First-principles calculations of Fischer-Tropsch processes catalyzed by nitrogenase enzymes

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The Fe(Mo/V)co Nitrogenase

Nitrogenases are a class of metalloenzymes that catalyze the reduction of N\(_2\) to NH\(_3\), a critical process in biology and nature. FeMoCo and FeVco are two notable variants distinguished by the transition metal in their cofactor. FeMoCo is the best known nitrogenase for NH\(_3\) synthesis, requiring only one H\(_2\) per N\(_2\) reduced.[1]

Not just N\(_2\) reduction

Recent experiments have shown FeMoco and FeVco can also reduce CO and CN\(^-\) into higher-order hydrocarbons,[2] indicating they may be suitable catalysts for Fischer-Tropsch synthesis, i.e., the conversion of CO and H\(_2\) into liquid fuels.

Protonation of the cofactor

Calculated free energy diagrams for protonating the 3 bridging μ\(_1\) S atoms of the cofactors containing Mo (blue) and V (grey). The black pathways represent the free energy at DV vs. RHE and the red pathways at the labeled potential.

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References


Summary

We have investigated the chemical pathways describing CO and CN\(^-\) reduction by nitrogenases. We find that the potential-limiting step of the (electro)reduction of CO into hydrocarbons is the protonation of CO to CHO\(^*.\) CN\(^-\) reduction is instead limited by the further reduction of HCN to CHNH\(^*-\). These steps become much more favorable if the under-coordinated bridging μ\(_1\) S atoms are available as adsorption sites. Our calculated pathways can account for the observed CO and CN\(^-\) reduction trends in both isolated cofactor variants, and suggest CH\(_2\)\(^*-\) as the primary building block of C-C species. Furthermore, the nitrogenases compare favorably to the best known metal surfaces CO electroreduction catalysts.

CO/CN\(^-\) reduction pathways

We find that the reduction pathways are qualitatively and quantitatively similar for the isolated cofactors, consistent with experiment.[2]

For CO, the potential-limiting step is the initial protonation to CHO\(^*\), which becomes much more favorable when one of the μ\(_2\) atoms is available as an adsorption site.

This same potential-limiting step compares favorably to Cu, currently the best known metal surface for the electroreduction of CO.[3,4]

For CN\(^-\), the potential-limiting step is the second protonation and adsorption of HCN to CHNH\(^*-\). We find CN\(^-\) reduction on non-μ\(_2\) sites requires a much smaller overpotential than for CO reduction, making CN\(^-\) reduction more facile for both cofactors.

Adjacent CH\(_2\)\(^*-\) can favorably couple to form C\(_2\)H\(_4\) and higher-order hydrocarbons.

Free energy diagrams for the reduction of CO and CN\(^-\) to CH\(_4\) by the isolated nitrogenase cofactors. The pathways are shown for adsorbates binding to an unprotonated μ\(_1\) site. The cartoon insets of the CH\(_2\)\(^*-\) intermediates are highlighted in bold, as they are believed to be the bifurcation of the methanation and hydrocarbon formation pathways, similar to conventional Fe-based Fischer-Tropsch catalysts.