

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

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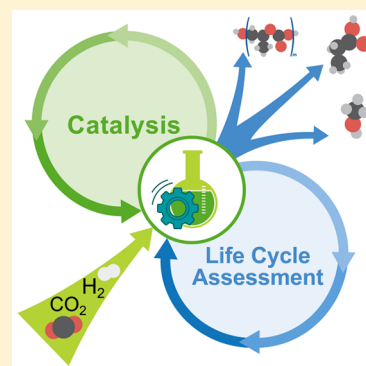
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**ABSTRACT:** CO<sub>2</sub> conversion covers a wide range of possible application areas from fuels to bulk and commodity chemicals and even to specialty products with biological activity such as pharmaceuticals. In the present review, we discuss 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<sub>2</sub> utilization as a measure for global CO<sub>2</sub> mitigation. Whereas the latter focuses on reducing the end-of-pipe problem “CO<sub>2</sub> emissions” from today’s 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<sub>2</sub>-based chemistry does not depend primarily on the *absolute* amount of CO<sub>2</sub> emissions that can be remediated by a single technology. Rather, CO<sub>2</sub>-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

|                                                                                                             |     |
|-------------------------------------------------------------------------------------------------------------|-----|
| 1. Introduction                                                                                             | 435 |
| 1.1. Challenges and Opportunities                                                                           | 435 |
| 1.2. Life Cycle for CO <sub>2</sub> -Based Products and Life Cycle Assessment Method Used                   | 436 |
| 2. Carbon Dioxide as a Building Block for Chemical Structures                                               | 439 |
| 2.1. Organic Carbonates                                                                                     | 439 |
| 2.1.1. Dimethyl Carbonate                                                                                   | 439 |
| 2.1.2. CO <sub>2</sub> -Based Routes to Polycarbonates                                                      | 443 |
| 2.2. Synthesis Gas                                                                                          | 446 |
| 2.2.1. Background and Motivation                                                                            | 446 |
| 2.2.2. Current Status of CO <sub>2</sub> Conversion to Synthesis Gas                                        | 447 |
| 2.2.3. Life Cycle Assessment of CO <sub>2</sub> Conversion to Synthesis Gas                                 | 449 |
| 2.2.4. Further Trends and Research Topics: Catalyst Design, Robust Processes, and Alternative Energy Inputs | 450 |
| 2.2.5. Coelectrolysis                                                                                       | 453 |

|                                                                |     |
|----------------------------------------------------------------|-----|
| 2.3. Carboxylic Acids and Carboxylation Reactions              | 454 |
| 2.3.1. Formic Acid                                             | 454 |
| 2.3.2. Carboxylation Reactions                                 | 459 |
| 2.4. Methanol and Methylation Reactions                        | 462 |
| 2.4.1. Methanol                                                | 462 |
| 2.4.2. Methylation Reactions                                   | 468 |
| 3. Carbon Dioxide as an Energy Vector for Transportation Fuels | 469 |
| 3.1. Addressing Global Warming Impacts and Local Emissions     | 469 |
| 3.2. Methane                                                   | 470 |
| 3.2.1. Background and Motivation                               | 470 |
| 3.2.2. Current Status of CO <sub>2</sub> Conversion to Methane | 470 |

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|                                                                                                                       |     |
|-----------------------------------------------------------------------------------------------------------------------|-----|
| 3.2.3. Life Cycle Assessment of CO <sub>2</sub> Conversion to Methane                                                 | 471 |
| 3.2.4. Further Trends and Research Topics: Highly Dynamic Processes and Catalysts                                     | 472 |
| 3.3. Fischer–Tropsch Products                                                                                         | 473 |
| 3.3.1. Background and Motivation                                                                                      | 473 |
| 3.3.2. Current Status of CO <sub>2</sub> Conversion to Fischer–Tropsch Products                                       | 474 |
| 3.3.3. Life Cycle Assessment of CO <sub>2</sub> Conversion to Fischer–Tropsch Products                                | 474 |
| 3.3.4. Further Trends and Research Topics: Processes and Catalysts for Dynamic Operation and Decentralized Production | 475 |
| 3.4. Oxygenates                                                                                                       | 477 |
| 3.4.1. Background and Motivation                                                                                      | 477 |
| 3.4.2. Current Status of CO <sub>2</sub> Conversion to Oxygenates                                                     | 477 |
| 3.4.3. Life Cycle Assessment of CO <sub>2</sub> Conversion to Oxygenates                                              | 478 |
| 3.4.4. Further Trends and Research Topics: Adopting the Fuel Design Process to CO <sub>2</sub> -Based Oxygenates      | 480 |
| 4. Conclusions and Future Perspectives                                                                                | 483 |
| Author Information                                                                                                    | 484 |
| Corresponding Authors                                                                                                 | 484 |
| ORCID                                                                                                                 | 484 |
| Notes                                                                                                                 | 484 |
| Biographies                                                                                                           | 484 |
| Acknowledgments                                                                                                       | 485 |
| References                                                                                                            | 485 |

