

Introduction to CO<sub>2</sub> utilisationCite this: *Green Chem.*, 2021, **23**, 3499Da-Gang Yu \*<sup>a</sup> and Liang-Nian He \*<sup>b</sup>

DOI: 10.1039/d1gc90036f

rsc.li/greenchem

The concentration of carbon dioxide (CO<sub>2</sub>), a well-known greenhouse gas, has been increasing in the atmosphere for hundreds of years, which is related to the frequent occurrence of extreme weather.<sup>1</sup> According to the Global Energy & CO<sub>2</sub> Status Report 2019, the emissions of CO<sub>2</sub> into the atmosphere have reached a worrisome level of 33.1 Gt each year.<sup>2</sup> The amount of CO<sub>2</sub> emission has been rising dramatically, endangering the balance of the natural ecosystem and threatening the survival of human beings. Therefore, the pursuit of capturing, storing and converting CO<sub>2</sub> to suppress the amount of CO<sub>2</sub> emission is urgent.

In the last decades, there have been considerable advancements in CO<sub>2</sub> chemistry and industry. The process of carbon dioxide capture and storage (CCS) removes CO<sub>2</sub> that would otherwise be emitted from fossil fuel power stations and other chemical plants through industrial processes and then allows it to be transported for permanent underground storage.<sup>3</sup> This process is effective, however, the process of carbon dioxide capture and utilization (CCU) is even more attractive due to the sustainability, nontoxicity and easy availability of CO<sub>2</sub>, and its potential to be transformed into diverse high value-

added chemicals.<sup>4</sup> Although the thermodynamic stability and kinetic inertness of CO<sub>2</sub> make it difficult for it to be utilized efficiently, many kinds of strategies have been developed to construct important hydrocarbon fuels, fine chemicals and pharmaceuticals from CO<sub>2</sub>.<sup>5</sup> Not only can the utilization of CO<sub>2</sub> help reduce the carbon content in the atmosphere, but it can also provide clean energy and value-added products for the future. Therefore, the process of CCU has received increasing attention from all over the world and great effort from science, industry and government agencies has been made to develop this process.<sup>6</sup> In terms of the CCU process, it covers a wide range of scientific problems including CO<sub>2</sub> hydrogenation, biological carbon fixation, CO<sub>2</sub> reduction and fine chemical production from CO<sub>2</sub>.

Carbon dioxide can act as an ideal carbon source to synthesize hydrocarbon fuels *via* photo-, transition metal, and electro-catalysis. One of the goals of CO<sub>2</sub> utilization is to acquire valuable products, such as CO, HCOOH and CH<sub>3</sub>OH, using homogeneous catalysts. In this respect, the latest advances in the field of the production of commonly used organic solvents from CO<sub>2</sub> are summarized and discussed by Wu and co-workers (DOI: 10.1039/d0gc03280h). Moreover, the Das group (DOI: 10.1039/D0GC04040A) provide an overview of the photochemical reductions of CO<sub>2</sub> to formic acid. A primary advantage of CO<sub>2</sub> reduction *via* photo-catalysis is that the selective reduction of CO<sub>2</sub> can be achieved by photocatalysts with reducing

capabilities. The relevant works in this realm are demonstrated well in a review from Dong, Lan and co-workers (DOI: 10.1039/d0gc01497d) on the selective reduction of CO<sub>2</sub> to HCOOH in H<sub>2</sub>O. Meanwhile, the He group (DOI: 10.1039/d0gc03111a) and the Li and Lu group (DOI: 10.1039/d0gc02836c) have realized the reduction of CO<sub>2</sub> to CO with a rhenium catalyst with bifunctional pyrene groups and a Z-scheme heterojunction of Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, respectively.

