



Review

Perspectives on atmospheric CO₂ fixation in inorganic and biomimetic structures



Niall J. English^{a,b,*}, Morad M. El-Hendawy^{a,c}, Damian A. Mooney^{a,b}, J.M.D. MacElroy^{a,b}

^a The SFI Strategic Research Cluster in Solar Energy Conversion, School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland

^b The Centre for Synthesis and Chemical Biology, School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland

^c Chemistry Department, Faculty of Science, Kafrelsheikh University, Kafrel, Egypt

Contents

1. Introduction	85
1.1. CO ₂ utilisation.....	86
1.2. CO ₂ sequestration.....	86
2. Lessons from nature on CO ₂ fixation	87
3. Towards the chemical transformation of CO ₂	89
3.1. Coordination modes in polynuclear metal–CO ₂ complexes.....	89
3.2. Cascade complexation to uptake CO ₂ as CO ₃ ²⁻ and MeCO ₃ ⁻ anions	90
3.3. CO ₂ fixation by bridged complexes.....	91
4. Computational studies of CO ₂ fixation	92
4.1. Bimetallic complexes	93
4.2. Rubisco	93
5. Conclusions	94
Acknowledgments.....	94
References.....	94

ARTICLE INFO

Article history:

Received 11 October 2013

Accepted 17 February 2014

Available online 28 February 2014

Keywords:

CO₂

Fixation

Metal complexes

Biomimetic

Cryptand

Rubisco

Molecular simulation

ABSTRACT

In this review, we examine the fixation of atmospheric carbon dioxide, primarily in inorganic and biomimetic structures, the latter of which can be seen to be inspired by Nature. We discuss coordination modes in polynuclear metal–CO₂ complexes, CO₂ fixation by metallic complexes (poly-nuclear), and fixation by assembly formation. While a number of enzymes exist for the purpose of fixing CO₂, we consider the broad processes exhibited by the enzymes carbonic anhydrase, urease and, more specifically, Rubisco, as well as the inspiration it provides in attempting to develop synthetic derivatives. Recently, *ab initio* and classical molecular simulation methods have been applied to the modelling of CO₂ fixation in Rubisco, and especially in inorganic and biomimetic compounds, which together yield useful insights which could prove useful in the development of next generation CO₂ fixation catalysts.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Anthropogenic CO₂ is often seen as a pollutant, strongly associated with climate change and linked with humanity's over-dependency on fossil fuels. Indeed, the atmospheric concentration of CO₂ has risen from around 280 ppm prior to the industrial age to a current level of around 400 ppm [1,2]. Despite this, it is still envisioned that by 2030 carbon-rich fossil fuels will still provide at least 80% of the world's energy generation. This, combined, with the

* Corresponding author at: The SFI Strategic Research Cluster in Solar Energy Conversion, School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland. Tel.: +353 1 7161646; fax: +353 1 7161177.

E-mail address: niall.english@ucd.ie (N.J. English).

expected growth of emerging economies, suggests an increase in CO₂ emissions by 50–100% during the same period, excluding radical changes in current energy generation and usage or a ‘paradigm shift’ in renewable energy technologies and economics [3].

In the following review, we try to draw together Nature’s mechanisms for both concentrating (the short-term raising of effective CO₂ levels within an organism) and fixing (longer-term incorporation into organic molecules) of atmospheric CO₂ with man’s attempts at biomimetic or synthetic analogues, particularly through the use of metallic complexes. We strongly believe that, like Nature, technologies for concentrating and fixing CO₂ need to be developed, or considered, in tandem in order to move from CO₂ as a pollutant to CO₂ as a resource, *i.e.* a feedstock for the production of valuable products.

In Section 1, we present the backdrop to this work, namely, the limitations associated with only considering CO₂ capture/concentration as an end in itself and the limited sinks available for captured CO₂. In Section 2, a review is made of the means employed by Nature for CO₂ concentration and fixation by focusing on examples of important enzymes involved in the process, in particular carbonic anhydrase and urea amidohydrolase (CO₂ concentration) and ribulose-1,5-bisphosphate (RuBP) carboxylase/oxygenase, or Rubisco (CO₂ fixation). Following on from this, Section 3 looks at many of the bio-inspired, biomimetic analogues that have been studied to date. These synthetically derived catalysts are bio-inspired, at least, in the sense that they have sought to provide a stable framework for a metal centre (or metal centres) to act upon CO₂. In Section 4, we present work that has been conducted in the modelling of the mechanisms of CO₂ conversion, in nature and using synthetic analogues, employing molecular simulation tools. The purpose of this section is to unite the themes of natural and synthetic through the prism of detailed computational investigations with the hope of providing further insight into the development of better catalysts. Finally, results are drawn together for a conclusion in Section 5.

