

Autocatalysis and CO₂: Carbon Capture and Utilization (CCU) Meets Natural Processes

Gabriela Gastelu,^[a] Pritha Saha,^[b] Paul J. Dyson,^{*,[c]} Martin Hulla,^{*,[b]} and Jorge G. Uranga^{*,[a]}

Autocatalytic reactions were proposed to play a key role at the beginning of life starting from the first reduction of CO₂ to formate, acetate and C₁–C₄ hydrocarbons. In carbon capture and utilization (CCU) processes, the same reactions were demonstrated to be autocatalytic and, in some cases, promoted by catalysts of the same composition. Through evolution, CO₂ reduction then turned into complex autocatalytic networks such as photosynthesis, where CCU chemists found inspiration for the development of more advanced systems for the synthesis of value-added chemicals. Less evolved systems than

photosynthesis, however, may be easier to emulate and provide valuable inspiration into CO₂ reduction chemistry for CCU. Other synthetic systems were also demonstrated to be autocatalytic demonstrating that CO₂ reactions and autocatalysis are closely connected. In this concept article, the relationship between natural, artificial and bio-inspired autocatalytic CO₂ reduction processes is summarized and discussed. The accomplishments resulting from the integration of autocatalysis and CCU strategies, along with their inherent benefits and future perspectives are also outlined.

Introduction

There is a broad agreement that autocatalytic CO₂ reduction played an essential role at the beginning of life when only small molecules such as CO₂, H₂, CH₄ and H₂S were present.^[1–4] According to deep-sea vent theory,^[2,5,6] the first organic molecules could have formed at hydrothermal vents on the seafloor, where magma heated seawater mixes with cold water at extreme pressures and pH values. Initially, mineral rich surfaces of the hydrothermal vents could have acted as heterogeneous catalysts for CO₂ reduction to formate and acetate,^[2,5] prior to the development of autocatalytic networks.

These networks comprise a set of molecular reactions that generate a compound, which, through catalysis of earlier reaction(s) in the network, promotes the synthesis of itself.^[7–9] Past the first reduction of CO₂, complex autocatalytic networks were proposed to describe the evolution of different biochem-

ical and biological processes, such as self-replicative systems,^[4,10] oscillating networks,^[11] and homochirality.^[12] Reduction of CO₂ also evolved into one of the most important autocatalytic networks in biology.

Photosynthetic reduction of CO₂ in green plants is catalyzed by ribulose-5-phosphate (R5P), which itself is produced during photosynthesis, making the entire process autocatalytic.^[13] By recombinant expression, this cycle has also been used to construct a non-natural carbon fixation pathway using an *Escherichia coli* strain for the biosynthesis of sugars.^[14,15] In these systems, CO₂ reduction and autocatalysis are closely connected and, based on deep-sea vent theory, may have been connected from the very beginning of life itself.

In synthetic chemistry, reduction of CO₂ is studied for its use in chemical reactions as part of the carbon capture and utilization (CCU) strategy for mitigation of climate change.^[16] Particularly striking are the similarities between the reaction conditions for CO₂ reduction to formate that operate between 21 and 200 °C, 10 to 210 bar pressure and pH > 7,^[17] and the hydrothermal conditions found below and at the deep-sea vent network called Lost city, where temperatures range between 2 and 200 °C, pressures between 75 and 95 bar and pH in the range of 9–11.^[5] Since autocatalytic reactions were hypothesized to take place at the hydrothermal vents, it should not be surprising that comparable manmade autocatalytic reductions of CO₂ are appearing in CCU chemistry.

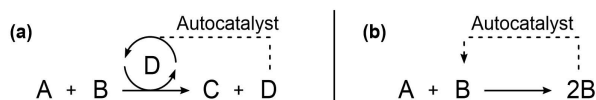
According to IUPAC, an autocatalytic reaction is defined as a reaction in which a product – any compound generated from the reaction – also acts as the reaction's catalyst.^[18] This compound can be a catalyst in a conventional sense, diminishing the activation barrier in a certain step (Scheme 1a) or it can become a substrate of a reaction step for its own production, thus, increasing conversion due to its appearance in the kinetic equation (Scheme 1b). Autocatalytic reactions are usually identified by a sigmoidal kinetic profile that arises from increasing concentrations of the catalyst. However, this can lead to

