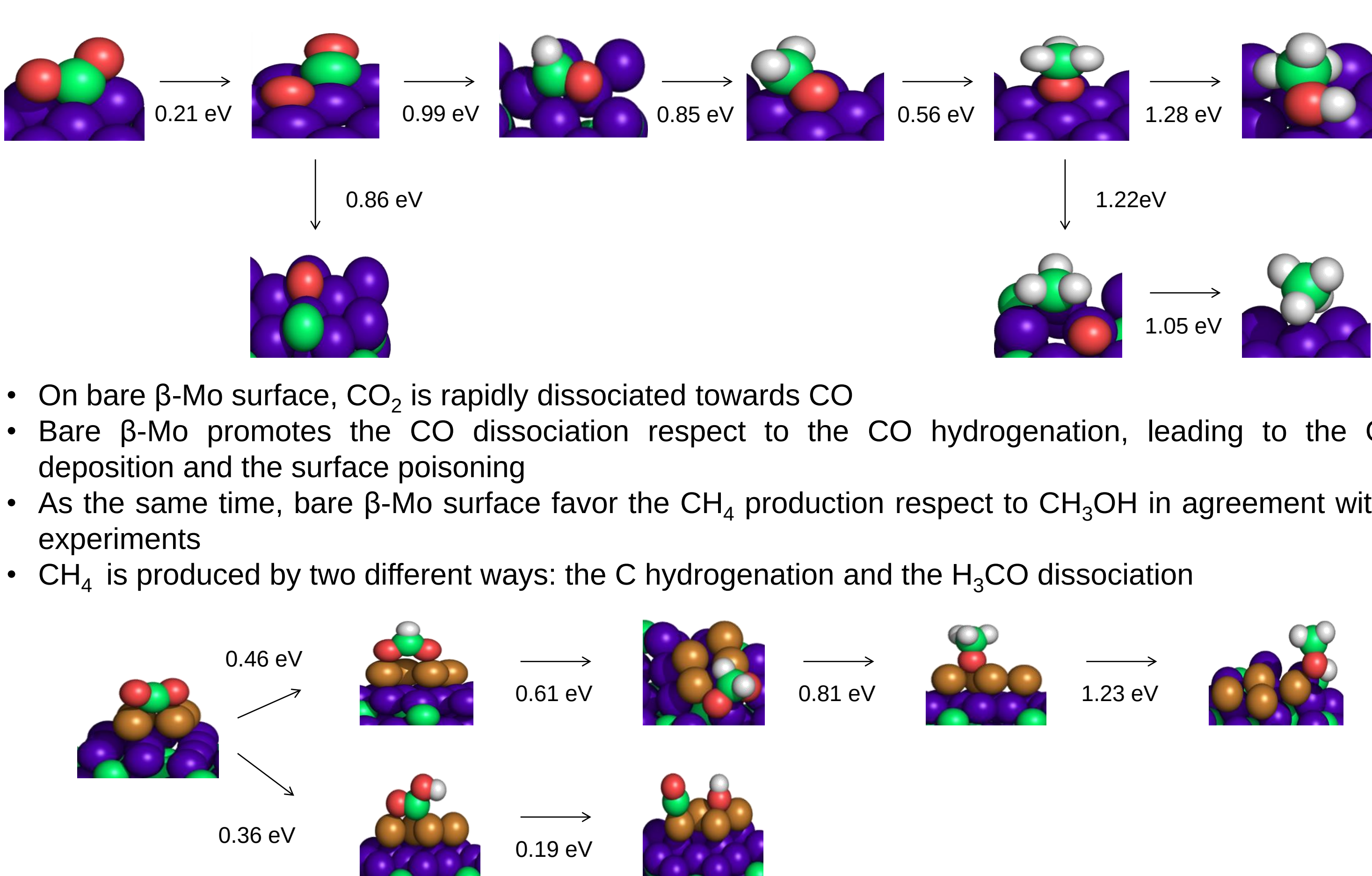
- β -Mo₂C(001) Mo termination is more reactive than C termination
- The Cu₄ cluster model have been used in previous studies^{3,4}

