

# Carbon Dioxide Utilization Coming of Age

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In the 1990s and early 2000s more and more detailed and alarming studies started to appear on the magnitude of the annual anthropogenic carbon dioxide (CO<sub>2</sub>) emissions and the associated undesired effects on the global climate.<sup>[1]</sup> In subsequent years, for example through the authoritative work by Hansen et al., this notion got much more solid footing.<sup>[2]</sup> Any attempt to reduce or mitigate the excess anthropogenic CO<sub>2</sub> emissions (presently on the order of 4 Gt carbon per year<sup>[3]</sup>) would require the simultaneous implementation of a broad spectrum of measures, including carbon capture and sequestration, switching to renewable energy sources, as well as efforts to reduce energy use and/or enhance efficiency, be it in industrial processes, heating and cooling of buildings, or transportation.<sup>[4]</sup> Some studies also started to suggest the utilization of CO<sub>2</sub> as a feedstock. For example, back in 2007 one of us (Dibenedetto) co-authored a perspective entitled “Utilisation of CO<sub>2</sub> as a chemical feedstock: opportunities and challenges,” in which they explored the potential of CO<sub>2</sub> as a raw material in the synthesis of chemicals such as carboxylates, carbonates, carbamates, fuels or other C1 molecules such as formic acid and methanol.<sup>[5]</sup> Now, ten years later, one can see that major progress has been made in several but not all of these areas. Furthermore, a variety of additional CO<sub>2</sub> utilization approaches has emerged since then. Indeed, carbon dioxide utilization has become a vibrant field of research: A quick Web of Science search for “carbon dioxide utilization” reveals that less than ten articles on this topic were published in 1990, a number that grew to 75 by 2000, 168 by 2010, and over 550 in 2016. Similarly, the citations per year have skyrocketed from only 11 in 1990, to 800 in 2000, over 4100 in 2010, and over 15k in 2016. Industry has also become involved significantly, as evidenced

by the ever-growing number of industrial patents and new processes.

A promising approach for CO<sub>2</sub> utilization, able to significantly contribute to the reduction of anthropogenic CO<sub>2</sub> emissions, would involve a way to activate the rather inert CO<sub>2</sub> molecule to then drive its selective conversion into a chemical or product for which there is a market. Ideally, the energy to drive such a process comes from renewable sources, and overall it needs to produce significantly less CO<sub>2</sub> than the amount being mitigated. Moreover, the process also has the potential to be economically viable at scale, so economics will be the driver for adoption of this new sustainable technology, instead of a reliance on regulation or incentives.


Indeed, the scientific community has pursued a wide range of CO<sub>2</sub> utilization options, several of which are represented in this Special Issue. At the onset, the reader will find reviews by Apayin et al. and Urakawa et al. on a broad range of heterogeneous catalysis approaches for the conversion of CO<sub>2</sub> to value-added intermediates. Interestingly, one of these also compares the relative performance of certain organometallic and semiconductor catalysts when used as homogenous catalysts, or when immobilized on an electrode. Kawi and coworkers review nickel-based catalysts for ‘dry reforming of methane’, the conversion of CO<sub>2</sub> plus methane to syngas, a mixture of hydrogen and carbon monoxide (CO), which serves as the feed for synthetic fuel production, which already is a known industrial-scale process (Fischer–Tropsch).

On the topic of homogenous catalysis, you will find a report by He et al., organometallic catalysts for the synthesis of oxazolidinones from ethanolamines and CO<sub>2</sub>. Keith et al. report on a computational study on how solvation affects the reaction between borohydrides and CO<sub>2</sub>, in support of developing better biomimetic hydride transfer catalysts. With respect to heterogeneous approaches, Mota et al. report on metal oxide catalysts for the direct carbonation of glycerol with CO<sub>2</sub> to yield glycerol carbonates, a versatile building block for chemical synthesis. Plucinski, Jones, and coworkers report a kinetic study on hydrogenation of CO<sub>2</sub> to hydrocarbons over iron on silica catalysts. Nervi and coworkers bridge homo- and heterogeneous catalysis in their study of manganese and rhenium organometallic catalysts for CO production. Provided they exhibit the right turnover numbers (activity) and selectivity for products for which there is a market, homogeneous and heterogeneous catalysis approaches will be easiest to adopt at scale due to familiarity of industry with such processes. In fact, some

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polymers are already being produced at scale in this way using CO<sub>2</sub> as the feed.

Another interesting approach is the photocatalytic reduction of CO<sub>2</sub> to CO or hydrocarbon species, a biomimetic approach often referred to as 'artificial photosynthesis'. It requires catalysts that directly utilize solar energy (and thus conserve fossil fuel resources) to drive the activation and subsequent conversion of CO<sub>2</sub>. In this issue, recent progress is reported on TiO<sub>2</sub> and Bi-containing heterogeneous photocatalysts for the photo-reduction of CO<sub>2</sub> to methane under visible light. He et al. report a good performance in CO<sub>2</sub> photoreduction using the most widely used TiO<sub>2</sub>-based coral-like nanostructures, while Peng et al. developed promising TiO<sub>2</sub> nanocubes decorated with Cu nanoclusters. Moreover, Zhou and co-workers show how smart assembly of a network structure using Bi-containing oxides can also enhance the CO<sub>2</sub> photoreduction activity. Undoubtedly, the continued smart design of nanostructured catalysts composed of semiconductors like TiO<sub>2</sub> or organic compounds, or even hybrid systems with enzymes, will lead to the production of value-added CO<sub>2</sub> reduction products, such as hydrocarbons, at high selectivity.