[a] G. Gastelu, Dr. J. G. Uranga
 Instituto de Investigaciones en Físico-Química Córdoba
 Universidad Nacional de Córdoba
 (INFIQC-CONICET), Córdoba, 5000 (Argentina)
 E-mail: jorge.uranga@unc.edu.ar

[b] P. Saha, Dr. M. Hulla
 Department of Inorganic Chemistry
 Faculty of Science
 Charles University
 12800 Praha 2 (Czech Republic)
 E-mail: martin.hulla@natur.cuni.cz

[c] Prof. P. J. Dyson
 Institute of Chemical Sciences and Engineering
 École Polytechnique Fédérale de Lausanne
 Lausanne (EPFL), 1015 (Switzerland)
 E-mail: paul.dyson@epfl.ch

© 2023 The Authors. ChemCatChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Scheme 1. General scheme of autocatalytic reaction when a product (a) acts as a conventional catalyst in its own production or (b) becomes a substrate of a step for its own production.

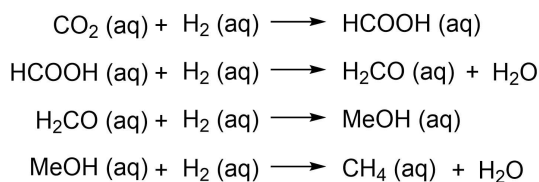
misclassifications as other reaction types lead to comparable kinetic profiles and, also, an autocatalytic reaction might not present sigmoidal kinetics.^[19] Decisive evidence of autocatalysis is the addition of the presumed 'autocatalyst' at the beginning of the reaction. Catalytic effects should then be observed on the initial rate of the reaction and, unless consumed in a secondary process, higher concentrations of the catalytic compound should be observed at the end of the reaction.

Compared to regular catalysis, autocatalysis presents several advantages such as no need to pre-synthesize the catalyst, lower catalyst cost and environmental impact as the autocatalyst is an inherent part of the reaction. In some cases, where the product of interest is the actual autocatalyst, the advantages are enhanced. For instance, product purification and accumulation are usually easier.

Formic acid/formate, formaldehyde, methanol and methane are produced from the reduction of CO₂ as potential autocatalysts (Scheme 2) and, depending on the reducing agent, water, silanols, borates and ketones, via transfer hydrogenations and metal oxides can be produced as autocatalysts. In this concept, the development of autocatalytic reactions involving CO₂ for the generation of value-added products, such as fuels or organic compounds, is discussed and compared to reactions proposed to take place at hydrothermal vents and in biological systems, demonstrating extensive overlap between the seemingly unrelated fields of research, which than can be used as a source of inspiration for the development of novel CO₂ reduction strategies. The discussion is divided into two sections depending on the source of the proposed autocatalyst, i.e. reductant-derived and CO₂-derived autocatalysts.

Reductant-derived autocatalysis

Metals in relatively low oxidation states, particularly Fe(II), are considered to be the primary reducing agents beneath hydrothermal vents. In a process, referred to as serpentinization, olivine is converted to serpentine at temperatures of around



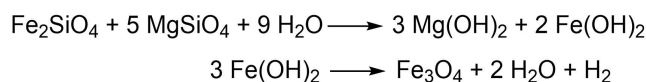
Scheme 2. Sequential reduction of CO₂ to formic acid, formaldehyde, methanol, and methane.

300 °C and iron hydroxide, produced in the reaction, is then oxidized to magnetite (Fe₃O₄), water and hydrogen (Scheme 3).^[20]

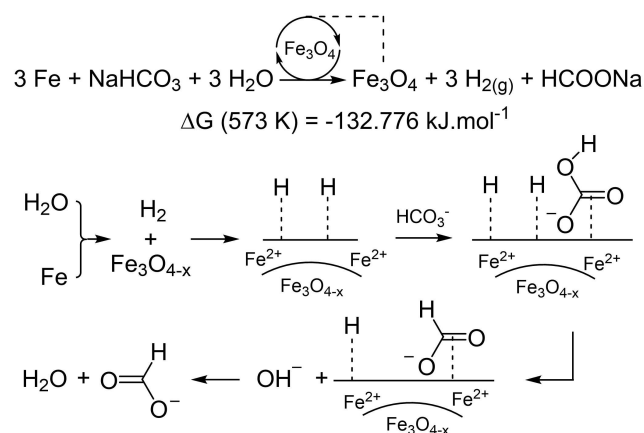
Hydrogen gas is then a source of chemical energy and a reducing agent that is available below and at hydrothermal vents. Carbon dioxide or bicarbonate, produced by the reaction of CO₂ with alkaline water, can be reduced by H₂ to form formic acid/formate, formaldehyde, methanol, methane and water (Scheme 2). Nevertheless, more methane than expected from standard geothermal processes was detected at some geothermal vents, which was hypothesized to be caused by the presence of catalytically active metals or metal alloys.^[21]

