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CO2绿色转化

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全球工业化水平的持续提升加速了煤、石油、天然气等化石燃料的消耗,大量二氧化碳(CO₂)被排放进大气,导致全球变暖和生态失衡,削减 CO₂ 排放、将 CO₂ 资源化成为亟需解决的问题。2010 年前后,美国、欧洲、日本相继开启以"人工光合成"为题的国家级科研项目,投入经费均在 1 亿美元以上。2011 年起,我国国家自然科学基金委、科技部相继资助了相关项目。2020 年 9 月,我国政府进一步提出力争在 2030 年前实现"碳达峰"、2060 年前实现"碳中和"的目标。

绿色植物或部分微生物通过"光合作用"将 CO_2 和 H_2O 转化为有机物,而通过催化剂在光能驱动下将 CO_2 与 H_2O/H_2 转化为燃料或化工原料,正是模拟了自然界的"光合作用",被称为"人工光合成"。当然, CO_2 的转化并不局限于太阳能驱动,利用非化石燃料产生的电能(如太阳能、风能、水能等)高效率驱动电催化、热催化 CO_2 还原也是可行途径之一。目前,基础研究的热点是光催化、光热催化以及电催化 CO_2 还原,这类具有能耗低、环境负荷小、反应效率高等至少一个特点的技术途径均属于" CO_2 绿色转化"的范畴,在未来工业化应用中具有较强的竞争力。

近年来,有关 CO₂转化的研究突飞猛进,但是仍面临一些关键性问题亟待解决。光催化途径利用最为温和的方式(常温、常压)将 CO₂转化为燃料或者化工原料,但是在反应效率和稳定性等方面还面临着巨大挑战。光热催化途径于2014年被报道之后,引起了广泛关注,它利用金属纳米粒子或窄带隙半导体材料进行光能到热能的转换进而驱动热催化反应。相比光催化,光热催化 CO₂还原的效率和稳定性得到显著提升,但是需要消耗氢气(H₂)提供氢源,应用中会造成生产成本上升。相比前两种方式,电催化 CO₂还原也比较温和,其能量利用效率最高,但是由于其反应环境为水溶液,CO₂还原与质子还原的竞争不可避免,提升产物的选择性面临瓶颈,液相或者气相产物的分离在一定程度上会增加生产成本。CO₂转化的经济性还需要考虑产物的附加值,光催化、电催化的产物主要集中在 C1 产物(主要包括一氧化碳、甲烷、甲醇、甲酸盐等),也有少数研究报道能够产出乙烷。光热催化途径则较有优势,以 CO₂和 H₂为原料的费托合成可以生成 C2~C7产物。可见,各种技术途径各具优势,但又面临不同的科学或技术困难,在未来应用中可能互为补充,在不同应用领域各展所长。

尽管 CO_2 转化的研究取得了长足进步,但是仍面临较多的挑战。在我国提出"碳达峰"、"碳中和"的目标后不久,《无机材料学报》编辑部即着手策划" CO_2 绿色转化"专栏。期待我国更多的科研工作者能够投入这项研究并加强合作,推动其从基础研究快速步入应用研究,并最终实现工业应用,使我国由碳排放大国转变为 CO_2 资源化利用的强国!



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Green Conversion of CO₂

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With the continuous progress of global industrialization, fossil fuels have been over-consumed, which results in a large amount of CO₂ discharged into the atmosphere and therefore causes negative effects such as global warming and ecological imbalance. Reducing CO₂ emissions and converting recycled CO₂ to value added chemicals have become important tasks. Around 2010, led by the United States of America, followed by Europe and Japan, tens of countries started their national scientific research projects entitled "artificial photosynthesis", with an investment as much as 100 million USDs. Since 2011, China has also funded similar projects by the National Natural Science Foundation of China and the Ministry of Science and Technology. In September of 2020, the Chinese government even put forward the goal of "carbon emission peak" by 2030 and "carbon neutrality" by 2060.

Green plants or microorganisms make organics from CO₂ and H₂O through "photosynthesis". The photocatalysts can convert CO₂ and H₂O/H₂ into fuels or chemicals under light irradiation, which simulates the natural "photosynthesis" and is entitled as "artificial photosynthesis". Nevertheless, the conversion of CO₂ is not limited to be driven by solar energy; alternatively, the electricity generated by non-fossil fuels to drive efficient electrocatalytic or thermocatalytic CO₂ reduction is also a feasible way. At present, the hot spots in basic research are photocatalysis, photothermocatalysis and electrocatalysis for CO₂ reduction. "Green conversion of CO₂" defines the technological approaches with at least one of the features of low energy consumption, low environmental load and high efficiency, which enables them competitive in future industrial applications.

In recent years, the study on CO₂ conversion has made rapid progresses, but some key problems are still to be solved. Photocatalysis provides the mildest way to convert CO2 into fuels or chemicals, which means the lowest cost in the future application, but currently faces great challenge in efficiency and stability. Not until photothermocatalytic CO₂ reduction was reported in 2014, it has attracted extensive attention. The catalysts realize light-to-thermal conversion and subsequently drive thermocatalysis. Compared with photocatalysis, the efficiency and stability of photothermocatalytic CO₂ reduction are significantly increased, but the consumption of H₂ as feedstock will result in additional cost. Electrocatalytic CO2 reduction is also a mild process, and its energy utilization efficiency is the highest among the three methods. However, due to the reaction environment of aqueous solution, there inevitably occurs the competition of CO₂ reduction and proton reduction; therefore, the improvement of product selectivity is still faced with a bottleneck. Moreover, the separation of liquid or gas phase products somewhat increases production cost. Importantly, the economy of CO₂ conversion should take account of the yield of value-added product. The products of photocatalysis and electrocatalysis mainly concentrated in C1 chemicals (mainly including carbon monoxide, methane, methanol, formic acid salt, etc.), and a few studies reported the production of ethane. However, the photothermocatalysis exhibits superior advantage in this aspect; for instance, the Fischer-Tropsch synthesis with CO₂ and H₂ as feedstocks to produce C2-C7 products has been reported. Each technological approach has its own advantages but faces different scientific or technical difficulties, which may complement each other and show its strengths in different application fields in the future.

Shortly after China put forward the goal of "carbon emission peak" and "carbon neutrality", the editorial board of *Journal of Inorganic Materials* organizes the special issue on "Green Conversion of CO₂". Although the investigation on CO₂ conversion has made great progress, but still faces various challenges. Looking forward to that more researchers devote to this study to promote it from the basic research to the industrial application, our continuous effort will make our country reverse the disadvantage of terrible carbon emission to the advantage of converting recycled CO₂ to resources effectively.