Experimental Data of Bare β -Mo₂C and Cu/ β -Mo₂C



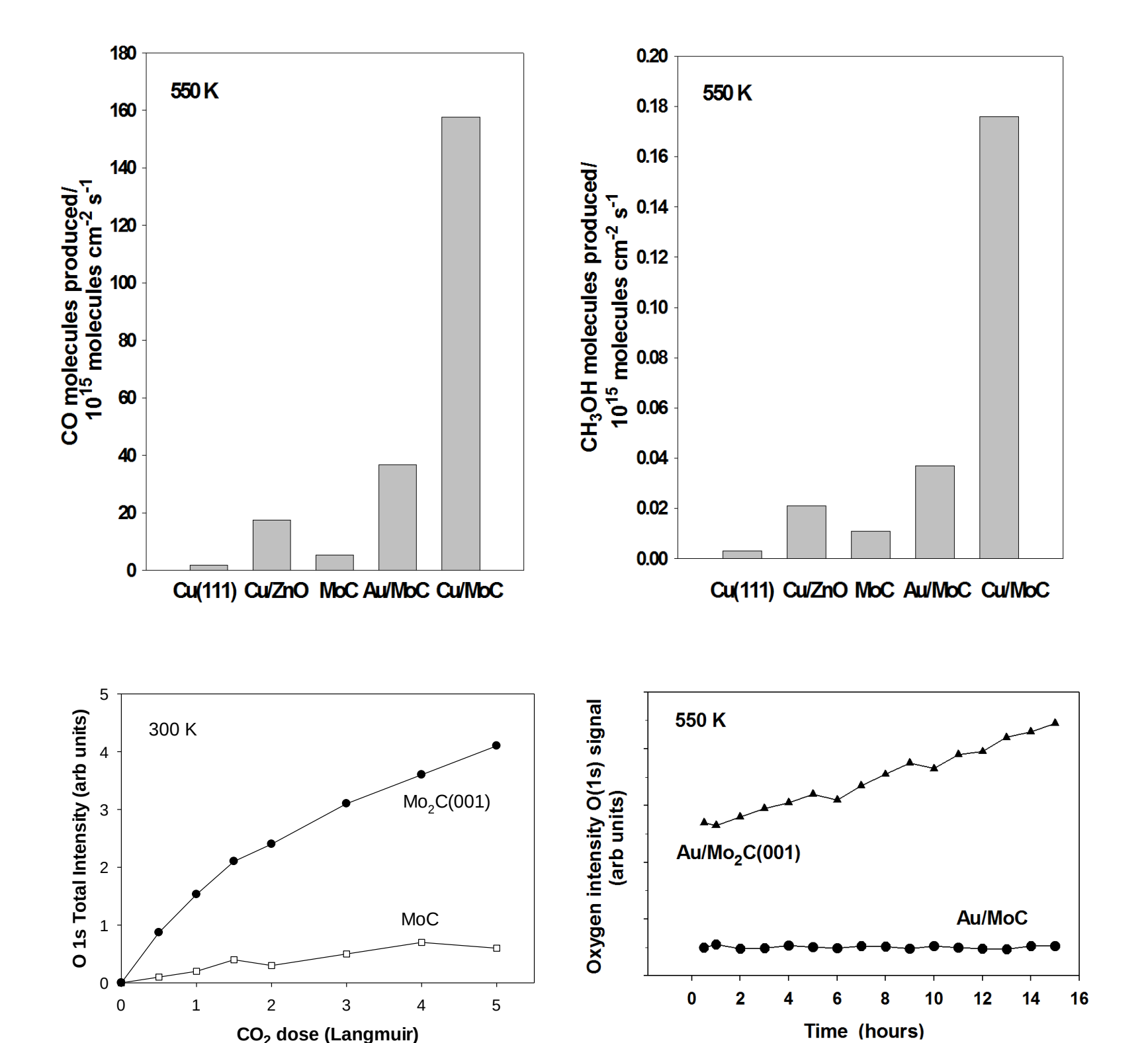
- The Arrhenius plots show that CO and CH₃OH are not the only products on the synthesis; CH₄ is the main product on bare β -Mo₂C
- The deposition of Cu clusters increase the amount of CO and CH₃OH as the same time that CH₄ production decreases
- The experiments exhibit that Cu clusters block the CO dissociation sites and avoid the CH₄ production
- Nevertheless, the optimum Cu coverage to produce CH₃OH is 0.4 ML, and consequently CH₄ is also produced
- Both bare and Cu supported β -Mo₂C surfaces are **poisoning** by the O related to CO dissociation
- The oxycarbide formation provokes a decay of the catalytic activity