In CCU research, partially reduced Fe₃O₄,^[22] ZnO,^[23] MnO^[24] and AlO(OH)^[25] were shown to be catalytically active for CO₂ reduction to formate (for comparison of the oxide catalysts see the following excellent review)^[26] and in some instances further reduction to methane was detected.^[26] When the corresponding metal is used as the reducing agent, the reaction becomes autocatalytic (Scheme 4). In particular, when iron(0) was used, the kinetic profile of the reaction matched autocatalytic reactions, which was confirmed by isolation of the Fe₃O_{4-x} produced, and its use as the catalyst for the reaction. Moreover, in the absence of catalytically active Fe₃O_{4-x} iron(0) is a poor reducing agent for CO₂ and low yields of formate are obtained.^[27]

Interestingly, bicarbonate catalyzes the water splitting reaction with iron(0) resulting in a small catalytic network, where bicarbonate promotes reaction of H₂O with Fe(0) to form H₂ and Fe₃O_{4-x}. The Fe₃O_{4-x} then catalyzes reduction of the bicarbonate to formate and water. Moreover, the produced formate is partially converted to acetate,^[28] the second compound proposed to appear in the origin of life.^[25] Bicarbonate



Scheme 3. Serpentinization of olivine, a geothermal process that produces H₂ gas.



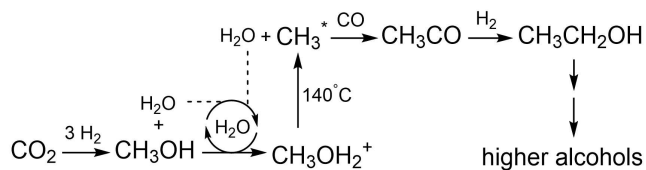
Scheme 4. Reduction of CO₂ with Fe(0) and the proposed reaction mechanism, adapted from ref. [22].

reduction proceeds at 300 to 325 °C and pH ~8.6, which matches the conditions proposed deep below hydrothermal vents of Lost City,^[20] while acetate formation is favored under slightly milder conditions,^[28] which inevitably appears as the system cools towards the actual hydrothermal vents, where hydrothermal fluids are vented at 40–91 °C.^[5]

Formation of Fe(OH)₂, postulated to take place during serpentinization of olivine, was not observed in the laboratory reactions. Instead, iron(II) carbonate was observed as an intermediate and hence a bicarbonate promoted pathway involving Fe(HCO₃), FeCO₃ and FeO was proposed for oxidation of iron(0) to Fe₃O₄.^[22,29] Nevertheless, intermediate hydroxides were reported with Al, Zn and Mn reducing agents, where Al(OH)₃,^[25] Zn(OH)₂^[30] and Mn(OH)₂^[24] form before their dehydration to the corresponding oxides. Although they are not as abundant as iron on the seafloor, zinc and manganese can still be found in μmol to mmol/kg quantities,^[31] sufficient to play a role in catalysis.

Beyond CO₂ reduction to formate and acetate, Fisher-Tropsch type processes and temperature/pressure driven equilibrium between low mass hydrocarbons were proposed to explain the detection of C₂–C₄ hydrocarbons at hydrothermal vents.^[21,32] In CCU chemistry C₂–C₄ alcohols were produced from the hydrogenation of CO₂. The reaction is catalyzed by Pt/Co₃O₄ at 140 °C and promoted by water.^[33] Water is also produced by the reduction of CO₂ with H₂, which makes the reaction partially autocatalytic. Water is presumed to be a source of radical or anionic OH and H reductants, which forms by water splitting on vacancies in Co₃O_{4-x} in a similar manner to Fe₃O_{4-x} in the reduction of CO₂ to formate, to promote protonation and dehydration of MeOH to catalyst bound –CH₃*. Fisher-Tropsch type processes were then proposed to yield higher alcohols from the –CH₃* fragment and CO, formed by the reverse water gas shift reaction. The reaction mechanism (Scheme 5) is evidenced by the use of D₂O and methanol-d₄, which yielded the corresponding deuterated C₂–C₄ products. Interestingly, the reaction also proceeds with naturally occurring Co₃O₄ in the absence of Pt(0), albeit at a lower rate.

