CHEMICAL REVIEWS

Review

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Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment

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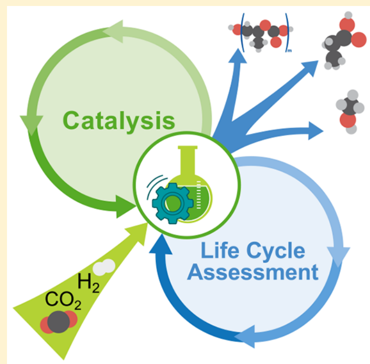
ABSTRACT: CO_2 conversion covers a wide range of possible application areas from fuels to bulk and commodity chemicals and even to specialty products with biological activity such as pharmaceuticals. In the present review, we discuss selected examples in these areas in a combined analysis of the state-of-the-art of synthetic methodologies and processes with their life cycle assessment. Thereby, we attempted to assess the potential to reduce the environmental footprint in these application fields relative to the current petrochemical value chain. This analysis and discussion differs significantly from a viewpoint on CO_2 utilization as a measure for global CO_2 mitigation. Whereas the latter focuses on reducing the end-of-pipe problem "CO_2 emissions" from todays' industries, the approach taken here tries to identify opportunities by exploiting a novel feedstock that avoids the utilization of fossil resource in transition toward more sustainable future production. Thus, the motivation to develop CO_2-based chemistry does not depend primarily on the *absolute* amount of CO_2 emissions that can be remediated by a single technology. Rather, CO_2-based chemistry is stimulated by the significance of the *relative* improvement in carbon balance and other critical factors defining the environmental impact of chemical production in all relevant sectors in accord with the principles of green chemistry.



CONTENTS

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1. INTRODUCTION

1.1. Challenges and Opportunities

The molecular transformation of carbon dioxide (CO_2) into value-added products has fascinated chemists ever since the advent of the area of catalysis. The "Sabatier reaction" converts a mixture of CO_2 and H_2 into methane, and its discovery has been pivotal in the development of the principle of catalysis in its modern understanding. The genuine challenge of "activating" a small and relatively unreactive molecule has stimulated the curiosity and creativity of generations of scientists. In particular, the ingenious and remarkably complex mechanism of nature's capability to build up enormous amounts of carbon-based materials in very short periods of time solely on the basis of CO_2, water, and sunlight is still humbling the prodigious progress of modern synthetic chemistry. While capitalizing on this natural process indirectly through the exploitation of fossil resources forms today the basis of our global energy system and material value chains, only very few chemical processes utilizing CO_2 as feedstock are of industrial relevance. Nonetheless, the utilization of CO_2 in the synthesis of urea from ammonia cannot be overestimated in its importance, both in market volume and in societal impact: With over 100 Mt/a capacity, urea production is among the largest processes synthesizing a carbon-containing product, and it is a vital component to provide nutrition for an ever-growing population by valorizing nitrogen for soil fertilization.

In recent years, the interest in catalytic conversion of CO_2 has experienced a very dynamic growth.[1−17] This increase results at least partly from scientific insight into the problems arising from continuous and ever-increasing emissions of CO_2 as waste material from fossil-based energy systems. Obviously, the exploitation of a waste stream of one sector as feedstock for the value chain of another industry can be economically and ecologically attractive, contributing to the concept of a circular economy.[18,19] In fact, this is how industrial organic chemistry started by valorizing coal tar as a cheap and abundant carbon source resulting from energy production in the 19th century. With CO_2, the perception is different, however. The discussion often solely takes the perspective of the fossil-based energy sector by focusing on "CO_2 mitigation" rather than looking at the opportunities for the chemical industry provided by "CO_2 utilization". Thus, both terminologies, "CO_2 mitigation" and "CO_2 utilization", are frequently—but wrongly—used interchangeably or even as synonyms.

The aim to reduce carbon dioxide emissions directly by converting CO_2 into chemicals or fuels has motivated a number of analyses on the potential amounts of CO_2 to be captured.[20,21] Such a perspective is motivated by searching for solutions to quantitatively reduce carbon dioxide emissions of the fossil-based energy system. Given the different scales of the energy sector and the material value chain, it should go without saying that the production of CO_2-based organic chemicals cannot provide a quantitative "sink" for carbon dioxide to reduce substantially the enormous CO_2 emissions from fossil power generation. Producing liquid fuels for transportation requires much more carbon and could therefore demand significant amounts of CO_2. However, the combustion of the fuel generates the equivalent amount of carbon dioxide and therefore does not lead to a direct net "consumption" of CO_2. *But even if CO_2 conversion cannot provide a silver bullet to solve the CO_2 mitigation problem, there are still very good reasons why CO_2 conversion will play an important role in moving toward a sustainable future.*

(1) CO_2 conversion for a less carbon-intensive and more benign chemical industry.

The focus on the global challenge of CO_2 mitigation is important, but it should not prevent us from identifying the potential benefit of CO_2 utilization for the chemical value chain. From this viewpoint, the question to be asked is as follows:

Can the use of CO_2 as feedstock reduce the carbon footprint and environmental impact of chemical production?

The efforts to minimize the carbon footprint of the petrochemical industry via process optimization and intensification are reaching ever-higher maturity, already approaching in certain cases saturation. Alternative feedstocks such as CO_2 (or biomass[22,23]) come into view to open new doors for disruptive changes. Hereby, the contribution of CO_2 conversion could be realized by two distinct approaches: First, CO_2 can be funneled into the existing treelike structure of the chemical industry at different positions via certain key components such as carbon monoxide, methanol, etc. Second, novel synthetic routes can be opened using a different combination of starting materials and reagents whereby CO_2 serves as a C_1 building block. In both cases, potential benefits from using CO_2 can go significantly beyond the reduction of global warming impact by addressing other important environmental impacts such as reducing fossil resource depletion or providing access to more benign production pathways.

(2) CO_2 conversion for the production of synthetic fuels.

The above analysis is very useful for the chemical sector, wherein the individual molecular structures define their use and lifetime. This is different for transportation fuels, where the

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