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Editorial

Can CO_2 and Renewable Carbon Be Primary Resources for Sustainable Fuels and Chemicals?

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With the increasing global population, the demands for fuels and chemicals are greater than ever. Greenhouse gas (GHG) emissions from the use of fossil fuel-based conventional feedstocks are also a matter of great concern. A revolution is needed to replace the conventional feedstocks, processes, and the materials that enable these processes with more sustainable alternatives such as renewable biomass, recycled carbon, and carbon dioxide (CO_2). In fact, we are at the verge of witnessing a shift from conventional fossil fuel-based petrochemical conversion to more sustainable processes that utilize unconventional feedstocks. Specifically, CO_2 can be viewed as a renewable source of carbon, which can be used as a C1 building block to valuable chemicals.

Replacing petrochemical-based hydrocarbons would require massive sourcing of renewable hydrogen and carbon. Advances are underway in producing so-called "green" hydrogen, as the costs of renewable energy has significantly reduced in recent times. However, major renewable energy sources, such as solar and wind, are distributed with intermittent supply and spatiotemporal variability and uncertainty. Natural gas-based hydrogen generation is mature, but we must remove CO_2 to make it sustainable. Significant scientific and research challenges need to be resolved in the areas of hydrogen generation, separation, storage, and utilization to envision a sustainable future hydrogen economy. On the other hand, CO_2 capture and utilization/storage (CCUS) not only shows great promise for decarbonizing the hydrogen, energy and manufacturing sectors, it allows one to tap into large volumes of CO_2 that are available from stationary/point sources (e.g., fossil power plants, cement, iron and steel, agricultural processing, etc.) and from air via direct air capture. CO_2 capture remains expensive, and the associated parasitic energy penalty remains high. CO_2 is a stable gas that is mostly available as a combustion product after we burn fossil fuels. The energetics of CO_2 utilization is a key challenge. We need novel materials, methods, and multiscale approaches before we envision large-scale implementation of CO_2 as a primary resource for fuels and chemicals. Biomass and recycled plastics can constitute a major portion of a future feedstock portfolio for both hydrogen and carbon toward meeting our increasing demands for hydrocarbons. To that end, the concepts of integrated biorefineries and circular economy require further work in terms of resource utilization, materials development, and process intensification, among others.

To overcome the intrinsic thermodynamic stability of CO_2, a large amount of chemical energy is required. Thermocatalytic CO_2 conversion is a known pathway for CO_2 upgrading and, for the *ACS Sustainable Chemistry & Engineering* (*ACS SCE*) journal, we pay attention to the wording used in the submitted papers. For example, the hydrogenation of CO_2 to methane implies the consumption of H_2, so it should not be presented as a process that allows "upgrading CO_2" on its own but as a reaction that allows "converting a CO_2 + H_2 mixture into methane (and water)". This point is crucial because the large majority of the hydrogen production worldwide is still by steam reforming of natural gas (a large CO_2 emitter). For a net positive utilization of CO_2, the hydrogen must be obtained from renewable resources. Thus, the implementation of any significant development made on the front of catalytic CO_2 hydrogenation will rely on our ability to develop effective, cheap, and sustainable means to produce "green hydrogen". As the GHG potential of methane is much higher than CO_2, one also needs to factor the net sustainability gain when methane is used as a fuel or reagent as part of chemical production.

Another aspect of CO_2 utilization that is often overlooked is the nature of the CO_2 feed. While academic studies are usually carried out on pure CO_2 streams, it should be kept in mind that the CO_2 has to be mined (from gas effluents or possibly directly from air), and then, the solid adsorbent or the liquid absorbent used for capture has to be regenerated to produce a concentrated CO_2 stream. This step is known to be energy consuming. The energy requirement and cost of CO_2 capture vary significantly with the source CO_2 composition, flow rate, required purity of captured CO_2 to meet the pipeline specifications (typically >95%), and extent of separation (i.e., CO_2 recovery).[22] Therefore, CO_2 capture itself is a key challenge toward CO_2-based sustainable feedstocks. This is why efforts are being made to develop combined processes,[1,2] where capture and transformation are being carried out synergistically on nonpure CO_2 streams (ideally targeting the gas effluents of point sources such as incinerators or cement factories). *ACS SCE* welcomes manuscripts that propose an integrated discussion on the transformation of CO_2 and on its sourcing (capture and purification).

The electrification of the chemical industry concept is gaining momentum both academically and industrially.[3] New

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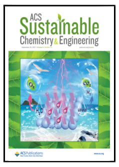

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reaction concepts that use electricity should enable renewable energy sources (e.g., wind and solar) to power chemical transformations and promote sustainability in the chemical industry. A core pillar of this transformation will be the electrochemical conversion of CO_2. Electrochemical CO_2 reduction offers a promising strategy to reduce the atmospheric CO_2 concentration and produce value-added chemicals and fuels at the same time. The reaction environment is friendly with ambient pressure and temperature. The electrochemical CO_2 conversion offers advantages such as benign conditions, controlled reaction conditions via applied potentials and/or currents, and easy coupling with renewable energies such as solar or wind with no extra CO_2 emission. In electrochemical CO_2 conversion processes, the electrocatalyst is key to overcome the high kinetic barriers for CO_2 activation, suppress the competitive reaction (e.g., hydrogen evolution reaction), and increase the selectivity toward the wanted products. Currently, the electrocatalysts used for CO_2 electrolysis can be generally classified into four groups including (i) non-Cu metal materials, (ii) carbon materials, (iii) molecular materials, and (iv) Cu-based catalysts. Electrolyzers for CO_2 conversion to CO and/or formic acid are reaching the pilot scale.[4] More valuable C_{2+} products, such as ethanol, ethylene, and acetate, can only be generated over the Cu-based materials, as well as several heteroatom-doped carbon materials.

