Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

EDITORIAL

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2021, **23**, 3499

DOI: 10.1039/d1gc90036f

rsc.li/greenchem

Introduction to CO_2 utilisation

Da-Gang Yu *[a] and Liang-Nian He *[b]

The concentration of carbon dioxide (CO_2), 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.[1] According to the Global Energy & CO_2 Status Report 2019, the emissions of CO_2 into the atmosphere have reached a worrisome level of 33.1 Gt each year.[2] The amount of CO_2 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_2 to suppress the amount of CO_2 emission is urgent.

In the last decades, there have been considerable advancements in CO_2 chemistry and industry. The process of carbon dioxide capture and storage (CCS) removes CO_2 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.[3] 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_2, and its potential to be transformed into diverse high value-added chemicals.[4] Although the thermodynamic stability and kinetic inertness of CO_2 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_2.[5] Not only can the utilization of CO_2 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.[6] In terms of the CCU process, it covers a wide range of scientific problems including CO_2 hydrogenation, biological carbon fixation, CO_2 reduction and fine chemical production from CO_2.

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_2 utilization is to acquire valuable products, such as CO, HCOOH and CH_3OH, using homogeneous catalysts. In this respect, the latest advances in the field of the production of commonly used organic solvents from CO_2 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_2 to formic acid. A primary advantage of CO_2 reduction *via* photo-catalysis is that the selective reduction of CO_2 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_2 to HCOOH in H_2O. Meanwhile, the He group (DOI: 10.1039/d0gc03111a) and the Li and Lu group (DOI: 10.1039/d0gc02836c) have realized the reduction of CO_2 to CO with a rhenium catalyst with bifunctional pyrene groups and a Z-scheme heterojunction of Co_1-C_3N_4@α-Fe_2O_3, 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_2O_3 catalyst to convert CO_2 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_2) catalyst and even the pretreatment temperature are all important for this CO_2 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_2 to CO, which is detailed in the article by Geng, Zeng and co-workers (DOI: 10.1039/d0gc02689a). Zhong, Jin and co-workers

[a]*Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, P. R. China. E-mail: dgyu@scu.edu.cn*
[b]*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_2 under an alkaline environment.

Besides photocatalysis and transition metal catalysis, other catalytic modes can also reduce CO_2 effectively Recently, Wu, Wu, Han and co-workers (DOI: 10.1039/d0gc03051a) have demonstrated an electrodeposited Cu–Pd bimetallic catalyst for the selective electroreduction of CO_2. 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_2 *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_2 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_2 using hydroxyl and azolate ionic liquids. CO_2 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_2 has proved its value as a renewable C_1 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_2 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_2 has been described as a method for the synthesis of γ-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_2. 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_2 and sulfur to synthesize sulfur-containing carbonyl compounds. Sodium trihydroxyaryl borates as robust tetracoordinate organoboron catalysts for reductive formylation of amines with CO_2 have been discussed in the work of Zhao, Wang, Li and co-workers (DOI: 10.1039/d0gc01741h). The transformation of low-concentration CO_2 to high value-added chemicals has become a major target in the capture of (waste) CO_2, as demonstrated by Zhou, Lu and co-workers (DOI: 10.1039/d0gc03009k) through the capture of low-concentration CO_2 by super-basic guanidines, yielding important oxazolidine-2-ones.

In addition to the potency of CO_2 as C_1 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_2, in which CO_2 plays the role of a weak oxidant. Liu, Zhang and co-workers (DOI: 10.1039/d0gc03333b) have demonstrated the application of CO_2 in multicolored light-emitting diodes. The neutral waterborne cationic polyurethane from CO_2-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_2 and furfuryl amines, as demonstrated by Cheng, Zhao and co-workers (DOI: 10.1039/d0gc03695a). CO_2 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_2 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_2 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. Meienshausen, 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.