Fueling the future: Investigation of hydrocarbon formation from CO by vanadium nitrogenase

Chi-Chung Lee[1], Simone Meinardi[2], Brian Chipman[1], Yilin Hu[1], Donald Blake[2], Markus Ribbe[1]

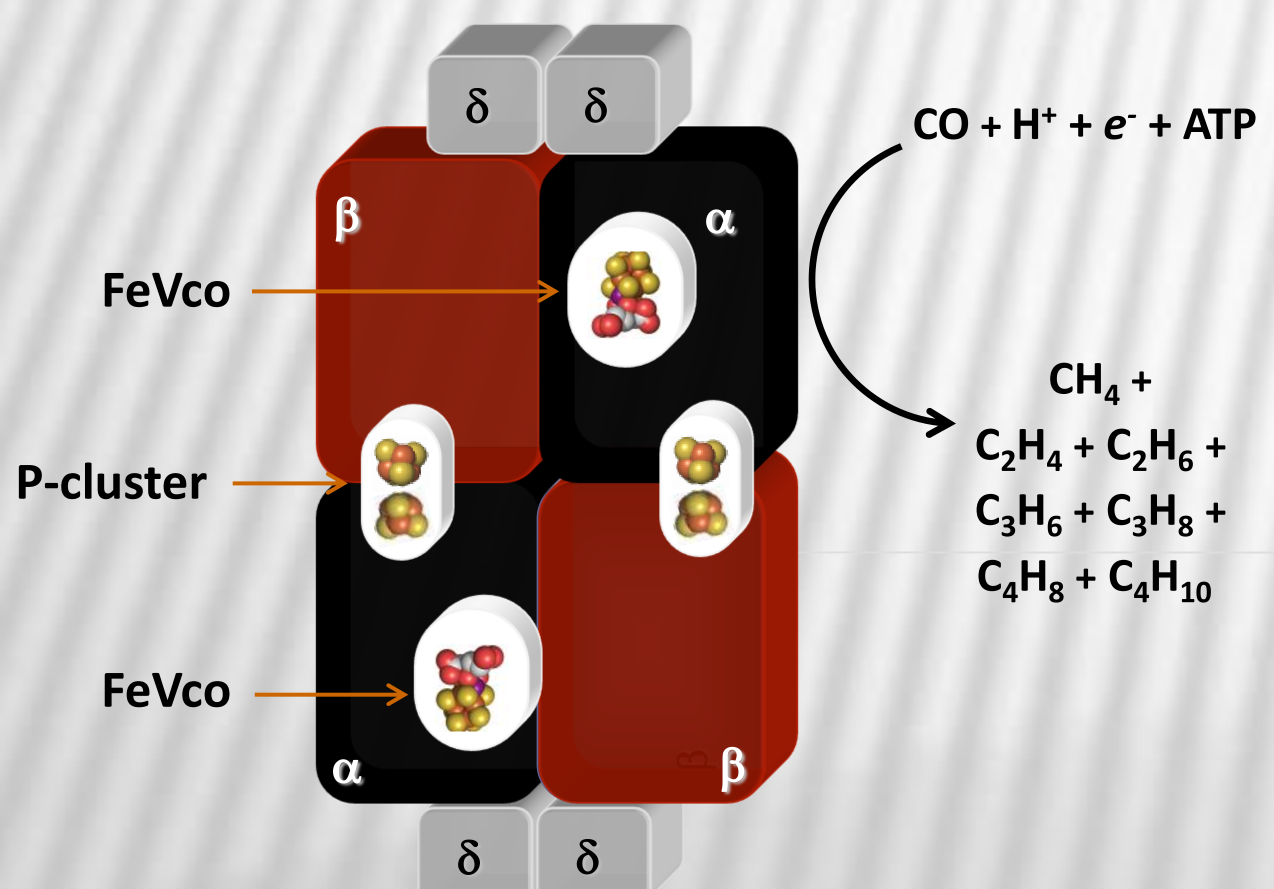
[1]Department of Molecular Biology & Biochemistry, University of California, Irvine , mribbe@uci.edu

[2]Department of Chemistry, University of California, Irvine , drblake@uci.edu

Vanadium nitrogenase (V-N_2ase) is a variant form of nitrogenase, an enzyme that is responsible for the conversion of atmospheric dinitrogen (N_2) to bio-available ammonia (NH_3). Like most nitrogenases, V-N_2ase consists of two proteins: a iron (Fe) protein and a vanadium-iron (VFe) protein. However, unlike its close relative, the commonly found molybdenum nitrogenase (Mo-N_2ase), the VFe protein consists of an $\alpha_2\beta_2\delta_4$ octameric quaternary structure, and it houses an unique P-cluster and an iron-vanadium cofactor (FeVco).

Recently, the Ribbe lab discovered that the V-N_2ase from *Azotobacter vinelandii* could generate small hydrocarbons (*i.e.*, C1–C4 alkanes and alkenes) from carbon monoxide (CO) and protons (H^+) in aqueous solution under ambient pressure and temperature.[1-3] However, the reaction stoichiometry and the complete product profile are yet to be established.

