Angewandte International Edition Chemie

Hydrogen Storage

DOI: 10.1002/anie.201402963

CO_2 Fixation through Hydrogenation by Chemical or Enzymatic Methods

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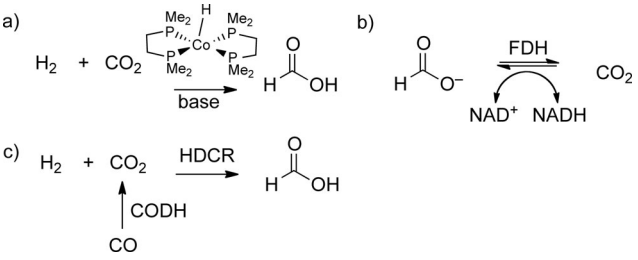
carbon dioxide · catalysis · enzymes · formic acid · microbiology

Today's CO_2 emissions predominantly arise from the combustion of fossil fuels and are estimated at 3.2 Gt per year. In fact, the concentration of CO_2 in the atmosphere has risen from a level of 280 ppm at the beginning of the Industrial Age in the mid-18th century to 383 ppm in 2010.[1] Hence, it may be that the ecological buffer capacity of the biosphere was reached already in the 1980s and that we are currently trespassing beyond nature's limits. Unfortunately, carbon is in its highest oxidation state in CO_2 and its transformation into other valuable chemicals requires high energy input. Apart from traditional synthetic applications such as the carboxylation of Grignard reagents, there are only a few large-scale industrial processes using CO_2, such as the synthesis of urea (ca. 95 million metric tonnes per year), and the Kolbe–Schmitt reaction for the synthesis of salicylic acid (70 kilotonnes per year). Moreover, carbon dioxide is added in small amounts to syngas for the production of methanol (20 million metric tonnes per year) and more recently for the synthesis of (poly)carbonates through the carboxylation of epoxides with an estimated production of 150 kilotonnes per year. However, keeping in mind the tremendous annual emission of carbon dioxide, any new large-scale chemical process for its fixation would still be only "a drop in the bucket". Nevertheless, the use of carbon dioxide as C1 source to produce chemicals and fuels can be the basis of a greener and more sustainable chemical industry. In this regard, recently significant progress has been achieved in the reduction of carbon dioxide or bicarbonate using organometallic and enzyme catalysis.

An interesting strategy to capture carbon dioxide is the combination with "green" hydrogen generated with renewable energy sources to produce formic acid or formate. This concept has the additional charm that a potential surplus of renewable energy is used to produce hydrogen as an alternative fuel, which can then be safely stored and transported because of the reversibility of the system.

In the past, chemical routes to transform CO_2 and H_2 into formate in the presence of organometallic homogeneous or heterogeneous catalysts often required high pressure and temperatures. Notably, significantly improved iridium catalysts[2] for the reversible hydrogenation of carbon dioxide as well as Co- and Fe-based catalysts working under ambient conditions[3] have been described recently. For all these catalysts rather high turnover frequencies (TOFs) were determined (Ir: TOF of 150000 h^{-1} at 200 °C with 30 bar CO_2 and 30 bar H_2; Co: TOF of 3400 h^{-1} at room temperature and 1 atm; 74000 h^{-1} at 20 atm; Fe: 770 h^{-1} at 80 °C and 60 bar; Scheme 1 a).



Scheme 1. a) Metal catalysts such as the recently described [Co{1,2-bis(dimethylphosphino)ethane}$_2$H] produce formic acid in the presence of a base at atmospheric pressure and room temperature. b) The well-studied formate dehydrogenase (FDH) from *C. boidinii* is very useful for regenerating the cofactor NAD^+, but only a few FDHs are known to catalyze the reverse formation of formic acid from CO_2 and H_2 with sufficient activity. c) The hydrogen-dependent carbon dioxide reductase (HDCR) from *A. woodii* can synthesize formic acid directly from CO_2 and H_2 with high turnover frequencies. In combination with a CO-dehydrogenase (CODH) one can even start from carbon monoxide. The required enzymes and cofactors are not shown for clarity.