Theoretical Results of Bare β -Mo₂C and Cu/ β -Mo₂C



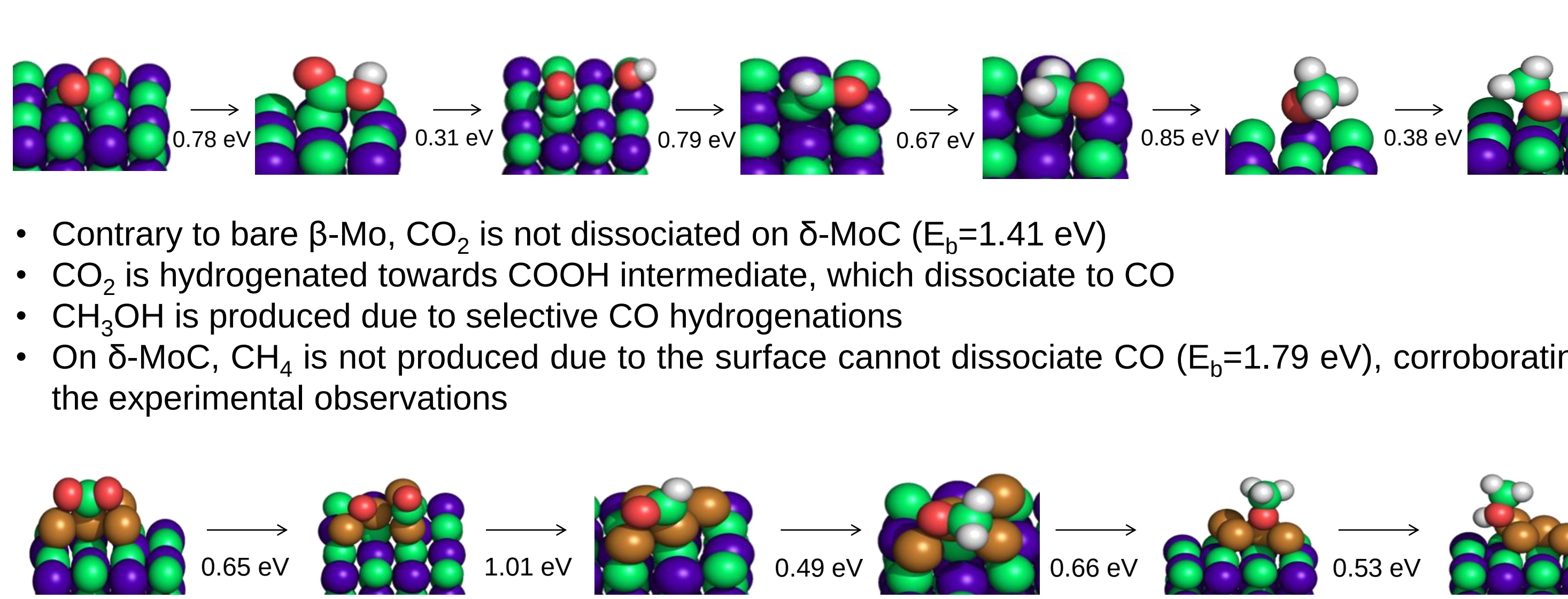
- On bare β -Mo surface, CO₂ is rapidly dissociated towards CO
- Bare β -Mo promotes the CO dissociation respect to the CO hydrogenation, leading to the O deposition and the surface poisoning
- As the same time, bare β -Mo surface favor the CH₄ production respect to CH₃OH in agreement with experiments
- CH₄ is produced by two different ways: the C hydrogenation and the H₃CO dissociation
- Cu supported clusters are not able to dissociate CO₂. CO and CH₃OH are produced due to the CO₂ hydrogenation towards COOH and HCOO intermediates
- Theoretical calculations confirm the experiments, since Cu clusters avoid the two pathways to form CH₄, the CO and H₃CO dissociations

Experimental Data of Bare δ -MoC and Cu/ δ -MoC



- Contrary to β -Mo₂C, δ -MoC and Cu/ δ -MoC does not produce CH₄
- Both Au/MoC and Cu/MoC produce more CO and CH₃OH than the model of the technical catalyst (Cu/ZnO)
- The interface between Cu-MoC is more efficient than the Au-MoC interface for CO and CH₃OH production
- In comparison with bare β -Mo₂C, the O poisoning is not detected on MoC
- Au-MoC and Au-Mo₂C have similar behavior than Cu-MoC and Cu-Mo₂C. The oxycarbide is not formed on MoC surface

Theoretical Results of Bare δ -MoC and Cu/ δ -MoC



- Contrary to bare β -Mo, CO₂ is not dissociated on δ -MoC ($E_b=1.41$ eV)
- CO₂ is hydrogenated towards COOH intermediate, which dissociate to CO
- CH₃OH is produced due to selective CO hydrogenations
- On δ -MoC, CH₄ is not produced due to the surface cannot dissociate CO ($E_b=1.79$ eV), corroborating the experimental observations
- In opposite to Cu/ β -Mo, CO₂ is dissociated on Cu/ δ -MoC
- Nevertheless, some steps like CO hydrogenation to HCO are favorable on bare regions
- Cu/ δ -MoC work as bifunctional catalyst; Cu cluster form CO and bare regions and the interface produce CH₃OH

Conclusions

- Experiments and calculations show that δ -MoC and Cu/ δ -MoC are more selective and active than β -Mo₂C and Cu/ β -Mo₂C due to the non CH₄ production and the non catalyst poisoning
- The support change the reactivity of the Cu clusters. The metal/C ratio on the carbide lead to different reactivity of bare and Cu supported surfaces
- Cu clusters on β -Mo₂C kill the surface sites to dissociate CO, avoiding the CH₄ formation and open a new route to produce CH₃OH
- The role of Cu clusters on δ -MoC is to dissociate CO₂ more rapidly than bare surface and catalyze some steps of CO hydrogenation towards CH₃OH

References

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Acknowledgments