Beyond the electrocatalysts, the cell and reactor designs become significant in CO_2 conversion processes. Traditionally, the reaction occurs in a H-type electrochemical cell where the catalyst is fully immersed into electrolytes, while CO_2 gas is generally bubbled into the electrolyte. However, these conventional electrochemical systems suffer from low CO_2 reduction rates, especially with water as the solvent. This is because CO_2 solubility in water at ambient operating pressures is very low (34 mmol/L) and can be increased with pressure only moderately, according to Henry's law. Such low solubilities limit achievable CO_2 reduction rates, regardless of the intrinsic activity of the electrocatalysts used. Thus, process intensification is needed for industrially relevant electrochemical CO_2 conversion.

A variety of strategies are being pursued to alleviate CO_2 starvation at electrode surfaces. One example is gas-diffusion electrode-based flow cells, including a three-electrodes flow cell and membrane electrode assembly, to overcome these limitations and significantly enhance electrocatalytic performance. These vapor-fed systems are ripe for additional research on understanding the complexity of the three-phase boundary and myriad of interfaces on the micrometer and nanometer scales. In addition to vapor-feed systems, organic-based CO_2-rich systems can also provide significant process intensification.[5] Under ambient conditions, CO_2 is close to its critical temperatures, and when it is mildly compressed to few tens of bars at ambient temperatures, its density transitions from a gas-like to liquid-like form. Thus, in its compressed state, the solubilities of CO_2 in most organic solvents increase dramatically, and the volume of the liquid phase expands, resulting in a CO_2-expandedliquid. These CO_2-expanded liquids can also be paired with supporting electrolytes (hence referred to as CO_2-expanded electrolytes) to enable electrochemical CO_2 conversion at multimolar liquid-phase CO_2 concentrations. This provides process intensification, but further work is needed on developing larger-scale flow reactors using condensed CO_2. However, it is anticipated that highly efficient and selective electrocatalysts used together with well-designed flow cells hold great promise for electrochemical CO_2 conversion in the industry in the near future.

As we continue to develop new approaches to utilize unconventional feedstocks for the chemical process industry, we also need to keep in mind the increased competition, stringent environmental regulations, and volatile markets. In recent times, these factors have contributed to renewed interest in process intensification methods to drastically reduce the size, cost, CO_2 emissions, and energy consumption. Process intensification synergistically combines multiple operations, such as separation, conversion, and intermittent storage, within a single piece of equipment. However, it is not trivial to identify the hotspots for process intensification to achieve sustainability goals. Another long-standing problem is to be able to systemically obtain out-of-the-box process solutions (an example is integrated CO_2 capture and conversion[2] with significantly less equipment and energy requirement). To that end, advances are made in computer-aided process intensification techniques. One example is the sustainable process design and intensification technique using the SPICE (synthesis and process intensification of chemical enterprises) framework.[6] SPICE departs from the classic unit operation-based representation of chemical processes and uses a new building block-based representation to achieve a seamless transition from the phenomena scale to the task/equipment scale to the flowsheet scale. SPICE enables "systematic innovation", which is to say that process designers and process engineers now can systematically discover out-of-the-box and optimal design/retrofitting solutions without exhaustively enumerating all plausible alternatives.

Significant progress in the development of homogeneous and heterogeneous catalysts for CO_2 hydrogenation to C1 products (e.g., formic acid, carbon monoxide, methane, and methanol) and C_{2+} products (chemicals containing two or more carbons) has been achieved. CO_2 hydrogenation by homogeneous (molecular) catalysts primarily produces methanol, formic acid/formate, and formamides.[7] Homogenous catalysts featuring phosphine, carbene, pincer, and proton-responsive bidentate ligands coordinated to platinum group metals like Ir, Ru, and Rh are known for CO_2 hydrogenation to formate. For example, an Ir^{III} trihydride pincer complex, [IrH3(PNP)][8] (PNP = 2,6-bis(di-isopropylphosphinomethyl)-pyridine, has the highest activity in CO_2 hydrogenation to formate at 3,500,000 turnover numbers (TON) and 150,000 h^{-1} turnover frequency (TOF). Another Ru^{II} pincer complex [RuH(Cl)(CO)(PNP′)][9] (PNP′ = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) has remarkable performance at TOF of 1,100,000 h^{-1} in an environmentally friendly solvent—aqueous media. The structure of pincer ligands impart high stability to the catalyst leading to high activities; notably, in some bifunctional systems, the metal and ligand work cooperatively, resulting in improved activities.[10] However, high operating temperatures and pressures (≥120 °C and 40 bar) mean an undesirable energy-intensive process from a scale-up viewpoint. A prominent class of CO_2 hydrogenation homogeneous catalysts are the half-sandwich Ir, Rh, and Ru complexes bearing bidentate N,N ligands with proton-responsive groups. The Ir version achieves a high activity in basic aqueous solution, at just 50 °C (TON = 153,000, pH 8.4). This system also converts CO_2 to formate at 25 °C and atmospheric pressure, albeit at low productivity (32 h^{-1}).[11] Even though some of these systems operate efficiently in aqueous media, the use of milder operating conditions (ambient temperature and pressure are ideal), elimination of additives such as bases and acids, and recyclable catalysts are important for achieving sustainability.

