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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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