

## Fischer–Tropsch Chemistry at Room Temperature?\*

Deidra L. Gerlach and Nicolai Lehnert\*

carbon monoxide · Fischer–Tropsch process · hydrocarbons · nitrogenase · vanadium

Methane is an abundant energy source and could be used as the basis for the production of chemical feedstocks; however, catalysts that effectively process this gas, for example for the production of larger hydrocarbons as fuel or olefins as monomers for polymerization, are rare. Currently, methane is first reformed to produce synthesis gas (CO and H<sub>2</sub>), which is then subjected to the Fischer–Tropsch (FT) process, whereby CO is reduced by H<sub>2</sub> over transition metals to produce larger-chain hydrocarbons. This process requires high temperature and high pressure to promote the formation of carbon chains containing more than two carbon atoms.<sup>[1]</sup> Nitrogenase is an enzyme that reduces N<sub>2</sub> to NH<sub>3</sub> through a process driven by adenosine triphosphate (ATP)<sup>[2]</sup> and is seemingly unrelated to the FT process. However, Ribbe and co-workers recently reported that vanadium nitrogenase (V nitrogenase) is in fact an FT catalyst at room temperature that is capable of reducing CO to yield light hydrocarbons by forming new C–C and C=C bonds!<sup>[3,4]</sup> This finding is surprising, as the much more prominent molybdenum nitrogenase is actually strongly inhibited by CO. In their most recent study, Ribbe and co-workers traced the source of hydrogen that is used by V nitrogenase for the production of hydrocarbons.<sup>[4]</sup> These exciting findings provide new insight into several unsolved matters with respect to the mechanism and evolution of the nitrogenase enzymes.

Mo nitrogenase is the most commonly found member of this enzyme family, and the most represented in the literature. In contrast, vanadium and iron-only (Fe) nitrogenases are generally only utilized by bacteria under unusual conditions, such as at lower temperature or when molybdenum-starved.<sup>[5]</sup> Each nitrogenase contains the active-site cofactor (FeMoco, FeVco, or FeFeco), a P cluster for electron transfer, and a binding site for the reduced Fe protein with two bound ATP moieties.<sup>[5]</sup> As of yet, only the structure of the FeMoco cluster has been determined crystallographically (Figure 1); however, on the basis of spectroscopic data and the similarity in sequence, the FeVco active-site cluster is usually thought to be similar to the FeMoco structure, with the replacement of Mo by V.<sup>[6]</sup>

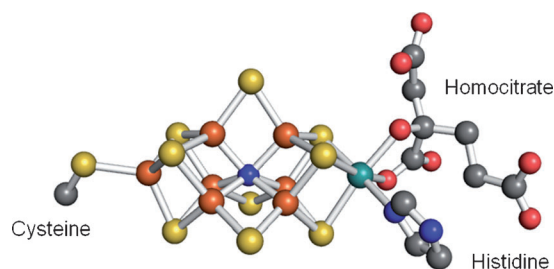


Figure 1. FeMoco structure modeled with N as the central atom (Mo teal, Fe orange, S yellow, C gray, N blue, O red).<sup>[8]</sup>

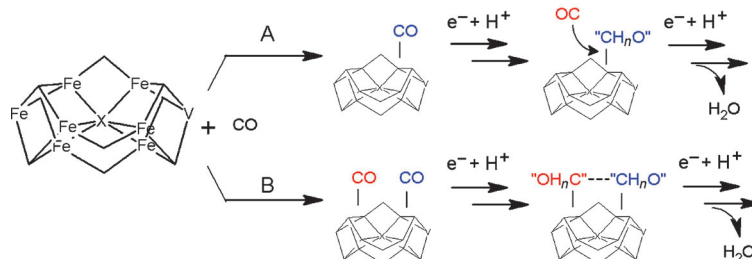
Although nitrogenases have been studied for many years, several unanswered key questions about these enzymes are of great current interest, in particular with respect to a) the mechanism of electron transfer and gating, b) the identity of the light, central atom (C, N, O) of the FeMoco cluster, and c) the substrate-binding site at the cofactor and the mechanism of N<sub>2</sub> reduction.<sup>[7,8]</sup> The potential differences between the three forms of the enzyme, that is, the exact effect of the unique metal in each of the cofactors, is also an exciting topic of current research.<sup>[9,10]</sup>

In the reduction of N<sub>2</sub> by nitrogenase, H<sup>+</sup> is concomitantly reduced to H<sub>2</sub>. Mo nitrogenase is capable of reducing other small unsaturated molecules, such as acetylene and ethylene, and the enzyme is inhibited by CO, CN<sup>-</sup>, and H<sub>2</sub>. V nitrogenase shows similar behavior with one significant discrepancy: CO does not inhibit the enzyme, but instead H<sub>2</sub> production is seen to decrease in the presence of CO, which indicates that the reduction of H<sup>+</sup> is being diverted.<sup>[9]</sup> In further investigations, Ribbe and co-workers found that in the presence of protons, CO is reduced to form light hydrocarbons, in particular ethylene, ethane, propylene, and propane.<sup>[3]</sup> In each of these products, new C–C bonds have been formed; thus, V nitrogenase can be classified as an FT catalyst.