In CCU processes, transition metal catalysis is expected to play an important role. This was exemplified in the use of an active Pt/In<sub>2</sub>O<sub>3</sub> catalyst to convert CO<sub>2</sub> to methanol, which was reported by Liu and co-workers (DOI: 10.1039/d0gc01597k). The catalyst loading methods, catalyst loading volume, loading ratios of the iridium/titanium oxide (Ir/TiO<sub>2</sub>) catalyst and even the pre-treatment temperature are all important for this CO<sub>2</sub> hydrogenation, as demonstrated in the work by Su, Huang and co-workers (DOI: 10.1039/d0gc02302g). A new avenue allowing precise control over the catalytic activity of metal catalysts is the stabilization of catalysts *via* the metal-oxide interface, as detailed in the article by Jung, Sun and co-workers (DOI: 10.1039/d0gc02279a). The controlled assembly of catalytic centers allows the tuning of the coordination number of metal catalysts with ligands, achieving the efficient reduction of CO<sub>2</sub> to CO, which is detailed in the article by Geng, Zeng and co-workers (DOI: 10.1039/d0gc02689a). Zhong, Jin and co-workers

<sup>a</sup>Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, P. R. China. E-mail: dgyu@scu.edu.cn

<sup>b</sup>State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, P. R. China. E-mail: heln@nankai.edu.cn

(DOI: 10.1039/d0gc02785e) have achieved an efficient green reduction of bicarbonate, which is produced by the capture of CO<sub>2</sub> under an alkaline environment.

Besides photocatalysis and transition metal catalysis, other catalytic modes can also reduce CO<sub>2</sub> effectively. Recently, Wu, Wu, Han and co-workers (DOI: 10.1039/d0gc03051a) have demonstrated an electrodeposited Cu–Pd bimetallic catalyst for the selective electro-reduction of CO<sub>2</sub>. Unlike molecular catalysts, Chen, Yan and co-workers (DOI: 10.1039/d0gc03506h) have made great efforts towards the selective reduction and subsequent valorization of the reduced forms of CO<sub>2</sub> *via* heterogeneous catalysis. Wang, Song and co-workers (DOI: 10.1039/d0gc03779f) have described another efficient process, where plasma-enabled catalysis is used for the hydrogenation of CO<sub>2</sub> to generate higher hydrocarbons. Wang and co-workers (DOI: 10.1039/d0gc03510f) have developed a highly efficient catalytic system used for the synthesis of alkylidene cyclic carbonates from CO<sub>2</sub> using hydroxyl and azolate ionic liquids. CO<sub>2</sub> reduction on graphdiyne is at an earlier stage of development for applications, therefore, density functional theory calculations can help further understand the mechanism of these reactions, as demonstrated by Wang, Wang and co-workers (DOI: 10.1039/d0gc03742g).

CO<sub>2</sub> has proved its value as a renewable C<sub>1</sub> resource to construct fine chemicals through different mechanisms. Compared to the widely investigated carbonylation from a series of carbonyl sources (*e.g.*, CO, COS or DMF), the transformations of CO<sub>2</sub> show the advantages of being green and economical, due to its abundance, availability, sustainability and nontoxicity. Such examples have been illustrated in the articles by D'Elia, Kleij and co-workers (DOI: 10.1039/d0gc03824e) and Guo, Lamb and co-workers (DOI: 10.1039/d0gc03465g). In a work by Chen, Xi and co-workers (DOI: 10.1039/d0gc02254c), the carboxylation of styrenes with amines and CO<sub>2</sub> has been described as a method for the synthesis of  $\gamma$ -aminobutyric acids *via* visible-light photoredox catalysis. In a related work,

Li and co-workers (DOI: 10.1039/d0gc02667k) studied the Rh-catalyzed regioselective arylcarboxylation of acrylamides with aryl boronic acids and CO<sub>2</sub>. Industrial ore calcination production always discharges unused sulfur as waste and so it can serve as a rich sulfur source for chemical synthesis. Therefore, Zhang, Yu and co-workers (DOI: 10.1039/d0gc03723k) have used both CO<sub>2</sub> and sulfur to synthesize sulfur-containing carbonyl compounds. Sodium trihydroxyaryl borates as robust tetracoordinate organoboron catalysts for reductive formylation of amines with CO<sub>2</sub> have been discussed in the work of Zhao, Wang, Li and co-workers (DOI: 10.1039/d0gc01741h). The transformation of low-concentration CO<sub>2</sub> to high value-added chemicals has become a major target in the capture of (waste) CO<sub>2</sub>, as demonstrated by Zhou, Lu and co-workers (DOI: 10.1039/d0gc03009k) through the capture of low-concentration CO<sub>2</sub> by super-basic guanidines, yielding important oxazolidine-2-ones.

