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VIEWPOINT

CO₂ Catalysis

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Over 90% of commercially available organic chemicals are sourced from crude oil. This is an unsustainable feedstock which will be exhausted at some time in the future. Indeed we may have already reached peak oil production. Biomass has the potential to provide an alternative, sustainable source of organic chemicals, but has issues associated with competing for land use with food production or natural habitat for wildlife and increased pollution caused by use of fertilizers, pesticides etc. Biomass is essentially just carbon dioxide which has been removed from the atmosphere and converted into organic chemicals using sustainable energy in the form of sunlight. Carbon dioxide is potentially the ultimate sustainable source of carbon on planet Earth; in 2014 anthropogenic carbon dioxide emissions were 36 Gt, corresponding to 9.8 Gt of carbon.[1] It is by far the biggest source of waste produced by human activities and Table 1 lists some of the largest point source producers of carbon dioxide to illustrate the scale and purities at which carbon dioxide is produced. The reuse of this waste is essential if we are to successfully transition to a circular economy.

Table 1. Major point sources of CO_2 emissions.[2]

| Source	Global CO_2 emissions (10^6 t CO_2 / year)	CO_2 purity (volume %)
Coal	14,200	12-15
Natural gas	6,320	3-5
Refineries	850	3-13
Cement production	2,000	14-33
Ethylene production	260	12
Iron and steel production	1,000	15
Natural gas production	50	5-70
Ammonia production	150	100

If not captured at source, then carbon dioxide is evenly distributed around the planet (currently at around 400 ppm atmospheric concentration), thus giving security of supply and is freely available to anyone who can make use of it. So then the question arises: can human kind mimic the activity of Nature in utilizing carbon dioxide as a chemical feedstock within chemical plants rather than within farmers' fields? This is the topic of this special issue of *ChemSusChem* which aims to demonstrate that catalysis is a key enabling technology for the valorization of CO_2.

When considering the utilization of carbon dioxide as a chemical feedstock, there are four key aspects to bear in mind:

1. How much CO_2 is directly utilized?
2. How much CO_2 emissions are avoided?
3. How long is the CO_2 sequestered for?
4. Where does the energy and other reactant(s) come from?

The importance of these four points can be illustrated by considering examples of carbon dioxide utilization that have already been commercialized. The chemical synthesis of urea (Scheme 1) is the largest scale chemical process operated by human kind. Around 157 Mt of urea is prepared from carbon dioxide and ammonia each year,[3] directly utilizing 115 Mt of carbon dioxide (point 1). As shown in Scheme 1, the synthesis of urea in this way is a highly exothermic process. However, this disguises the fact that the ammonia needed for urea synthesis is prepared from nitrogen and hydrogen and the hydrogen is obtained by steam reforming of methane (a fossil fuel) in a highly endothermic process (ΔH_r = +247 kJ mol^{-1}) which requires large amounts of (fossil fuel derived) energy and generates large amounts of waste carbon dioxide (point 4). It is some of this carbon dioxide which is utilized for urea production, but even so, as shown in Table 1, ammonia production is a net emitter of 150 Mt of carbon dioxide each year. Finally, virtually all the urea manufactured each year is used as fertilizer. As part of this application, the urea is hydrolysed back to ammonia and carbon dioxide and the carbon dioxide is emitted to the atmosphere. Thus, although it is prepared on a very large scale, urea only sequesters carbon dioxide for a few months between its production and use (point 3).

$$CO_2 + 2NH_3 \xrightarrow{\Delta H_r = -101 \text{ kJmol}^{-1}} H_2N\text{-CO-}NH_2 + H_2O$$
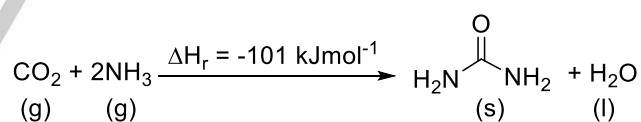
Scheme 1. Synthesis of urea.

The synthesis of salicylic acid from carbon dioxide and phenolates (Scheme 2) is an even older industrial process, dating back to the 19th century.[4] This is still an important process as it is the first step in the industrial synthesis of aspirin, but only about 90 Kt of salicylic acid are prepared this way each year, directly consuming just 29 Kt of carbon dioxide (point 1). Once again, this is an exothermic reaction, but the phenol with which the carbon dioxide is reacted is petrochemically derived (point 4). How long the carbon dioxide is sequestered for depends on how long the aspirin is stored for (by both retailers and consumers) prior to use, but is likely to be on a timescale of months to years (point 3).
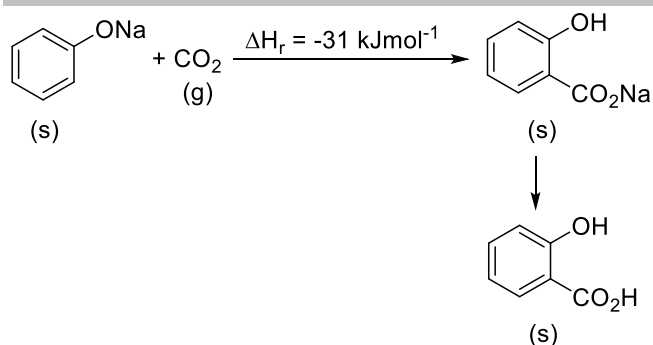
Scheme 2. Synthesis of salicylic acid.