1.1. CO₂ utilisation

As summarised by Mikkelsen et al. [4], there are three main ways in which to reduce the amount of CO₂ in the atmosphere. These are: (1) improved efficiency in energy generation and usage and embracing alternative energy sources, (2) capture and storage of CO₂ and, finally, (3) utilisation of CO₂ as a chemical feedstock. It is the latter of these (CO₂ utilisation) that forms the impetus for the work summarised here. Changing the focus from CO₂ as pollutant to CO₂ as feedstock, necessarily implies a change of perspective. Firstly, this offers a more sustainable ultimate outcome; secondly, it can lead to the development of new chemicals, materials (including polymers), as well as low-molecular weight fuels (with a source of cheap hydrogen); thirdly, it could lead to the replacement of other, more dangerous chemicals (*e.g.*, phosgene or isocyanates) and, finally, foster the realisation that CO₂ is a valuable commodity.

Typically, utilisation of CO₂ can be categorised as:

- (i) Technological use (*i.e.*, CO₂ is not converted into other species): the properties of CO₂ that make this gas particularly useful for many applications are inertness, acid character, relatively low critical temperature and pressure and high density. Moreover, the CO₂ is non-conducting, a good solvent in dense phase, bacteriostatic, and constitutes a fungicide and pesticide leaving no residues. Technological applications include food processing, carbonated beverages, metal fabrication, agriculture, etc.
- (ii) Biological use (CO₂ is fixed in terrestrial or aquatic biomass).
- (iii) Chemical use (CO₂ is converted into chemical feedstocks): currently, use of CO₂ as a chemical feedstock is limited with output by far exceeding this. In addition, some of the largest uses

for CO₂ are associated with short-life sinks including carbonated drinks, fire extinguishers and in cooling applications. Also, when considering the use of CO₂ as a feedstock, care must be taken to assess the overall net CO₂ avoided in production processes. This latter point is significant when one considers the not-insignificant costs associated with CO₂ sequestration.

Presently, the main industrial uses for CO₂ are shown in Table 1. Taking into consideration that anthropogenic emissions of CO₂ account for over 24 Gt of CO₂ per annum, the current chemical feedstock quantities associated with this table represent only 0.5% of this today [5]. Special mention should be given, at this point, to supercritical CO₂ as an environmentally benign or green, solvent, while at the same time being relatively non-toxic, naturally abundant, and is non-flammable. This has been mooted as a sustainable, long-term substitute for various organic solvents in a number of processes [6]. Nonetheless, as can be appreciated, there is significant scope for more widespread utilisation thereof.

Taking into consideration the aforementioned table, it becomes clear that the widespread utilisation of CO₂ is, in the main, directly linked with both the provision of low-cost capture technologies [7], as well as the development of viable chemical pathways for its use as feedstock [8–10].

1.2. CO₂ sequestration

In relation to the capturing and storing (sequestering) of CO₂, there have been a number of developments on both a (near-) geological scale and also in, for instance, flue-gas exhaust and other sources from industry (so-called Carbon Capture and Storage, CCS). The motivation has chiefly been in the mitigation of CO₂ emissions to control, or limit, putative global warming. In terms of geologically inspired approaches, the injection of (supercritical) CO₂ into porous rock deposits (either sub-ocean or subterranean) is a prime example; however, there have been concerns raised about the energy efficiency of such approaches, sustainability from a life-cycle perspective, long term stability and also even the possibility of increasing the likelihood of seismic activity [11,12]. Also, the prospect of CO₂ storage in clathrate hydrates has received increasing attention in recent years, and, indeed, the concept of displacing methane by CO₂ in methane hydrate deposits in the ocean depths or the permafrost has been proposed (although this is technically and operationally very demanding) [13]. One of the key challenges with regard to the displacement of methane from hydrate deposits (whether with or without replacement by CO₂) is the danger of releasing sizeable amounts of methane into the atmosphere, which would be expected to have a severely deleterious effect, given that methane has a global-warming potential approximately 25 times worse than CO₂; this may result in a *de facto* ‘runaway greenhouse effect’ with widespread melting of hydrate deposits as ocean and permafrost temperatures rise [14–16], on the perhaps questionable assumption that global-warming and atmospheric greenhouse-gas content act in tandem in a classic, straightforward ‘feedback loop’.

The removal of CO₂ from industrial emissions is growing in importance [17]. Traditional approaches include absorption (both physical and chemical), adsorption, cryogenic techniques and membranes [18]. However, when applied to power generation, capturing (typically) 90% of otherwise emitted CO₂, current technologies add 44–87% to the capital cost of a reference plant and 42–81% to the cost of electricity. Put another way, plants with CO₂ capture require 24–42% more fuel per MWh relative to a similarly sized plant without capture. It is estimated tentatively that roughly half of this additional energy is required for solvent regeneration and around one third for compression of CO₂ [18].

Recently, North and co-workers have built on their earlier work with cyclic carbonates [19] to devise bimetallic aluminium-based

Download English Version:

<https://daneshyari.com/en/article/1300986>

Download Persian Version:

<https://daneshyari.com/article/1300986>

[Daneshyari.com](https://daneshyari.com)