The development of electrocatalysts for CO<sub>2</sub> reduction has seen most interest within the CO<sub>2</sub> utilization community. Seminal work by Hori in the early 1990s classified the transition metals with respect to their selectivity for different products: methane, ethylene, ethanol, propanol, CO, formate, and hydrogen.<sup>[6]</sup> By 2013 when one of us wrote a perspective on this topic<sup>[7]</sup> only 300 or so publications had appeared on cathodic CO<sub>2</sub> electroreduction, a number that has risen to over 950 by now. Over the years, multiple computational efforts have led to mechanistic insights that explain the activity and selectivity of different electrocatalysts. In this issue, Rossmeisl, Strasser, and coworkers report a computational study on the identification of four intermediates that are key in predicting product selectivity. The role of the electrolyte in electrocatalytic systems is nicely highlighted in the study by Broekmann, Vestzergom, et al. on the effect of water content (and associated changes in diffusivity, conductivity, and proton availability) in ionic-liquid-based electrolytes. One of us (Kenis and coworkers) contributes a story on a strategy for the synthesis of a low-Au-loading catalyst that exhibits high activity for the conversion of CO<sub>2</sub> to CO. Also hybrid systems, such as enzymes immobilized on electrodes in the contribution by Pant et al., are being studied. Despite significant progress—especially with respect to catalysts for CO and formate—catalysts that are selective for the production of methanol, or for C<sub>2</sub> and higher hydrocarbons remain elusive. Moreover, achieving high activity at high energy efficiency remains a challenge. Indeed, it would help if the electrocatalysis community would focus more on improving the anode side, as it is by far the most energetic demanding for the overall CO<sub>2</sub> electrolysis process.

This issue also includes a few reports on materials for CO<sub>2</sub> capture, for example from flue gas to generate the concentrated CO<sub>2</sub> streams required for most CO<sub>2</sub> utilization approaches.

Wang et al. report on the use of polyallylamine and polyethyleneimine functionalized mesoporous silica—so-called molecular basket sorbents—for CO<sub>2</sub> capture. Two other contributions focus on enhancing the stability of existing classes of materials: Xie, Li, and coworkers report on base-stable metal–organic frameworks for CO<sub>2</sub> capture, while Müller et al. describe how CaO-based CO<sub>2</sub> sorbents can be stabilized using metal oxides. Bu et al. analyze the energy requirements of CO<sub>2</sub> mineralization, an approach that has tremendous potential to help reduce anthropogenic CO<sub>2</sub> emissions, where the product is used as construction material for roads and buildings, as mine filling and/or for land reclamation.

**I**ntegration of CO<sub>2</sub> capture with a chemical conversion strategy constitutes a significant area of opportunity. Direct conversion of CO<sub>2</sub> when it has been captured has the potential to drastically enhance the overall energy efficiency because it eliminates the typically energy-intensive CO<sub>2</sub> release step of traditional CO<sub>2</sub>-capture approaches. Wang and Kang report on such an approach: the use of zinc imidazolate functionalized metal–organic frameworks for CO<sub>2</sub> capture, as well as subsequent electrochemical reduction of CO<sub>2</sub> to CO.

**I**n summary, over the last fifteen years, the study of carbon dioxide utilization has grown from almost non-existent to a very vibrant field of research. Researchers have grasped the opportunity to contribute to developing technologies capable of helping to address the biggest global challenge of our lifetime. Progress in some of the approaches to CO<sub>2</sub> utilization has been so rapid that they are now being evaluated for economic viability and scale up. To aid these efforts, the academic community should pay increased attention to the investigation of durability associated with various CO<sub>2</sub> capture and conversion systems. Undoubtedly, other CO<sub>2</sub> utilization approaches also will reach a similar technology readiness level in the next 5–

10 years. Despite this progress and promise, one should not lose sight of the fact that even if one were to synthesize all 250 global commodity chemicals using CO<sub>2</sub> as the feedstock, one would only mitigate approximately 10% of the 4 Gt annual global excess anthropogenic carbon emissions. Carbon dioxide utilization in terms of chemical production will be a necessary strategy (or ‘wedge’<sup>[4]</sup>) in parallel to the implementation of other CO<sub>2</sub>-emission reduction wedges such as transitioning to renewable energy sources, further electrification of the transportation sector, advanced weathering, reforestation, and so on. Of course, if CO<sub>2</sub> utilization would expand to include the production of building materials and transportation fuels, its potential contribution to reducing CO<sub>2</sub> emissions would be dramatically enhanced, but certainly the latter is currently not cost competitive with fuel production from fossil resources. Further progress in some of the catalytic CO<sub>2</sub> utilization approaches described herein with respect to enhancing energy efficiency may change this picture.

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