Methanol was also produced by thermal reduction of CO/H₂, CO₂/H₂ and CO/CO₂/H₂ mixtures with Cu catalysts,^[34] and in the case of CO₂ reduction, water, produced in the reaction, was demonstrated to act as an autocatalyst. In the absence of added water, the reaction had up to 1.5-hour delay before steady state methanol synthesis was achieved. Nevertheless, it should be noted that large(r) quantities of water simultaneously decreased the steady state methanol yield. Based on DFT calculations^[35]



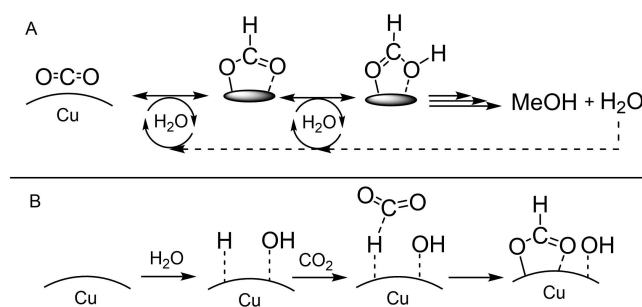
Scheme 5. Reduction of CO₂ to ethanol and higher alcohols catalyzed by Pt/Co₃O₄ with water as a co-catalyst. Species marked with * indicate attachment to the catalyst surface.

and ²H and ¹³C labelling experiments,^[34] a water promoted carboxyl intermediate was originally proposed to form in the reaction. However, more recent studies support a different pathway, where surface bound –H*, –OH* and –O* species, formed by splitting and disproportionation of water molecules on the Cu surface, facilitate CO₂ reduction to formate and destabilize its binding to the surface thereby promoting further reactions (Scheme 6).^[36] Subsequent reductions from formate to methanol were also demonstrated to be autocatalytic but with methanol as the catalyst (vide infra).^[37]

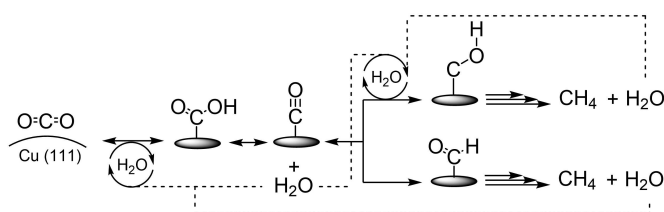
Copper surfaces are also used in CCU for electrochemical reduction of CO₂ to C₂–C₄ hydrocarbons and alcohols.^[38] Based on DFT calculations, the electrochemical reduction(s) on Cu surface(s) are promoted by water produced in the reaction and they proceed via surface bound –COOH*, –CO*, –COH* or –CHO* intermediates, prior to reduction to –CH*, –CH₂* and –CH₃* and formation of hydrocarbons by Fisher-Tropsch type processes^[39] that are also water promoted in the electrochemical reduction of CO₂.^[40] Initially, water was proposed to promote formation of the –COH* intermediate instead of –CHO* (Scheme 7)^[41] but more recent DFT and microkinetic studies indicate that this also depends on the surface coverage by intermediate –CO*^[40] and the type of the surface (e.g. Cu(111) vs Cu(211)), and that water also promotes formation of the very first –COOH* intermediate in the reaction.^[42]

CO₂-derived Autocatalysts

Methanol and formic acid/formate are potential CO₂-derived autocatalysts. Indeed, any compound produced from CO₂



Scheme 6. Thermal hydrogenation of CO₂ to methanol on copper based on DFT and microkinetic simulations A) Water catalyzed steps in the CO₂ reduction to methanol B) proposed role of water in the reduction of CO₂ to formate.

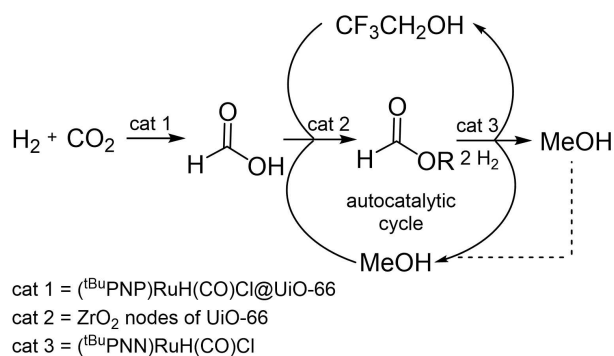


Scheme 7. Effect of water on the proposed pathways for the electrochemical reduction of CO₂ to methane catalyzed by Cu. Proton transfers are omitted for clarity.

