CO_2 Reduction

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Efficient Activation of the Greenhouse Gas CO_2

Ulf-Peter Apfel and Wolfgang Weigand**

carbon dioxide · niobium · photochemistry · reduction · water–gas shift reaction

Dedicated to Professor Peter Klüfers on the occasion of his 60th birthday

There is evidence that 3.8 billion years ago the geochemically important reduction of CO_2, a principal component of volcanic exhalation gases, to CO played a pivotal role for the periodic formation of biomolecules.[1] According to the water–gas shift reaction, CO_2 could be reduced by dihydrogen to afford CO under these prebiotic conditions.[2,3] Additionally, the possible prebiotic importance of CO was postulated by Wächtershäuser and Huber in the context of the iron–sulfur-world hypothesis.[4] They showed that CO can react to thioacetic acid methylester in the presence of methylthiol and NiFe-sulfides with subsequent hydrolysis to acetic acid.[4] This reaction is assumed to be important in the chemoautotrophic origin of life in which primitive organisms consumed CO or CO_2 from volcanic or hydrothermal sites for the formation of carbon–carbon bonds.[1,4,5]

Over the following billions of years enzymes catalyzing the CO/CO_2 equilibrium have taken on the role of NiFe-sulfides in organisms. CO is widely utilized in organisms as a reductant[6] [Eq. (1)], signaling molecule,[7] and for the synthesis of *S*-acetyl-CoA by acetyl-CoA synthase (ACS),[8] which is analogous to the inorganically catalyzed prebiotic synthesis of thioacetic acid methylester.

$$CO + H_2O \rightleftharpoons CO_2 + \underbrace{2e^- + 2H^+}_{H_2} \qquad (1)$$

In organisms, the selective and reversible conversion of CO into CO_2 is catalyzed by the enzyme CO-dehydrogenase (CODH).[9] Two different types of CODH are found in nature and can be classified into Mo-Cu ($CODH_{Mo}$) and Ni-Fe containing ($CODH_{Ni}$) enzymes.[10] Whereas $CODH_{Mo}$ is found in aerobic organisms, $CODH_{Ni}$ is found in anaerobic organisms. Structure determination of the active sites in the $CODH_{Ni}$ enzymes of *Rhodospirillum rubrum*[11] and *Carboxydothermas hydrogenoformans*[12] revealed a [Ni-4Fe-5S] cluster (Figure 1). It was suggested that the Ni^{II} atom is the catalytic center for the oxidation of CO to CO_2 and a plausible catalytic pathway is described.[13] This pathway includes the formation of a $\{Ni^{II}Fe^{II}(OH)\}$ species and subsequent nucleophilic attack of the hydroxy ligand by incoming CO.

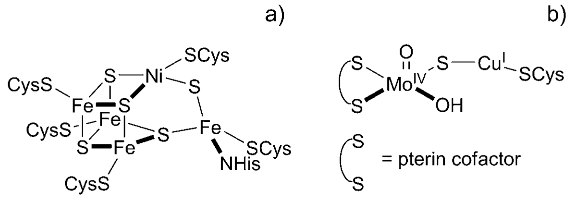

Figure 1. Active site structures of a) the anaerobic functioning $CODH_{Ni}$ from *Carboxydothermus hydrogenoformans* and b) the aerobic functioning $CODH_{Mo}$ from *Oligotropha carboxidovorans*.

In contrast, the $CODH_{Mo}$ active site found in *Oligotropha carboxidovorans* provides a $\{Mo^{IV}(=O)(OH)\text{-}S\text{-}Cu^{I}\}$ system (Figure 1).[14] The CO_2 formation is suggested to start by nucleophilic attack of the hydroxy ligand at the CO.[14] In contrast to the Ni-containing systems, this initial activation is followed by insertion of CO into the $S{-}Cu^{I}$ bond and elimination of CO_2. In both enzymes, a direct reversible two-electron transfer was observed.

Current active-site model complexes of both CODH enzymes provide solely two consecutive one-electron reduction/oxidation steps and promote either CO oxidation or CO_2 reduction.[15] Recently, Armstrong et al. described a light-driven two-electron reduction of CO_2 to give exclusively CO.[16] They attached a photoactive $[Ru^{II}(bipy)_2\text{-}(4,4'\text{-}(PO_3H_2)\text{-}bipy)]Br_2$ (RuP; bipy = 2,2′-bipyridyl) unit and the CO_2-reducing enzyme CODH I from *Carboxydothermas hydrogenoformans* (Ch) to TiO_2 nanoparticles (Scheme 1). The usual TiO_2-based systems provide only a single electron transfer ($E = -1.9$ V versus the standard hydrogen electrode (SHE) in H_2O; pH 7),[17] giving a highly reactive $CO_2^{\bullet -}$ radical.[18] In contrast, the system developed by Armstrong and co-workers was able to bypass the formation of this radical by a direct two-electron transfer ($E = -0.46$ V versus SHE in H_2O; pH 6).[19] This transfer leads to a fast and highly selective reduction of CO_2 to CO (250 $\mu mol\,h^{-1}$ CO per g of TiO_2) under irradiation with sunlight without the typical side products, such as methanol or methane. In addition, the same group had already shown that the water–gas shift reaction could be influenced in such a way that mainly CO_2 and H_2 was obtained when CODH I was connected to a hydrogenase enzyme on graphite micro pellets.[19] The TiO_2 nanoparticles thereby serve as an electron relay between the ruthenium dye

