



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

Joel B. Varley and Jens K. Nørskov

### The Fe(Mo/V)co Nitrogenase



### Summary

We have investigated the chemical pathways describing CO and CNreduction 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  $\mu_2$  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<sub>2</sub>\* as the primary building block of C-C species. Furthermore, the nitrogenases compare favorably to the best known metal surfaces CO electroreduction catalysts.

for NH<sub>3</sub> synthesis, requiring only one H<sub>2</sub> per N<sub>2</sub> reduced.[1]

### Not just N<sub>2</sub> 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<sub>2</sub> into liquid fuels.



**Protonation of the cofactor** 

# 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  $\mu_2$  atoms \_is available as an adsorption site.

This same potential limiting= step compares favorably  $t\bar{0}$ Cu, currently the best known metal surface for the electroreduction of CO.[3,4]

For CN<sup>-</sup>, the potentiallimiting step is the second\_ protonation and adsorption of HCN to CHNH\*. We





Calculated free energy diagrams for protonating the 3 bridging  $\mu_2$  S atoms of the cofactors containing Mo (blue) and V (grey). The black pathways represent the free energy at 0 V vs. RHE and the red pathways at the labeled potential.

### Acknowledgements

Support from the Global Climate and Energy Project (GCEP) at Stanford University is gratefully acknowledged.

### References

- [1] B. Hinneman and J.K. Nørskov, *Top. Catal.* **37**, 55 (2006).
- [2] Y. Hu, C.C. Lee, M.W. Ribbe, Science **333**, 753 (2011); C.C. Lee, Y. Hu,
  M.W. Ribbe, Angew. Chem. Int. Ed. **51**, 1947–1949 (2012).
- [3] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov,
  - Energy Environ. Sci. **3**, 1311 (2010).

find  $CN^{-}$  reduction on non-  $\mu_{2}$  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  $C_2H_4$  and higherorder hydrocarbons.

#### Free energy diagrams

for the reduction of CO and CN to CH<sub>4</sub> by the isolated nitrogenase cofactors. The pathways are shown for adsorbates binding to an unprotonated  $\mu_2$  site. The cartoon insets of the CH<sub>2</sub>\* intermediates are highlighted in bold, as they are believed to be the bifurcation of the methanation and hydrocarbon formation