Cyclic carbonates are produced commercially by the reaction between carbon dioxide and epoxides (Scheme 3).[5] This has been a commercial process since the 1950's, though the scale of production has been around just 80 Kt per annum,[3,4] directly utilizing 40 Kt of CO_2 each year. However, the market for cyclic carbonates is experiencing rapid growth as they are the electrolytes used in lithium ion batteries which power all the portable electronic devices which are so essential to modern life. Should electric cars capture a significant share of the transport market, then demand for cyclic carbonates will increase even more substantially (point 1). This is yet another highly exothermic reaction of carbon dioxide, though unlike the synthesis of urea and salicylic acid, cyclic carbonate synthesis does not occur spontaneously and the reaction requires a catalyst. The catalysts currently used commercially are quaternary ammonium salts which have relatively low catalytic activity, and as a result the synthesis of cyclic carbonates has to be carried out at elevated temperatures and pressures. This requires energy (from fossil fuels) and results in the synthesis of cyclic carbonates as currently commercialized being a net emitter rather than consumer of carbon dioxide (0.9 t of CO_2 emitted for every t of cyclic carbonate produced). More active catalysts are, however, available and they allow the synthesis of cyclic carbonates to occur at room temperature and atmospheric pressure which would obviate the need for energy input and the associated carbon dioxide emissions. Thus, commercial adoption of these catalysts would result in a significant reduction in total carbon dioxide emissions associated with the synthesis of cyclic carbonates (point 2).
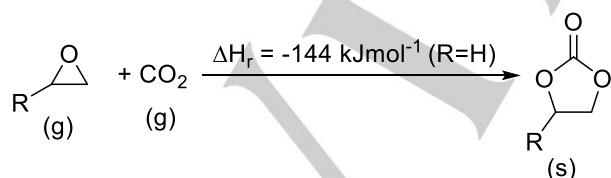

Scheme 3. Synthesis of cyclic carbonates.

Mobile electronic devices have a lifetime measured in years and this is likely to increase to decades for electric cars so cyclic carbonates have the potential to sequester carbon dioxide for much longer than urea or salicylic acid (point 3). The commercially most important cyclic carbonate is ethylene carbonate (R = H in

Scheme 3) and this requires ethylene oxide as a reactant. At present, ethylene oxide is manufactured from crude oil by cracking to ethylene followed by epoxidation. However, in 2016 Croda announced that they were building a plant for the commercial production of ethylene oxide from bioethanol,[6] so in a few years' time it will be possible to manufacture ethylene carbonate in which every atom is sustainably sourced.

Polyurethanes are produced by the reaction between a bis-isocyanate and a polyol. In Bayer's (now Covestro's) implementation of this process, the polyol is a polyether prepared by the polymerization of propylene oxide using an initiator with multiple OH groups (Scheme 4). In their DREAM process, Bayer showed that up to 10% of the propylene oxide within the polyol could be replaced by carbon dioxide giving a polyether-polycarbonate-polyol.[7] At these levels of carbon dioxide incorporation, the physical properties of the resulting polyurethane are essentially unchanged. The global market for polyurethanes is around 18 Mt per year and 10% carbon dioxide in the polyol corresponds to around 4% carbon dioxide in the polyurethane, giving the technology the potential to directly utilize 0.7 Mt of carbon dioxide each year (point 1). Importantly, each carbon dioxide incorporated into the polymer replaces a propylene oxide molecule which no longer needs to be manufactured from crude oil. A life cycle analysis[8] of the DREAM process showed that the carbon dioxide emissions avoided by manufacturing less propylene oxide were far more important than the carbon dioxide directly utilized in this process (point 2). Covestro were due to start production of polyurethane foam prepared by the DREAM process for use in mattresses towards the end of 2016. Mattresses have a lifetime measured in years to decades so the carbon dioxide could be sequestered for a significant period of time (point 3).
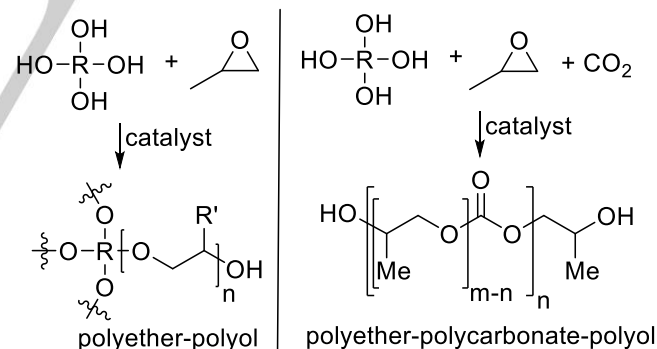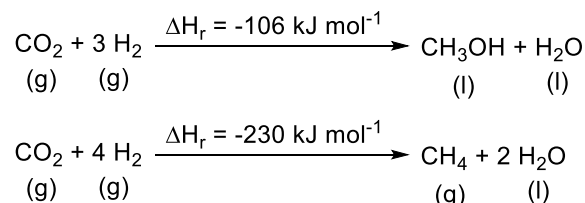

Scheme 4. Synthesis of polyols.