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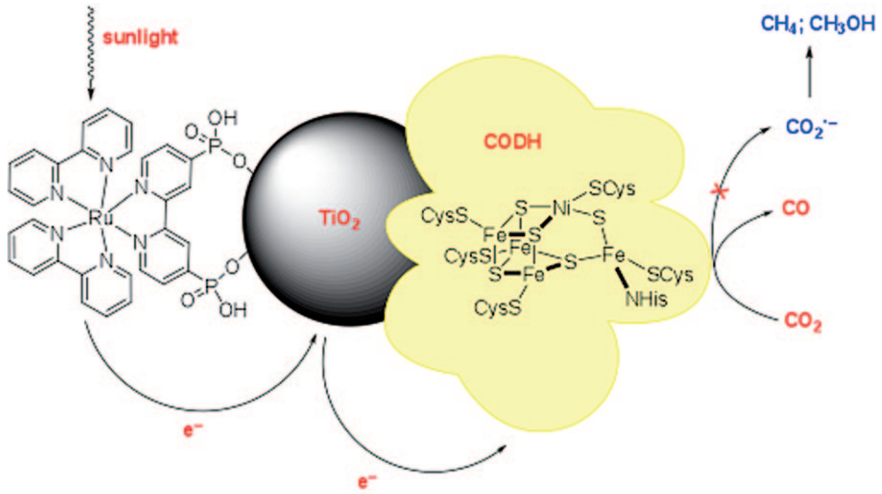
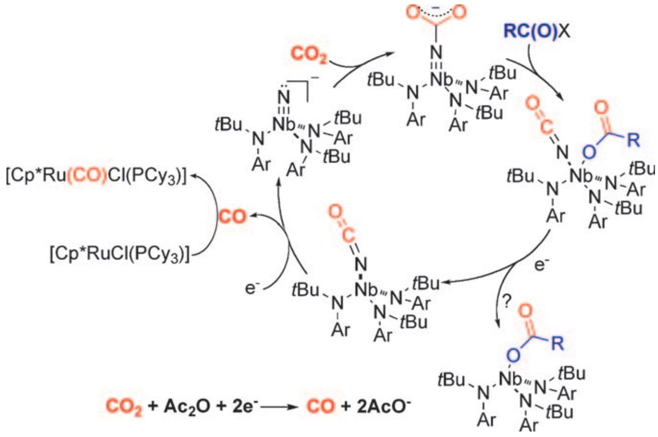
[*] Dr. U.-P. Apfel, Prof. Dr. W. Weigand
Institut für Anorganische und Analytische Chemie
Friedrich-Schiller-Universität Jena
August-Bebel-Strasse 2, Jena (Germany)
Fax: (+49) 3641-948-102
E-mail: peter.apfel@uni-jena.de
wolfgang.weigand@uni-jena.de



Scheme 1. The reduction of CO_2 to CO, supported by a photoactive dye and a $CODH_{Ni}$-enzyme bound to a TiO_2 nanoparticle. Adapted from Ref. [16].

and the CODH I enzyme. However, it was reported that the catalytic rate was mainly dependent on the amount of enzyme and decreases upon prolonged irradiation. This loss of activity was attributed to the photoinstability of the conglomerate RuP-TiO_2-CODH, possibly caused by the labile connection of the enzyme to TiO_2 particles.

Similar fascinating results were obtained by Cummins et al. who described the two-electron reduction of CO_2 formally bypassing the $CO_2^{\bullet -}$ radical.[20] In contrast to the functionalization of a whole enzyme, they used a ligand-based reduction of CO_2, supported by a Nb^V nitrido complex. In contrast to other CO_2-activating metal complexes, strong metal–oxygen bonds, responsible for low catalytic turnover, are avoided by the CO_2 activation through the nitrido ligand. Thus a direct oxygen transfer to an external oxygen-acceptor system was established. Thereby, the nitrido ligand reacts with CO_2 to give a carbamate species (Scheme 2). This result was impressively confirmed by X-ray crystallography, whereby a significant increase of the C–O bond length compared to that in free CO_2 was observed. Additionally, they were able to confirm CO_2 as the source for carbamate formation by ^{13}C-labeling experiments. The deoxygenation of this stable carbamate by reaction with electrophiles RC(O)X such as acetic anhydride resulted in an isocyanato acetato complex (Scheme 2). This crucial step involves an oxygen atom transfer from the carbamate to the carbonyl compound (in this case acetic anhydride). Again, the Cummins group could show, using ^{13}C-labeling techniques, that the carbamate is transformed to an isocyanate which remains coordinated (Scheme 2). Subsequently, a preferential dissociation of the acetate ligand occurs by a one-electron reduction step. This dissociation can be induced either by electrochemical reduction or by treatment with SmI_2. Additional one-electron reduction led to CO release and re-forms the Nb^V nitrido complex. However, the critical point of this reaction remains the dissociation of the acetate group, which is in competition to the cleavage of the isocyanate group (Scheme 2). The final loss of the CO group was confirmed in an elegant way by the reaction with [Cp*RuCl(PCy_3)] which gives [Cp*RuCl(PCy_3)(CO)] (Cp* = C_5Me_5) and shows a prominent color change of the reaction mixture upon CO binding.



Scheme 2. Simplified mechanistic pathway for the CO_2 reduction by ligand-based reduction on Nb^V nitrido complexes. Adapted from Ref. [20].

These outstanding results will open new pathways to convert CO_2 selectively into CO and may open an alternative way to provide a reactive C_1 building block for several reactions (e.g. water–gas shift reaction, hydroformulation, Monsanto process) in future. This might also be a versatile way to reduce the CO_2 concentration and a giant stride for reducing greenhouse gases. However, beside these convenient reaction conditions, two crucial points are remaining, namely the photoinstability of the RuP-TiO_2-CODH and the competitive loss of the isocyanate during the catalytic cycle, need to be solved. Further stimulating investigations based on the findings of Armstrong et al. and Cummins et al. might therefore be expected.

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