CO_2 to MeOH is most efficient when alcohols or amines are used first to convert CO_2 to formamides, alkyl formates, or carbamates, which are further reduced to obtain methanol. Generally, homogeneous catalysts are not as highly active in hydrogenation beyond the process leading to formate; however, some Ru^{II} complexes exhibit activity in amine-assisted methanol synthesis from CO_2[12] and in direct CO_2 conversion to methanol.[13] Further catalyst development is required, particularly those that exhibit high activity at mild operating conditions and are derived from abundant sources or waste metals recovered from mine tailings or e-waste. The quest to develop efficient and inexpensive catalysts based on earth-abundant metals has led to several catalysts, including Fe, Mn, Co, and Cu, with promising activities in CO_2 hydrogenation to formate, methanol, and formamides.[14,15] Some catalysts show greater activities than known noble metal catalytic systems.[16] Although several catalytic systems show high activity, further development of highly active catalytic systems into chemical processes is less explored. If the main goal is to create innovative homogeneous catalytic hydrogenation systems that might lead to practical schemes for recycling CO_2, efforts should also be directed toward process design such as in the following examples: (1) the continuous-flow hydrogenation of supercritical CO_2 to produce pure formic acid in a single process that incorporates easy separation of the solvent, product, and catalyst[17] and (2) the synthesis of formamides in a miniplant scale catalyzed by a Ru pincer complex.

The hydrogenation of CO_2 into CO, CH_4, CH_3OH, dimethyl ether, olefins, aromatics, hydrocarbons, and higher alcohols has been extensively studied in the field of heterogeneous catalysis. Numerous catalysts based on metals, oxides, and their alloys, such as Cu, Ru, Rh, Pt, Pd, Au, Ir, Co, Fe, Ni, Re, and In, have been developed for the CO_2 hydrogenation reaction, especially targeting higher activity and selectivity. CO_2 conversion is limited by the thermodynamics, but the product selectivity can be fine-tuned by catalyst design to avoid the thermodynamically most stable product methane[18] and by chosen operating conditions, such as low temperature and high pressure to increase methanol yield under supercritical flow conditions.[19] The classical methanol synthesis (from CO/H_2) catalysts, based on $Cu/ZnO/Al_2O_3$, have also been investigated and improved for the direct hydrogenation of CO_2 to methanol, while a remarkably productive process for the synthesis of methanol was achieved at high pressure and by increasing the H_2/CO_2 feed ratio.[20] Combined with zeolites, one-step integrated processes for the CO_2 conversion into dimethyl ether and other liquid products are achievable. Several studies have not only addressed the catalysts and process-technical aspects but also provide insightful views on the reaction thermodynamics, mechanism, and kinetics from theoretical studies. The literature is vast, but development of efficient catalysts to break the thermodynamic barriers of CO_2 hydrogenation reaction continues to be of extreme importance.

Lastly, as we continue to develop new catalysts, solvents, adsorbents, membranes, and other materials toward utilizing CO_2 and renewable or recycled carbon as primary feedstocks for sustainable future, we foresee new challenges in terms of operability, safety, controllability, flexibility, resilience, and system integration of new processes and plant configurations that will use these materials.[21] Process system engineering methods and tools will play important roles in balancing the trade-offs between various economic, environmental, and sustainability goals. Specifically, we need to be cognizant about the variability, uncertainty, and spatiotemporal distribution associated with CO_2 sources. The selection of appropriate CCUS materials, processes, and technologies will largely depend on the CO_2 source compositions and flow rates and the distances between sources and utilization sites.[22] Synergistic integration of renewables and flexible carbon capture with individual fossil power plants will need to be considered. Furthermore, just focusing on converting CO_2 to chemicals will not be economically sustainable in the long term, since the large volume of available CO_2 is likely to saturate the chemical market quickly. A more sustainable pathway would involve combining CO_2 with renewable hydrogen toward producing alternatives to liquid transportation fuels and plastics. Overall, a holistic approach with a systems perspective will be necessary to determine the optimal pathways following informed decisions through systematic technoeconomic and life cycle analysis (TEA and LCA). Model-based and computer-aided multiscale design, simulation, and optimization of molecules, processes, and supply chains will be useful, all in conjunction with experimental synthesis and scale up.

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Notes

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