The final application of carbon dioxide to be discussed here is its reduction to methanol or methane for use as fuels (Scheme 5).[9] These processes have almost unlimited potential scale due to their ability to provide drop in replacements for existing liquid and gaseous fossil fuels (point 1). Both are apparently exothermic processes, but large amounts of hydrogen are required and as discussed above for urea production, the production of hydrogen by steam reforming is a highly endothermic process (point 4) and a major emitter of carbon dioxide. Fuels will only sequester carbon dioxide for a very short period of time (days to weeks) after which the fuel will be burnt to release its energy and the carbon dioxide

(point 3). However, by producing the fuel from carbon dioxide, the whole process is potentially carbon neutral and the carbon dioxide emissions associated with burning the corresponding amount of fossil fuel are avoided (point 2).

$$CO_2(g) + 3 H_2(g) \xrightarrow{\Delta H_r = -106 \text{ kJ mol}^{-1}} CH_3OH(l) + H_2O(l)$$

$$CO_2(g) + 4 H_2(g) \xrightarrow{\Delta H_r = -230 \text{ kJ mol}^{-1}} CH_4(g) + 2 H_2O(l)$$

Scheme 5. Synthesis of methanol and methane.

The challenge in converting carbon dioxide to fuel is developing a sustainable source of hydrogen. This will have to be from water and is most directly achieved by electrolysis, though this is a very energy intensive process and under normal circumstances cannot compete with other applications of the electricity. However, Carbon Recycling International has demonstrated commercial methanol production in Iceland for a number of years, using locally available, green geothermal electricity to produce the hydrogen.[10] The technology could be applied elsewhere provided low cost (preferably renewable) electricity is available. One potential application under investigation is to associate such electrolysis facilities with wind farms. When the wind blows at times of low demand for electricity (e.g. at night), the surplus electricity would be used to generate hydrogen for conversion to methane or methanol which can later be used as fuels at times of high demand.

It is often argued that the challenge in carbon dioxide utilization is its high thermodynamic stability and so reactions that involve CO_2 conversion require energy inputs. This editorial so far has focused on commercial applications of carbon dioxide which are exothermic and so illustrate that the challenge is not necessarily the thermodynamic stability of carbon dioxide. Rather, the challenge is that many reactions of carbon dioxide have high activation energies and so require a catalyst to lower the kinetic barrier and allow the reaction to occur under reasonable reaction conditions. It is for this reason that the focus of this special issue is on CO_2 catalysis as a means to valorize this waste material into potential new products, and to improve the efficiency of already existing technologies. The articles contained in this special issue illustrate the breadth of research in carbon dioxide utilization and have been supplied by some of the leading researchers in this area providing either heterogeneous or homogeneous catalysis approaches. It is our hope that they will inform and inspire the broad community working on CO_2 valorization, especially the next generation of scientists for whom developing technology to facilitate a circular economy will be essential to a future sustainable development of human kind.

References

1. https://www.co2.earth/global-co2-emissions
2. 'Carbon Capture' J. Wilcox, Springer, New York, 2012.
3. I. Omae, *Coordination Chem. Rev.* **2012**, *256*, 1384–1405.
4. C. Federsel, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2010**, *49*, 6254–6257.
5. a) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353–1370; b) J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966–1987.
6. http://ethanolproducer.com/articles/12058/croda-to-manufacture-surfactant-from-ethanol-opening-new-market
7. J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner, C. Gürtler, *Green Chem.* **2014**, *16*, 1865–1870.
8. N. von der Assen, A. Bardow, *Green Chem.* **2014**, *16*, 3272–3280.
9. a) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, Etsuko Fujita, *Chem. Rev.* **2015**, *115*, 12936–12973; b) E. Alberico, M. Nielsen, *Chem. Commun.* **2015**, *51*, 6714–6725; c) M. Behrens, *Angew. Chem. Int. Ed.* **2016**, *55*, 14906–14908; d) J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, *RSC Adv.* **2015**, *5*, 22759–22776; e) H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70–88; f) B. Miao, S. S. K. Ma, X. Wang, H. Su, S. H. Chan, *Catal. Sci. Technol.*, **2016**, *6*, 4048–4058; g) M. A. A. Aziz, A. A. Jalil, S. Triwahyono, A. Ahmad, *Green Chem.* **2015**, *17*, 2647–2663; h) M. D. Porosoff, B. Yan, J. G. Chen, *Energy Environ. Sci.* **2016**, *9*, 62–73; i) A. Bansode, A. Urakawa, *J. Catal.* **2014**, 309, 66-70.
10. http://carbonrecycling.is/