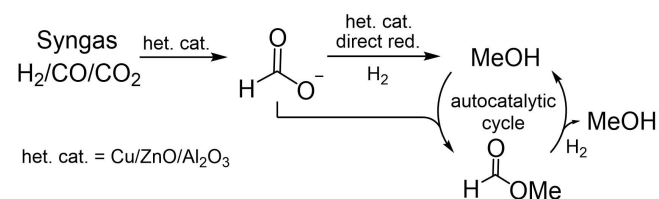
reduction can be considered a potential autocatalyst through a catalytic network.^[2] In nature, the best known example is ribulose-5-phosphate (R5P) in photosynthesis.^[13] Inspired by protein assemblies in the photosynthetic cycle, a multicomponent catalytic process for the hydrogenation of CO₂ to methanol was assembled, and when isolated from one another in a metal-organic framework (MOF) UiO-66, three consecutive reactions take place (Scheme 8).^[43] In the first reaction, CO₂ is reduced to formic acid by H₂. In the second reaction, formic acid is esterified with an alcohol, and in the third reaction, the ester is hydrogenated to methanol and the original alcohol. In the first cycle, 2,2,2-trifluoroethanol (TFA) was used as the only alcohol but, when methanol is produced by the system, the process becomes autocatalytic as methanol takes part in the esterification reaction.

The reactions are sequentially catalyzed by (^tBuPNP)RuH(CO)Cl@UiO-66 (1@UiO-66), ZrO₂ nodes of the MOF, and (^tBuPNN)RuH(CO)Cl (2) in the reaction solution.^[43] Modification of 1@UiO-66 MOF by amination/protonation to UiO-66-NH₃⁺ and also encapsulation of 2 within UiO-66 MOF increases the turnover frequency (TOF) of the catalytic system for the reduction of CO₂ to methanol to 9100 h⁻¹ at 70 °C and 40 bar total pressure.^[44]

Methanol was also proposed as an autocatalyst in its own synthesis from a mixture of H₂/CO/CO₂ catalyzed by Cu/ZnO/Al₂O₃^[37] at 250 °C, 41 bar and H₂/CO/CO₂ = 67.6/29.6/2.8 mol%. In the absence of methanol, the reaction proceeds by direct hydrogenation of formate to methanol, but while methanol is produced, the reaction proceeds by formate esterification and hydrogenation (Scheme 9), as in the MOF UiO-66 systems,^[43,44] which was confirmed by methanol addition at the beginning of



Scheme 8. Reduction of CO₂ to methanol via esterification with CF₃CH₂OH or MeOH catalyzed MOF embedded catalyst sequence.



Scheme 9. Direct reduction of CO₂ to methanol catalyzed by Cu/ZnO/Al₂O₃ and an alternative autocatalyzed mechanism in the presence of MeOH.

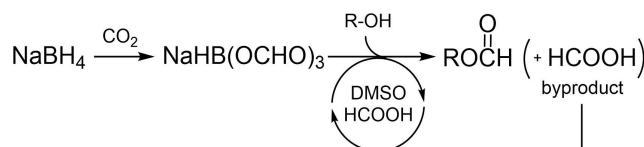
the reaction.^[37] In contrast, the reaction is inhibited by water, which is in line with poor hydrolytic stability of methyl formate.^[45] Nevertheless, it should be noted that small quantities of water were shown to be autocatalytic for the synthesis of methanol from CO₂/H₂ on Cu and only large quantities inhibited the reaction (vide supra),^[34] which was recently confirmed on Cu/ZnO catalyst.^[46]

Interestingly, the esterification reaction of alcohols with formate, also referred to as *O*-formylation, can be catalyzed by formic acid.^[47] In a two-step process, CO₂ is reduced by NaBH₄ to sodium triformato borohydride Na[BH(OCHO)₃], which then acts as the *O*-formylating agent of alcohols (Scheme 10). The second step is catalyzed by formic acid and the products of the reaction are formate esters and more formic acid from the hydrolysis of Na[BH(OCHO)₃]. Under kinetic conditions, increasingly higher yields of formate esters are then obtained during recycling of the formic acid-solvent mixture. The formate esters produced are high value-added products and demonstrate the use of CO₂-derived autocatalyst(s) for more complex compounds of interest.