In addition to the potency of CO<sub>2</sub> as C<sub>1</sub> source, it can also act in other roles in organic synthesis. Cui, Shi and co-workers (DOI: 10.1039/d0gc03705b) have reported the oxidative dehydrogenation of light alkanes with CO<sub>2</sub>, in which CO<sub>2</sub> plays the role of a weak oxidant. Liu, Zhang and co-workers (DOI: 10.1039/d0gc03333b) have demonstrated the application of CO<sub>2</sub> in multicolored light-emitting diodes. The neutral waterborne cationic polyurethane from CO<sub>2</sub>-polyol could act as a water-dispersible binder to overcome the bottleneck in heavy metal-free anti-corrosion coatings, as demonstrated by Wang and co-workers (DOI: 10.1039/d0gc02592e). Moreover, polyurethane-urea adducts could be synthesized from CO<sub>2</sub> and furfuryl amines, as demonstrated by Cheng, Zhao and co-workers (DOI: 10.1039/d0gc03695a). CO<sub>2</sub> is taken up by organisms through carbon fixing enzymes and generates important intermediate metabolites for cell growth, and a thermodynamic view of biological carbon fixation is detailed in the report by Li, Zhang and co-workers (DOI: 10.1039/d0gc03493b).

In summary, we have committed to ensuring that CO<sub>2</sub> utilisation contributes

to its full potential in tackling the major global energy challenge. It is clear that the highlighted papers in this themed collection have demonstrated the urgency of reducing greenhouse gas emissions in response to climate change and the energy dilemma. Beyond any doubt, there is significant work left to be done in the field of CCU. These works not only provide hope for turning CO<sub>2</sub> into valuable hydrocarbon fuels and fine chemicals, but also provide some guidelines on CCU to contribute to a more sustainable future for human beings.



Prof. Da-Gang Yu  
Sichuan University



Prof. Liang-Nian He  
Nankai University

## Acknowledgements

We thank the National Natural Science Foundation of China (21822108) and National Key Research and Development Program of China (2016YFA0602900) for financial support.

## References

- 1 M. Meinshausen, N. Meinshausen, W. Hare, S. C. B. Raper, K. Frieler, R. Knutti, D. J. Frame and M. R. Allen, *Nature*, 2009, **458**, 1158–1162.
- 2 <https://www.iea.org/reports/global-energy-co2-statusreport-2019>.
- 3 D. M. Reiner, *Nat. Energy*, 2016, **1**, 15011–15017.
- 4 M. He, Y. Sun and B. Han, *Angew. Chem., Int. Ed.*, 2013, **52**, 9620–9633.
- 5 (a) Q.-W. Song, Z.-H. Zhou and L.-N. He, *Green Chem.*, 2017, **19**, 3707–3728; (b) C.-K. Ran, X.-W. Chen, Y.-Y. Gui, J. Liu, L. Song, K. Ren and D.-G. Yu, *Sci. China: Chem.*, 2020, **63**, 1336–1351; (c) Z. Zhang, L. Gong, X.-Y. Zhou, S.-S. Yan, J. Li and D.-G. Yu, *Acta Chim. Sin.*, 2019, **77**, 783–793; (d) X. He, L.-Q. Qiu, W.-J. Wang, K.-H. Chen and L.-N. He, *Green Chem.*, 2020, **22**, 7301–7320; (e) L. Song, Y.-X. Jiang, Z. Zhang, Y.-Y. Gui, X.-Y. Zhou and D.-G. Yu, *Chem. Commun.*, 2020, **56**, 8355–8367; (f) J.-H. Ye, T. Ju, H. Huang, L.-L. Liao and D.-G. Yu, *Acc. Chem. Res.*, 2021, DOI: 10.1021/acs.accounts.1c00135.
- 6 (a) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742; (b) J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem., Int. Ed.*, 2016, **55**, 7296–7343.