A comparison of the catalytic properties of the FT process and this new reactivity of V nitrogenase is of course intriguing. Importantly, Ribbe and co-workers have shown that when H<sub>2</sub> is added to the CO gas, CO reduction by V nitrogenase is inhibited.<sup>[3]</sup> Hence, it can be concluded that the mechanism of the reduction of CO by V nitrogenase to hydrocarbons does not follow the exact same mechanism as the FT process, but that reducing equivalents of “H” are delivered by a different means in the enzyme. This issue was addressed further by Ribbe and co-workers, and the source of hydrogen and carbon in the formed hydrocarbons has now been identified.<sup>[4]</sup>

[\*] D. L. Gerlach, Dr. N. Lehnert  
Department of Chemistry, University of Michigan  
930 N University, Ann Arbor, MI 48109 (USA)  
Fax: (+1) 734-615-3790  
E-mail: lehnertn@umich.edu

[\*\*] We acknowledge Prof. Dimitri Coucouvanis for valuable discussions.



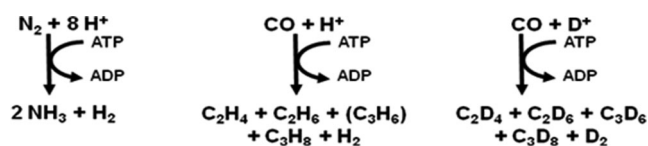
**Scheme 2.** Two general mechanistic strategies for the reduction of CO by V nitrogenase to form hydrocarbons.

When labeled  $^{13}\text{CO}$  was used, GC–MS indicated the formation of the complementary  $^{13}\text{C}_2\text{H}_4$ ,  $^{13}\text{C}_2\text{H}_6$ , and  $^{13}\text{C}_3\text{H}_8$  hydrocarbons. Hence, the carbon atoms found in the hydrocarbons originate solely from the carbon monoxide that is reduced. Similarly, when  $\text{D}_2\text{O}$  buffer was used for the reduction of CO, the detection of hydrocarbons by GC–MS revealed  $\text{C}_2\text{D}_4$ ,  $\text{C}_2\text{D}_6$ , and  $\text{C}_3\text{D}_8$ .<sup>[4]</sup> Additional mass shifts were observed when  $^{13}\text{CO}$  was reduced in  $\text{D}_2\text{O}$ : this reaction yielded  $^{13}\text{C}_2\text{D}_4$ ,  $^{13}\text{C}_2\text{D}_6$ , and  $^{13}\text{C}_3\text{D}_8$ . This evidence clearly suggests that the proton source (water) serves as the supply of hydrogen atoms for the production of hydrocarbons by V nitrogenase. Finally, Ribbe and co-workers allowed the cofactor to select either  $\text{H}^+/\text{D}^+$  or  $\text{H}_2/\text{D}_2$  as the hydrogen source for the production of the light hydrocarbons in the reduction of CO.  $\text{H}_2$  or  $\text{D}_2$  were supplied at ratios in which V nitrogenase produces these gases to mimic the steady  $\text{H}_2$  supply available to the FeVco during the reduction of CO. When 1.2 or 5.5%  $\text{D}_2$  (remaining composition is CO) was supplied to simulate the amount of  $\text{H}_2$  produced in 10 min and 1 h, respectively, in the presence of  $\text{H}^+/\text{H}_2\text{O}$  buffer, only nondeuterated hydrocarbons were detected.<sup>[4]</sup> These results again confirm that protons from water serve as the hydrogen source for the hydrocarbons produced in the reduction of CO by V nitrogenase. Thus, V nitrogenase could have a comparable mechanism to that of the FT process, but the hydrogen source in each case is distinctly different. Furthermore, there is an interesting H versus D isotope effect, where propylene is only produced in detectable quantities in the presence of  $\text{D}^+/\text{D}_2\text{O}$ ; this observation indicates that propylene should be a substrate for V nitrogenase.<sup>[4]</sup> The production of  $\text{C}_3$  hydrocarbons by V nitrogenase is approximately 100 times slower than the production of  $\text{C}_2$  chains, which indicates that there is a barrier to chain growth. Scheme 1 summarizes the unique reactivity of V nitrogenase.