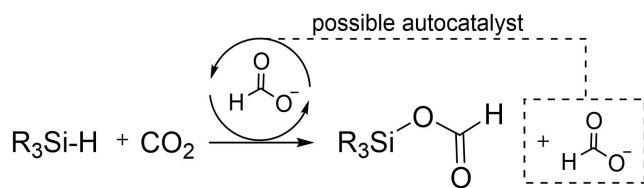
In principle, a similar approach could be applied to the reduction of CO₂ with hydrosilanes, which is catalyzed by nucleophilic and basic anions (Scheme 11).^[48,49] It was proposed that a formate intermediate is key for the reaction to proceed, which was confirmed by the use of formate salts directly as the catalyst. Moreover, the product of this reduction is a silyl formate, which can readily hydrolyze to formic acid/formate, and hence the reaction may be driven toward an autocatalytic pathway under the appropriate reaction conditions.

Summary and Outlook

Although the current number of examples reporting autocatalysis for CO₂ utilization are limited, they have shown important advantages for the development of efficient CCU strategies. In carbon dioxide reduction, autocatalysts can be derived either from the reductant itself or directly from CO₂. The investigation



Scheme 10. *O*-formylation of alcohols with CO₂ catalyzed by formic acid produced as a byproduct in the reaction.



Scheme 11. Potential autocatalytic cycle for the reduction of CO₂ by hydrosilanes catalyzed by formate.

of reductant-derived autocatalysis has revealed a significant connection with geochemistry and the genesis of primary molecules. This relationship is reflected in the case of CO₂ reduction to formate and acetate, where metal oxides generated through water splitting, ultimately act as catalysts in the subsequent reduction of CO₂. In this case, clear links can be established between evolutionary theories and artificial CCU, by considering the analogous reaction conditions and resulting products.

In the case of CO₂-derived autocatalysts, photosynthesis is the primary source of inspiration for the development of chemical pathways towards CO₂ reduction. Inspired by it, sequential reduction of CO₂ was achieved autocatalytically and with high turnover frequencies. Nevertheless, there are six known biological pathways for CO₂ fixation, including photosynthesis,^[50] and their prebiotic analogues, which can provide further inspiration into alternative and more importantly autocatalytic CO₂ fixation strategies.

Autocatalytic strategies, where the desired product is also the autocatalyst, are particularly beneficial as the amount of catalyst increases over time and there is no need to separate it from the product. However, in theory any product of CO₂ reduction can act as an autocatalyst, which was demonstrated on *O*-formylation of alcohols, which is catalyzed by formic acid that is generated as a by-product of the reaction.

It is noteworthy that formic acid and the formate anion are two of the more common reaction by-products in CO₂ reductions and both can directly participate in catalysis. However, most of the CCU strategies already described do not take advantage of their formation. Consequently, valuable compounds with good catalytic potential end up as waste. This issue could be effectively addressed by simple modifications to reaction conditions, and exploring these adaptations is essential for more efficient CCU applications. Alternative CO₂ derived products should also be considered as potential autocatalysts and then we may observe the formation of synthetic autocatalytic networks for CO₂ reduction in the future.

In summary, the combination of autocatalysis and CCU strategies has numerous advantages, such as reduced production costs, easier purification steps, straightforward recycling and increased efficiency with reduced environmental impact. Hence, it is a powerful tool for the development of improved CCU strategies to afford high efficiency and improved reaction kinetics, on the path towards sustainable carbon.

Acknowledgements

We thank the Czech Science foundation (GAČR 21-27431M), Saint Gallen Leading House Program and the ACS Green Chemistry Institute for funding our research in this domain. Gabriela Gastelu thanks CONICET for a fellowship. Open Access funding provided by École Polytechnique Fédérale de Lausanne.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: Autocatalysis · CO₂ utilization · Carbon capture and utilization · CCU · Organocatalysis · Heterogeneous catalysis · Biomimetic synthesis