## 1. INTRODUCTION

### 1.1. Challenges and Opportunities

The molecular transformation of carbon dioxide (CO<sub>2</sub>) into value-added products has fascinated chemists ever since the advent of the area of catalysis. The “Sabatier reaction” converts a mixture of CO<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> as feedstock are of industrial relevance. Nonetheless, the utilization of CO<sub>2</sub> 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<sub>2</sub> has experienced a very dynamic growth.<sup>1–17</sup> This increase results at least partly from scientific insight into the problems

arising from continuous and ever-increasing emissions of CO<sub>2</sub> 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.<sup>18,19</sup> 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<sub>2</sub>, the perception is different, however. The discussion often solely takes the perspective of the fossil-based energy sector by focusing on “CO<sub>2</sub> mitigation” rather than looking at the opportunities for the chemical industry provided by “CO<sub>2</sub> utilization”. Thus, both terminologies, “CO<sub>2</sub> mitigation” and “CO<sub>2</sub> utilization”, are frequently—but wrongly—used interchangeably or even as synonyms.

The aim to reduce carbon dioxide emissions directly by converting CO<sub>2</sub> into chemicals or fuels has motivated a number of analyses on the potential amounts of CO<sub>2</sub> to be captured.<sup>20,21</sup> 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<sub>2</sub>-based organic chemicals cannot provide a quantitative “sink” for carbon dioxide to reduce substantially the enormous CO<sub>2</sub> emissions from fossil power generation. Producing liquid fuels for transportation requires much more carbon and could therefore demand significant amounts of CO<sub>2</sub>. 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<sub>2</sub>. *But even if CO<sub>2</sub> conversion cannot provide a silver bullet to solve the CO<sub>2</sub> mitigation problem, there are still very good reasons why CO<sub>2</sub> conversion will play an important role in moving toward a sustainable future.*

(1) CO<sub>2</sub> conversion for a less carbon-intensive and more benign chemical industry.

The focus on the global challenge of CO<sub>2</sub> mitigation is important, but it should not prevent us from identifying the potential benefit of CO<sub>2</sub> utilization for the chemical value chain. From this viewpoint, the question to be asked is as follows:

*Can the use of CO<sub>2</sub> 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<sub>2</sub> (or biomass<sup>22,23</sup>) come into view to open new doors for disruptive changes. Hereby, the contribution of CO<sub>2</sub> conversion could be realized by two distinct approaches: First, CO<sub>2</sub> 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<sub>2</sub> serves as a C<sub>1</sub> building block. In both cases, potential benefits from using CO<sub>2</sub> 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<sub>2</sub> 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

point of reference is not a given molecular structure, but the function of the fuel to provide effective and clean propulsion. This function could be fulfilled by a wide range of possible molecular fuel components, and shifting the raw material and energy input from fossil to renewable expands the molecular diversity even further. This new degree of freedom of “fuel design” should be optimized such that the overall well-to-wheel environmental footprint associated with the propulsion efficacy as the function is served best.<sup>24</sup> Consequently, the question to be asked here would be as follows:

*Can CO<sub>2</sub> serve effectively as an energy vector to harvest renewable electricity into the mobility and transportation sector?*

Again, two scenarios may be distinguished: First, CO<sub>2</sub> and renewable hydrogen can be utilized to produce hydrocarbons that are largely identical to today's pool of fuels (gasoline, diesel, or liquefied natural gas, LNG). Second, the opportunity to produce novel molecular structures can lead to advanced fuels, allowing combination of reductions in global warming impact with improvements in other highly relevant impact categories such as local pollutant emission.

In the present review, we address the above two questions regarding the potential role of CO<sub>2</sub> conversion for a sustainable development in an interdisciplinary approach between chemistry and systems engineering from a life cycle perspective. The perspective and methodology of life cycle assessment for CO<sub>2</sub> conversion are briefly introduced and reviewed in [section 1.2](#). In [section 2](#), we focus on the conversion of carbon dioxide to chemicals, while addressing the production of fuels in [section 3](#). Since the present review is aimed at taking the viewpoint of sustainability of CO<sub>2</sub> conversion, we focused in the review on processes and reaction types for which a life cycle assessment study has been conducted and connected it to chemically related transformations of CO<sub>2</sub>. In each subsection, we briefly recall the molecular basis of the synthetic process of today's industry and discuss the possible CO<sub>2</sub>-based alternatives. We then review and analyze the currently available life cycle assessments (LCAs) for the CO<sub>2</sub>-based processes. Reflecting the scope of these studies, the focus of the analyses is on the global warming impact. However, other potential benefits are also discussed where appropriate. Attempts are made to derive lessons learned from the available LCAs for future research efforts in catalysis, and recent trends and achievements for the chemically related conversions are highlighted. Vice versa, this approach may help to identify research topics and assessment criteria for future LCA studies to analyze potential incentives and obstacles for sustainable CO<sub>2</sub> conversion pathways.