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Promising alternatives to such man-made catalysts are biological systems and the use of isolated enzymes (for recent reviews see Refs. [1,4]). Although four major pathways of biological CO_2 fixation have been discovered (namely the Calvin–Benson–Bassham cycle, the Arnon–Buchanan cycle, the Wood–Ljungdahl pathway, and acyl-CoA carboxylase pathways), none of them allows a direct and energy-efficient synthesis of formic acid directly from CO_2 and H_2. Notably,

already 50 years ago the so-called "Knallgas" bacterium from *Hydrogenomonas* sp. was described as being able to incorporate CO_2 and H_2 to synthesize energy-storage materials such as poly-β-hydroxybutyric acid.[5]

One possible enzymatic alternative is the use of formate dehydrogenase (FDH),[6] for instance from *Candida boidinii*, which was first described in the pioneering work of the Kula group in 1976[7] (Scheme 1b). This enzyme requires the cofactor NADH, which made it very attractive for the efficient regeneration of NAD^+ from formic acid on an industrial scale yielding CO_2 as a by-product to synthesize optically pure nonnatural amino acids through the reductive amination of α-keto acids catalyzed by amino acid dehydrogenases.[8a,b] Unfortunately, this FDH was found to be almost inactive in the reverse reaction required to make formic acid from CO_2. More recently alternative FDHs have been described. One enzyme originates from the anaerobic acetogen strain *Clostridium carboxidivorans* DSM15243.[9] This FDH, recombinantly expressed in *E. coli*, was found to be oxygen-tolerant and highly active in the desired NADH oxidation. Furthermore, its binding affinity for formate was at least 30 times lower than that of the FDH from *C. boidinii*, making it much more useful for the formation of formate. Another enzyme, which is found in *Clostridium autoethanogenum* grown in the presence of carbon monoxide, is an NADPH-dependent, selenocysteine- and tungsten-containing FDH which is part of a complex composed of seven subunits.[10a,b] One of the other subunits is an [FeFe]-hydrogenase, and together all of the subunits catalyze the reversible coupled reduction of ferredoxin and $NADP^+$ with H_2 or formate and the reversible formation of H_2 and CO_2 from formate. A major disadvantage is that all of these FDHs require NAD(P)H in stoichiometric amounts.

In 2010 Glueck et al.[1] stated in their review: "*Based on lead-sequence data, genome mining will certainly provide more oxygen-stable (de)carboxylases possessing a broad substrate tolerance in the near future.*" Indeed, when Poehlein et al.[11] studied the acetogenic bacterium *Acetobacterium woodii* to determine how this microorganism can synthesize acetate from CO_2 and H_2, they could postulate, based on its genome sequence, a hydrogen-dependent carbon dioxide reductase (HDCR). In a very recent publication, Schuchmann and Müller[12] studied this enzyme in detail and confirmed that HDCR can directly convert molecular hydrogen and CO_2 into formate (Scheme 1c). Biochemical characterization of the purified enzyme revealed that it is composed of four subunits: two large subunits formed by the (presumably selenium- and molybdenum-containing) formate dehydrogenase and an [FeFe]-hydrogenase, accompanied by two small electron-transfer subunits. HDCR hydrogenates CO_2 at 30 °C with a TOF of 101 600 h^{-1}, which is significantly better than chemical catalysts (but not 1500 times higher as stated in their publication; see TOFs given above for the Co complex). Interestingly, HDCR could also accept reduced ferredoxin instead of hydrogen for CO_2 reduction. Schuchmann and Müller proposed a combination of the HDCR with a carbon monoxide dehydrogenase (CODH) from the same strain to allow the complete conversion of gas mixtures composed of H_2, CO, and CO_2. Whether the FDH from *Clostridium* sp. or the HDCR are indeed a practical solution for large-scale storage and transportation of hydrogen remains to be demonstrated keeping in mind the overall complexity of these oxygen-sensitive enzymes and the challenge of establishing an efficient whole-cell system under anaerobic conditions. At least it is now evident that nature provides useful biocatalysts for this highly desired reaction.

What are the future challenges in catalytic carbon dioxide reductions? For large-scale industrial implementation, even better catalysts are needed. With regard to basic science, the hydrogenation of carbon dioxide with simultaneous C–C bond formation represents one of the grand challenges. As an example, the low-temperature and selective Fischer–Tropsch reaction can be considered.

Received: March 3, 2014
Published online: April 6, 2014

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