VFe Protein & CO Reduction



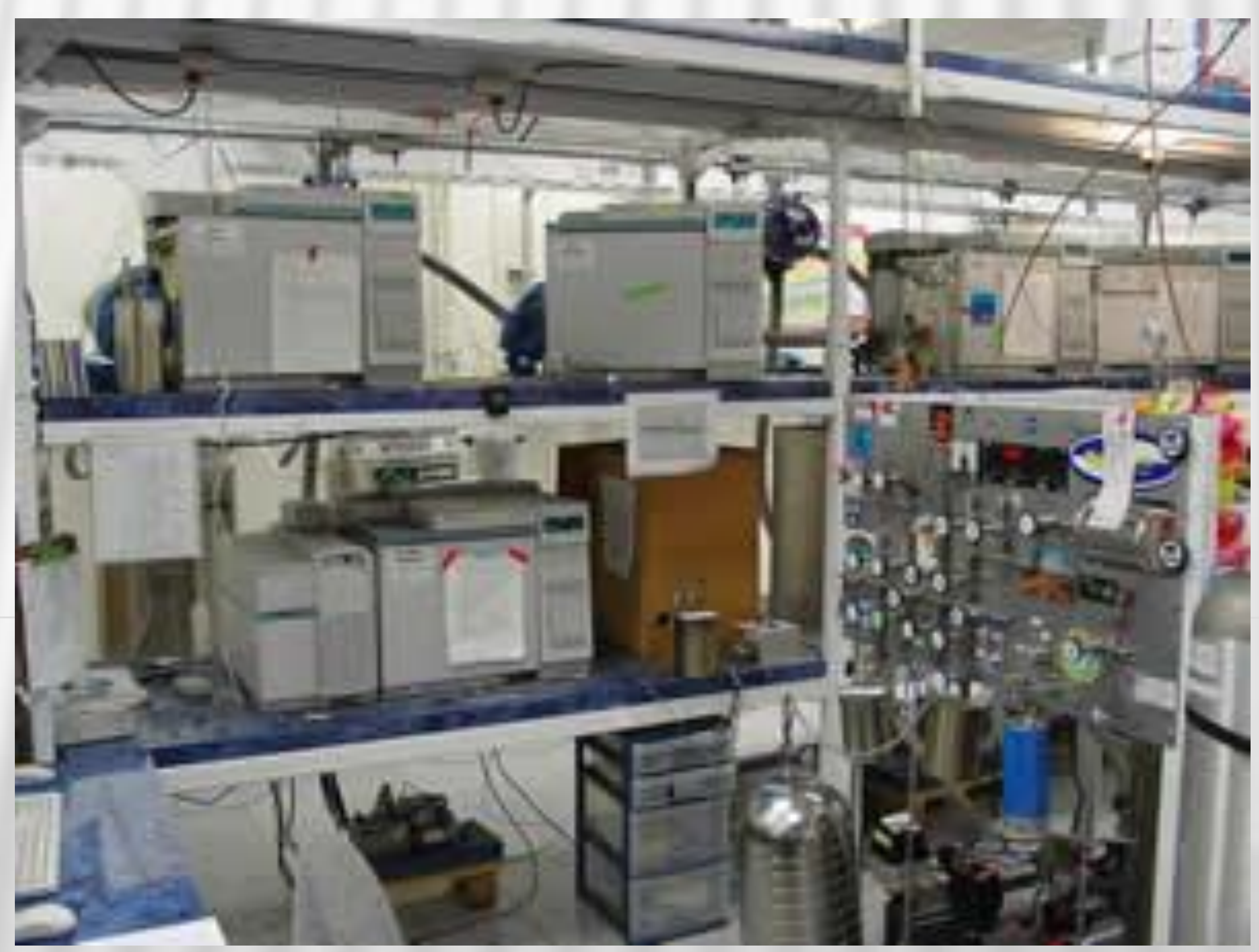
References

(1) Lee, C. C., Hu, Y., Ribbe, M. W. (2010) *Science,* **329**, 642. (2) Lee, C. C., Hu, Y., Ribbe, M. W. (2011) *Angew. Chem. Int. Ed. Engl.,* **50**, 5545-5547. (3) Hu, Y., Lee, C. C., Ribbe, M. W. (2011) *Science* **333**, 753-755.

The objective of this proposal is to combine the biochemical expertise of the Ribbe group and the analytical experience of the Blake group to determine the identities and quantities of the missing products of CO reduction by V-N_2ase. The outcome of this study will lay the foundation for future mechanistic studies of this important reaction.

The approach

- CO turnover samples will be prepared in the Ribbe lab using large quantities of V-N_2ase.
- The headspace content of these samples will be first transferred to 1.5L air canisters, and then applied to the state-of-the-art gas analytical system of the Blake lab.
- The sample is then chilled, enriched, cleaned and spitted into multiple lines that are analyzed by different GC, GC-MS setups. Various products can be simultaneously detected and quantified.



One of the GC/GC-MS setups in the Blake lab. It consists of 2 GC systems, each equipped with different columns and detectors, and 1 GC-MS system. Simultaneous detection and quantification of various compounds can be achieved through such a setup.

Expected Outcome & Future Directions

✓ Potential CO reduction products, including alkanes, alkenes, arenes, alcohols, aldehydes, ketones and organic acids, can be simultaneously measured at part-per-trillion (ppt) level. This approach ensures the complete profiling of all products of this reaction.

✓ CO consumption can also be measured independently and, together with the quantification of products, the preliminary reaction stoichiometry can be elucidated.

✓ Based on the distribution of the products, such as the ratio of oxygenated and non-oxygenated products, mechanistic insights could be gained into this reaction. Experiments can be conducted further under different conditions, such as different substrate concentrations, and proton/electron fluxes, to establish the mechanism of the V-N_2ase-catalyzed CO reduction.

Potential Industrial Applications

V-N_2ase provides a biological alternative to the industrial Fischer-Tropsch process for the production of hydrocarbon fuel from waste (*i.e.*, CO), with the added benefit that H_2 will be produced instead of consumed. Such a prospect prompts us to better understand the mechanism of this reaction, which will provide the basis for designing the next-generation cost-effective, eco-friendly biomimetic catalysts for production of fuel and other useful organic products, thereby bringing us a step closer toward solving the worldwide energy problems.

Acknowledgements

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