In summary, Ribbe and co-workers have provided clear evidence for the production of hydrocarbons with new C–C and C=C bonds from the reduction of CO by V nitrogenase,<sup>[3]</sup> and that the source of hydrogen atoms in these hydrocarbons

is water.<sup>[4]</sup> The difference between the ability of V nitrogenase to reduce CO and the inhibition of Mo nitrogenase by CO is truly remarkable. It can be speculated that the unique metal that is bound to the homocitrate, among other differences, is fundamental to the tuning of the activity of the cofactor. Recent spectroscopic and computational results for Mo nitrogenase advocate for the binding of  $\text{N}_2$  and CO at the six central iron atoms of the FeMoco, not the terminal Fe or Mo atom.<sup>[7c,11]</sup> If V nitrogenase binds CO similarly, two general mechanistic possibilities arise for the formation of the hydrocarbon chains (Scheme 2). In mechanism A, CO could bind end-on to a central iron atom and then undergo reduction and protonation to form a reduced “ $\text{CH}_n\text{O}$ ” species that is reactive towards a second molecule of CO, forming a new C–C or C=C bond by CO insertion into the Fe–“ $\text{CH}_n\text{O}$ ” bond. Alternatively (mechanism B), two CO molecules could bind simultaneously to the central  $\text{Fe}_6$  core in close proximity. The bound CO molecules could then undergo reductive coupling to form new C–C or C=C bonds. The oxygen atom of CO is likely eliminated in the form of water in these reactions. It can be further postulated that the same binding site is used for the binding of  $\text{N}_2$  and CO by V nitrogenase on the basis of the evidence that the production of  $\text{NH}_3$  and  $\text{H}_2$  decreases with the presence of CO, which indicates that the substrates are competing for the same binding site. On the basis of the formed products, V nitrogenase seems in fact able to catalyze FT-type chemistry at room temperature; however, the method of “H” delivery in the two processes is certainly different. Nevertheless, the ability of bacteria to catalytically produce light hydrocarbons is of much interest in the field of biofuel production, and researchers in this area have already begun to investigate the potential of converting syn gas into ethanol by using iron–sulfur proteins.<sup>[12]</sup> The results of Ribbe and co-workers will ignite more efforts in this important area of research.

Received: April 29, 2011  
 Published online: July 14, 2011



**Scheme 1.** Proposed schemes for the reduction of  $\text{N}_2$  (left) and CO in the presence of  $\text{H}^+$  (middle) and  $\text{D}^+$  (right) by V nitrogenase.<sup>[5]</sup>

- [1] C. K. Rofer-DePoorter, *Chem. Rev.* **1981**, *81*, 447–474.
- [2] B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3011.
- [3] C. C. Lee, Y. Hu, M. W. Ribbe, *Science* **2010**, *329*, 642.
- [4] C. C. Lee, Y. Hu, M. W. Ribbe, *Angew. Chem.* **2011**, *123*, 5659–5661; *Angew. Chem. Int. Ed.* **2011**, *50*, 5545–5547.
- [5] R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013–3030.
- [6] R. R. Eady, *Coord. Chem. Rev.* **2003**, *237*, 23–30.

- [7] a) J. W. Peters, R. K. Szilagy, *Curr. Opin. Chem. Biol.* **2006**, *10*, 101–108; b) H. J. Xie, R. B. Wu, Z. H. Zhou, Z. X. Cao, *J. Phys. Chem. B* **2008**, *112*, 11435–11439; c) Z. Y. Yang, L. C. Seefeldt, D. R. Dean, S. P. Cramer, S. J. George, *Angew. Chem.* **2011**, *123*, 286–289; *Angew. Chem. Int. Ed.* **2011**, *50*, 272–275; d) D. Lukoyanov, V. Pelmenschekov, N. Maeser, M. Laryukhin, T. C. Yang, L. Noodleman, D. R. Dean, D. A. Case, L. C. Seefeldt, B. M. Hoffman, *Inorg. Chem.* **2007**, *46*, 11437–11449; e) K. Danyal, D. Mayweather, D. R. Dean, L. C. Seefeldt, B. M. Hoffman, *J. Am. Chem. Soc.* **2010**, *132*, 6894–6895; f) K. Danyal, B. S. Inglet, K. A. Vincent, B. M. Barney, B. M. Hoffman, F. A. Armstrong, D. R. Dean, L. C. Seefeldt, *J. Am. Chem. Soc.* **2010**, *132*, 13197–13199; g) I. Dance, *Inorg. Chem.* **2011**, *50*, 178–192.
- [8] F. A. Tezcan, J. T. Kaiser, D. Mustafi, M. Y. Walton, J. B. Howard, D. C. Rees, *Science* **2005**, *309*, 1377–1380.
- [9] C. C. Lee, Y. Hu, M. W. Ribbe, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 9209–9214.
- [10] N. C. Smythe, R. R. Schrock, P. Müller, W. W. Weare, *Inorg. Chem.* **2006**, *45*, 9197–9205.
- [11] U. Huniar, R. Ahlrichs, D. Coucouvanis, *J. Am. Chem. Soc.* **2004**, *126*, 2588–2601.
- [12] H. N. Abubackar, M. C. Veiga, C. Kennes, *Biofuels Bioprod. Biorefin.* **2011**, *5*, 93–114.
-