Accelerating CO_2 Conversion through Microdroplet Chemistry

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Standfirst | When scaled down to the nano- or micrometer range, microdroplets feature a high surface-to-volume ratio and exhibit properties such as strong interfacial effects, electric fields, acidic environments, radical generation, and enhanced reducing power. These features accelerate reaction rates and enable otherwise unfavorable CO_2 conversion reactions under mild conditions.

Main text

The conversion of CO_2 into fuels and chemicals is a key strategy in global carbon mitigation efforts. Microdroplet chemistry can enhance this process by accelerating CO_2 conversion reaction rates and enabling new reactions.[1] Chemical reactions can occur up to a million times faster in microdroplets than in bulk solutions.[2] This phenomenon is attributed to several factors, including increased surface area-to-volume ratio, rapid mixing, and the presence of unique interfacial effects and an unusual physicochemical environment.[3] This area of study has implications in various scientific disciplines, including organic synthesis, analytical chemistry, environmental science, materials science, and biomedical applications.[3] The large-scale industrial application of microdroplet technology is currently limited by its small-scale production capacity. However, it holds significant potential as an efficient tool in industrial processes for reaction screening, enabling the discovery of new reactions and the optimization of catalysts and conditions.[4] Its ability to accelerate reaction rates, minimize reagent consumption, and explore new chemical pathways highlights its promise for broader industrial adoption.[3,4] Here, we will explore the role of microdroplets in CO_2 conversion and provide insights into their potential as a future clean technology, Figure 1.

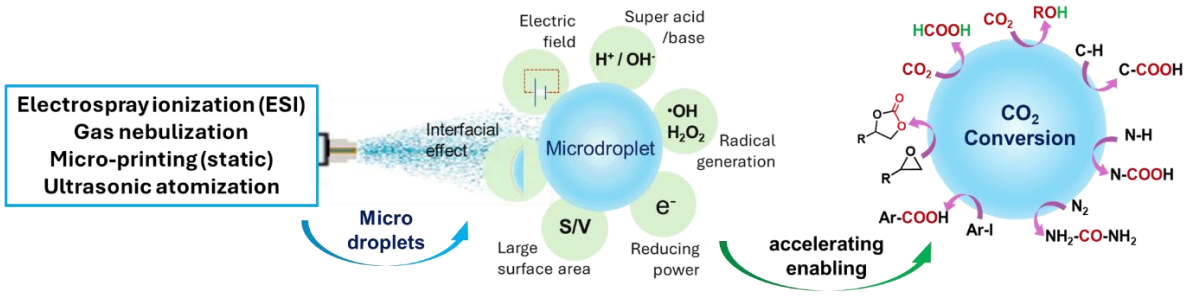

Figure 1. Microdroplets can be produced using a variety of methods. With a high surface-to-volume ratio, microdroplets exhibit properties of strong interfacial effects, electric fields, acidic

environments, radical generation, and enhanced reducing power, which substantially accelerate and facilitate various CO_2 to chemicals reactions.

Microdroplets formation

Microdroplets for chemical reaction are typically generated through pressure atomization, pneumatic atomization, ultrasonic atomization and electrospray atomization.[3] Microdroplets generated under various approaches have common characteristics, such as high surface area, partial solvation at the surface, ordered molecular orientation, reagent confinement, and pH alteration that create an extensive interfacial region where distinct catalytic and reactive species can form, markedly enhancing reaction rates. Electrospray microdroplets can have a strong electric field at the surface, generate radicals, additional reducing power which can alter reaction mechanisms and impact the thermodynamics of redox reactions, often leading to faster reaction rates and the formation of products that are not typically observed in bulk-phase reactions.

CO_2 reduction in water

Benefits on its reducing environment, microdroplet can facility CO_2 reduction under very mild conditions.[3] Room-temperature N_2 gas nebulized water microdroplets with a 1,2,3-triazole (Tz) catalyst can directly convert CO_2 gas in formic acid,[5] whereas microdroplets generated by directly spraying a water solution containing a Cu(II) catalyst into the air can substantially enhance CO_2 to formate conversion, with a reaction rate up to 4000 times higher.[6] These enhancements are attributed to the larger gas−liquid contact surface area and strong electric field at or near the microdroplet interfaces.

Similarly, in a photocatalytic static microdroplet system, CO_2 conversion rate is two orders of magnitude higher than in the corresponding bulk phase reaction.[7] The yields of HCOOH produced using hydrated WO_3 in microdroplets reached 2536 μmol/h·g compared to just 13 μmol/h·g in the bulk reaction. The strong electric field at the gas-liquid interface of microdroplets enhances the separation of photogenerated electron-hole pairs, thereby accelerating the reaction.

Direct carboxylation

Direct C-H activation and coupling with CO_2 is a sought-after reaction for converting CO_2 into valuable chemicals and fuels that can occur at room temperature within an electrospray ionization microdroplet environment.[8,9] Negatively charged water microdroplets facilitate the generation of hydroxyl radicals at the water-gas interface, which initiates the formation of organic radicals (α-carbon of ketones and iodopentafluorobenzene) and coupling with CO_2 to form carboxylic acids. These findings demonstrate a pathway for converting CO_2 into valuable carboxylate organic products that can be applied, for example, in the pharmaceutical industry.

The synthesis of cyclic carbonates from CO_2 has also been validated in microdroplet environment that favoured a cycloaddition reaction of CO_2 and epoxides by improving gas-liquid mass transfer.[4] The reaction has been demonstrated at pilot scale (400 g of total mass) with 5% decrease in reaction conversion efficiency, and further simulation of industrial-scale (1350 g of total mass) reactor efficiency showed a 17% decrease in conversion rate compared

to the lab-scale (50 g of total mass). This indicates the feasibility of microdroplet reactors in industrial applications.

Carbon-nitrogen bond formation

Microdroplet technology can also enable a one-step synthesis of urea from CO_2 and N_2 at room temperature, using a $CuBi_2O_4$ mesh as heterogeneous catalyst.[10] These microdroplets pass through catalyst mesh and produce urea within 0.1 milliseconds without any external voltage. The water microdroplets act as both the hydrogen source and electron transfer medium for the N_2 and CO_2 interacting with $CuBi_2O_4$ to facilitate the multiple steps reaction: N_2 absorption, $N{\equiv}N$ bond cleavage, nitrogen hydrogenation, and C−N bond formation. This approach enables the synthesis of urea by coupling N_2 fixation with CO_2 utilization. However, catalyst efficiency and stability as well as process scalability issues need to be addressed.

Microdroplets can also accelerate reactions between amines and CO_2 to form carbamic acid, which could benefit common carbon fixation processes, including those used in industrial CO_2 scrubbing systems.[1]

The need for scaling and standardization

In summary, microdroplets could be highly effective tools for converting CO_2 into fuels and fine chemicals. Their small volume and unique properties not only accelerate reaction rates and reduce reagent consumption but also facilitate the rapid discovery of novel compounds and synthetic pathways. However, fully understanding the fundamental mechanisms driving accelerated CO_2 conversions in microdroplets remains a challenge. The overall mass and energy balances of most microdroplet-promoted reactions are still not well understood. Moreover, translating microdroplet chemistry to large scales, developing standardized methods and protocols for microdroplet experiments is essential for ensuring reproducibility and broader application. Continued research and technological advancements, especially long lasting or continuous microdroplet system, will further enhance our understanding and utilization of microdroplet processes, opening new avenues for innovation in CO_2 utilization and across various scientific disciplines.

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Competing interests

The authors declare no competing interests