- [1] A. Pross, R. Pascal, *Open Biol.* **2013**, *3*, 120190.
- [2] M. Preiner, J. C. Xavier, A. Do Nascimento Vieira, K. Kleinermanns, J. F. Allen, W. F. Martin, *Interface Focus* **2019**, *9*, 1–8.
- [3] D. G. Blackmond, *Angew. Chem.* **2009**, *121*, 392–396.
- [4] P. V. Coveney, J. B. Swadling, J. A. D. Wattis, H. C. Greenwell, *Chem. Soc. Rev.* **2012**, *41*, 5430–5446.
- [5] W. Martin, J. Baross, D. Kelley, M. J. Russell, *Nat. Rev. Microbiol.* **2008**, *6*, 805–814.
- [6] S. F. Jordan, H. Ramm, I. N. Zheludev, A. M. Hartley, A. Maréchal, N. Lane, *Nat. Ecol. Evol.* **2019**, *3*, 1705–1714.
- [7] M. Eigen, P. Schuster, *Naturwissenschaften* **1977**, *64*, 541–565.
- [8] S. N. Semenov, L. J. Kraft, A. Ainla, M. Zhao, M. Baghbanzadeh, V. E. Campbell, K. Kang, J. M. Fox, G. M. Whitesides, *Nature* **2016**, *537*, 656–660.
- [9] D. G. Blackmond, *Chem. Rev.* **2020**, *120*, 4831–4847.
- [10] S. A. Kauffman, *J. Theor. Biol.* **1986**, *119*, 1–24.
- [11] V. Vasas, C. Fernando, M. Santos, S. Kauffman, E. Szathmáry, *Biol. Direct* **2012**, *7*, 1.
- [12] M. Steel, W. Hordijk, J. C. Xavier, *J. R. Soc. Interface* **2019**, *16*, 20180808.
- [13] D. A. Walker, R. M. Lilley, *Plant Physiol.* **1974**, *54*, 950–952.
- [14] N. Antonovsky, S. Gleizer, E. Noor, Y. Zohar, E. Herz, U. Barenholz, L. Zelcbuch, S. Amram, A. Wides, N. Tepper, D. Davidi, Y. Bar-On, T. Bareia, D. G. Wernick, I. Shani, S. Malitsky, G. Jona, A. Bar-Even, R. Milo, *Cell* **2016**, *166*, 115–125.
- [15] E. Herz, N. Antonovsky, Y. Bar-On, D. Davidi, S. Gleizer, N. Prywes, L. Noda-Garcia, K. Lyn Frisch, Y. Zohar, D. G. Wernick, A. Savidor, U. Barenholz, R. Milo, *Nat. Commun.* **2017**, *8*, 1705–1705.
- [16] A. Kätelhön, R. Meys, S. Deutz, S. Suh, A. Bardow, *Proc. Natl. Acad. Sci. USA* **2019**, *166*, 11187–11194.
- [17] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, *118*, 372–433.
- [18] P. Müller, *Pure Appl. Chem.* **1994**, *66*, 1077–1184.
- [19] A. K. Horváth, *Phys. Chem. Chem. Phys.* **2021**, *23*, 7178–7189.
- [20] M. Schulte, D. Blake, T. Hoehler, T. McCollom, *Astrobiology* **2006**, *6*, 364–376.
- [21] G. Proskurowski, M. D. Lilley, J. S. Seewald, G. L. Früh-Green, E. J. Olson, J. E. Lupton, S. P. Sylva, D. S. Kelley, *Science (80-)* **2008**, *319*, 604–607.
- [22] J. Duo, F. Jin, Y. Wang, H. Zhong, L. Lyu, G. Yao, Z. Huo, *Chem. Commun.* **2016**, *52*, 3316–3319.
- [23] F. Jin, X. Zeng, J. Liu, Y. Jin, L. Wang, H. Zhong, G. Yao, Z. Huo, *Sci. Rep.* **2014**, *4*, 4503.
- [24] L. Lyu, X. Zeng, J. Yun, F. Wei, F. Jin, *Environ. Sci. Technol.* **2014**, *48*, 6003–6009.
- [25] G. Yao, X. Zeng, Y. Jin, H. Zhong, J. Duo, F. Jin, *Int. J. Hydrogen Energy* **2015**, *40*, 14284–14289.
- [26] X. Liu, H. Zhong, C. Wang, D. He, F. Jin, *Energy Sci. Eng.* **2022**, *10*, 1601–1613.
- [27] F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei, R. L. Smith Jr, *Energy Environ. Sci.* **2011**, *4*, 881.
- [28] B. Jin, L. Luo, L. Xie, *ACS Omega* **2021**, *6*, 11280–11285.
- [29] X. Zeng, G.-D. Yin, Y.-Y. Zhou, J.-F. Zhao, *Molecules* **2022**, *27*, 7371.
- [30] Y. Le, H. Zhong, Y. Yang, R. He, G. Yao, F. Jin, *J. Energy Chem.* **2017**, *26*, 936–941.
- [31] K. L. Von Damm, *Geophys. Monogr. Ser.* **1995**, *91*, 222–247.
- [32] W. F. Giggenbach, *Geochim. Cosmochim. Acta* **1997**, *61*, 3763–3785.
- [33] Z. He, Q. Qian, J. Ma, Q. Meng, H. Zhou, J. Song, Z. Liu, B. Han, *Angew. Chem. Int. Ed.* **2016**, *55*, 737–741.
- [34] Y. Yang, C. A. Mims, D. H. Mei, C. H. F. Peden, C. T. Campbell, *J. Catal.* **2013**, *298*, 10–17.
- [35] Y.-F. Zhao, Y. Yang, C. Mims, C. H. F. Peden, J. Li, D. Mei, *J. Catal.* **2011**, *281*, 199–211.
- [36] D. Xu, P. Wu, B. Yang, *J. Phys. Chem. C* **2019**, *123*, 8959–8966.
- [37] J. Thrane, S. Kuld, N. D. Nielsen, A. D. Jensen, J. Sehested, J. M. Christensen, *Angew. Chem. Int. Ed.* **2020**, *59*, 18189–18193.

