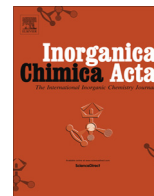




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## Review article

## Molybdenum and tungsten-containing formate dehydrogenases: Aiming to inspire a catalyst for carbon dioxide utilization

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## ABSTRACT

The global energy demand and the present high dependence on fossil fuels have caused an unprecedented increase in the Earth's atmosphere carbon dioxide concentration. Its exponential and uncontrollable rise is responsible for large and unpredictable impacts on the world climate and for ocean acidification, thus, being a major concern for the ecosystems and human's daily life. On the other hand, the carbon dioxide abundance and low cost make it an interesting source for the production of chemical feedstocks and fuels. Yet, the thermodynamic and kinetic stability of the carbon dioxide molecule makes its utilization a laboratorial/industrially challenging task.

In this Review, we propose to use the molybdenum and tungsten-containing formate dehydrogenase (FDH) enzymes as a model to understand the mechanistic strategies and key chemical features needed to reduce carbon dioxide to formate. We will highlight the present knowledge about the structure of FDHs, with particular emphasis on active site features, reaction mechanism and ability to reduce carbon dioxide to formate. The information gathered aims to inspire the development of new efficient (bio)catalysts for the atmospheric carbon dioxide utilization, to produce energy and chemical feedstocks, while reducing an important environmental pollutant.

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**Abbreviations:** EPR, electron paramagnetic resonance spectroscopy; FDH, formate dehydrogenase; M, metal (refers to molybdenum and/or tungsten); Mo-FDH, molybdenum-containing formate dehydrogenase; W-FDH, tungsten-containing formate dehydrogenase; XAS, X-ray absorption spectroscopy.

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## 1. The “carbon dioxide crisis

The global energy demand and the present high dependence on fossil fuels have caused the increase in the atmospheric carbon dioxide concentration for the highest values since records began [1]. Due to its significant green-house effect, carbon dioxide rise is responsible for large and unpredictable impacts on the world climate, besides being responsible for ocean warming and acidification (its major sink) [2,3]. While some authors defend that these alterations are no longer reversible, the carbon dioxide emissions must be greatly decelerate. Future energy sources should be carbon-neutral and based on solar, wind and geothermal energy and new methods to store, transport and use “on demand” the energy from these sources must be developed.

One solution to control the “carbon dioxide crisis” (alongside all other efforts to reduce emissions) would be the use of a renewable energy to scavenge the atmospheric carbon dioxide and convert it back into fuel [4]. Certainly, the carbon dioxide abundance makes it an attractive source for the production of fuels and other synthetic value-added chemicals and there is a huge interest in the development of strategies to efficiently scavenge and activate the atmospheric carbon dioxide [1,5–8]. One of the major challenges

is the thermodynamic and kinetic stability of the carbon dioxide molecule that makes its laboratory/industrial activation a very difficult task. Nature, on the contrary, has found several different strategies to activate and use carbon dioxide [9–12], applying different chemical approaches, with specific enzymes, to cleave the C–O bond (reduction to carbon monoxide) and form C–C (e.g., addition to ribulose 1,5-bisphosphate) and C–H bonds (reduction to formate) [8–14]. Understanding the chemical strategies already tested and proved by Nature (reaction mechanisms and key chemical features) would certainly contribute to the development of new efficient (bio)catalysts for the atmospheric carbon dioxide utilization [1,8,15–21].

This Review will be focused on the carbon dioxide reduction to formate catalyzed by formate dehydrogenase (FDH) enzymes. Formate is an interesting carbon dioxide product for several reasons: it is the first (and stable) intermediate in the reduction of carbon dioxide to methanol or methane; it is used as a chemical building block in industry; it is a viable energy source, easier to store and transport than dihydrogen (formate and dihydrogen are oxidized at similar potentials) and fuel cells that use formate are being developed. All these positive outcomes make worthwhile systematic investigations to develop more efficient (bio)catalysts

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