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Editorial

Valorization of Carbon Dioxide through Molecular Catalysis

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In times of shortage of resources and climate modification, chemistry can deliver solutions and counteract our today's challenges. Global warming, caused by increasing emissions of greenhouse gases such as carbon dioxide (CO_2), methane and others, has been recognized as a serious environmental problem. A possible solution is the reduction of CO_2 emissions, mainly through the reformulation of the processes for energy production from carbonaceous resources. Another option is the CO_2 utilization as a renewable resource, i.e. the reuse of existing CO_2 as a source of carbon for producing chemicals. Nowadays, the utilization of CO_2 as a new feedstock for commodity and specialty chemicals is intensively discussed. The advantages in the development of reliable methods to fixate and activate the CO_2 molecule are mainly two : 1- the alleviation of climate modifications caused in part by increasing CO_2 emissions; 2- the progressive substitution of the current limited carbon resources (coal, petroleum, and natural gas) into CO_2. Carbon dioxide is a renewable C1-feedstock; it is environmentally friendly and easily available from decomposition of organic matter or artificially. The concept behind its utilization is the following: the direct energy supply via combustion of fossil energy carriers produces CO_2, which can be converted back into the energy carrier, thereby leading to an artificial carbon cycle. The result would be double : the recycling of CO_2 and the balancing of the anthropogenic emission into the atmosphere. However, the chemistry of CO_2 shows relevant limitations, due the chemical inertness of CO_2 : a systematic use of CO_2 would only be possible if the CO_2 molecule could be catalytically activated. For this reason, the scientific community is dedicating a crescent number of study projects to the resolution of the problem with the aim to develop effective catalytic species for the valorization of CO_2 as well as of other renewable carbon feedstock, such as natural gas and biomasses (starch, lignin, and cellulose).

The classic heterogeneous catalysis fails to convert CO_2 at mild conditions, which is the principal limiting factor for a large-scale plant activity. On the other hand, homogeneous catalysis operates at milder conditions. In terms of energy balance, catalytic performance, reusability, and scale-up perspectives, the most promising transformations of CO_2 in C_1 or higher chemicals with molecular catalysts are : 1- the reduction to CO; 2- the hydrogenation with H_2 to methanol; 3- the formation of carbonates and polycarbonates. The reduction reactions, although particularly attractive, are not efficient enough and involve hydrogen, an expensive reactant. On the other hand, the synthesis of carbonates and polycarbonates via CO_2 and epoxides is an established procedure supported by the utilization of high-performance metal catalysts. In the field of the molecular catalysts, metal-free catalytic species find a progressively important position. Although they were not so common and explored, the application of metal-free catalysis – i.e., organocatalysts and Lewis pairs based catalysts – would easily out compete metal catalysts in price, stability, and remarkably, green accessibility since heavy metal waste or complicated recovery would be avoided. In the last years, many efforts were produced to define effective routes for the conversion of CO_2 to usable starting materials for further transformations utilizing metal-free catalysts but the accomplishments have been below a feasible real-world day-to-day process to date. Reliable results in development of eco-friendly species for applications in the aforementioned field will strongly contribute in solving urgent problems concerning energy and sustainability themes.

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