- [38] S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.* **2019**, *119*, 7610–7672.
- [39] X. Nie, M. R. Esopi, M. J. Janik, A. Asthagiri, *Angew. Chem. Int. Ed.* **2013**, *52*, 2459–2462.
- [40] J. Santatiwongchai, K. Faungnawakij, P. Hirunsit, *ACS Catal.* **2021**, *11*, 9688–9701.
- [41] X. Nie, W. Luo, M. J. Janik, A. Asthagiri, *J. Catal.* **2014**, *312*, 108–122.
- [42] B. Zijlstra, X. Zhang, J. X. Liu, I. A. W. Filot, Z. Zhou, S. Sun, E. J. M. Hensen, *Electrochim. Acta* **2020**, *335*, 135665.
- [43] T. M. Rayder, E. H. Adillon, J. A. Byers, C. K. Tsung, *Chem* **2020**, *6*, 1742–1754.
- [44] T. M. Rayder, A. T. Bensalah, B. Li, J. A. Byers, C. K. Tsung, *J. Am. Chem. Soc.* **2021**, *143*, 1630–1640.
- [45] O. Jogunola, T. Salmi, J. Waärnä, J. P. Mikkola, E. Tirronen, *Ind. Eng. Chem. Res.* **2011**, *50*, 267–276.
- [46] X. Wang, H. Zhang, *J. Catal.* **2022**, *406*, 145–156.
- [47] G. Gastelu, D. Savary, M. Hulla, D. Ortiz, J. G. Uranga, P. J. Dyson, *ACS Catal.* **2023**, *13*, 2403–2409.
- [48] K. Motokura, C. Nakagawa, R. A. Pramudita, Y. Manaka, *ACS Sustainable Chem. Eng.* **2019**, *7*, 11056–11061.
- [49] K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji, T. Baba, *Chem. Lett.* **2015**, *44*, 1217–1219.
- [50] K. B. Muchowska, S. J. Varma, J. Moran, *Chem. Rev.* **2020**, *120*, 7708–7744.

Manuscript received: July 18, 2023

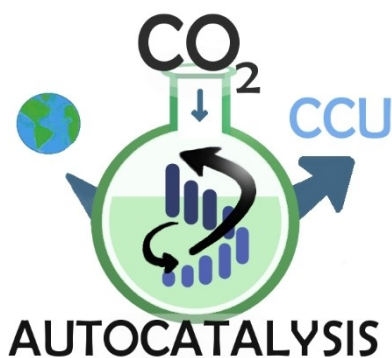
Revised manuscript received: September 18, 2023

Accepted manuscript online: September 22, 2023

Version of record online: September 22, 2023

CONCEPT

Autocatalytic reactions played a pivotal role in prebiotic chemistry and the origin of life. Their significance has inspired the integration of autocatalysis in CCU strategies giving rise to more advanced systems which are critically summarized in this concept article.



G. Gastelu, P. Saha, Prof. P. J. Dyson,
Dr. M. Hulla*, Dr. J. G. Uranga**

1 – 7

**Autocatalysis and CO₂: Carbon
Capture and Utilization (CCU) Meets
Natural Processes**