## 1.2. Life Cycle for CO<sub>2</sub>-Based Products and Life Cycle Assessment Method Used

The chemical utilization of the greenhouse gas CO<sub>2</sub> seems intuitively positive for the environment.<sup>11,17,25–29</sup> However, environmental benefits from CO<sub>2</sub> conversion cannot be taken for granted: Transformation of the thermodynamically stable and kinetically inert CO<sub>2</sub> molecule usually requires some form of energy, and the generation of this energy will in turn also be associated with CO<sub>2</sub> emissions.<sup>30</sup> There are CO<sub>2</sub>-based products which are thermodynamically more stable than CO<sub>2</sub>, such as inorganic carbonates obtained from mineralization.<sup>31,32</sup> In principle, these products could thus avoid the need for additional energy. These products are therefore currently studied for potential applications, e.g., in the building sector,<sup>33,34</sup> but they are beyond the scope of the present paper. In the present review, we focus on CO<sub>2</sub>-based chemicals

and fuels, which all require some form of energy inputs since they have a higher Gibbs enthalpy of formation than CO<sub>2</sub>. This also means that they are typically reconverted to CO<sub>2</sub> at their end-of-life.

To account for all processes along the life cycle of a product, the method of life cycle assessment (LCA) has been established and standardized by the International Standards Organisation (ISO) in the ISO norms 14040<sup>35</sup> and 14044.<sup>36</sup> LCA collects all mass and energy flows exchanged with the environment over the life cycle of a product and determines their potential environmental impacts. Thereby, life cycle assessment avoids shifting environmental impacts between different stages of production and application and between different environmental impacts. According to ISO,<sup>35,36</sup> an LCA study is performed in four phases:

- (1) Goal and scope definition, where the intended use of the LCA study is specified and used to decide (a) the implementation of the LCA methodology regarding the products considered and/or compared, (b) the functional unit which serves as a reference to compare LCA results and quantifies the functions of a product, (c) the system boundary, (d) the level of detail, and (e) the environmental impact categories taken into account.
- (2) Inventory analysis, where input/output data are collected.
- (3) Impact assessment, where the inventory data are related to the potential significance regarding environmental impacts.
- (4) Interpretation, where the results are discussed and reviewed.

[Figure 1](#) illustrates the LCA approach for CO<sub>2</sub>-based products. The life cycle comprises the entire value chain from

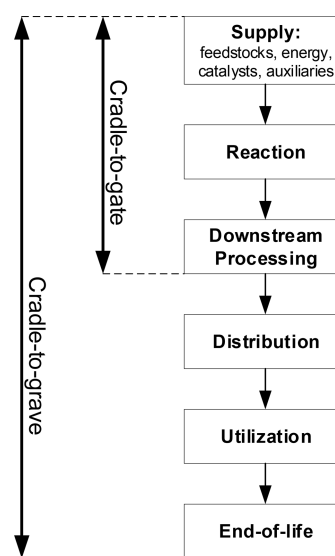


**Figure 1.** Life cycle stages of CO<sub>2</sub>-based products with scope shown for cradle-to-gate and cradle-to-grave assessments.

upstream supply processes for feedstocks, energy, catalysts, and further auxiliaries to the reaction step itself and the following downstream processing to obtain the final product at the factory gate, which is then distributed, used, and finally reaches its end-of-life.

While the present review is focused on the actual chemical transformation of CO<sub>2</sub>, we want to emphasize that there are

Table 1. Scenarios 2020 and Best Case for the Global Warming Impact of Upstream Processes for CO<sub>2</sub>-Based Products Used in This Review

|                        | scenario 2020                              |                                                         | scenario best case                                                  |                                                       |
|------------------------|--------------------------------------------|---------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------|
|                        | process                                    | GW                                                      | process                                                             | GW                                                    |
| CO <sub>2</sub> supply | capture from coal power plant <sup>a</sup> | −0.83 kg of CO <sub>2</sub> equiv/kg of CO <sub>2</sub> | use of already purified but emitted CO <sub>2</sub>                 | −1 kg of CO <sub>2</sub> equiv/kg of CO <sub>2</sub>  |
| H <sub>2</sub> supply  | steam methane reforming <sup>b</sup>       | 10.6 kg of CO <sub>2</sub> equiv/kg of H <sub>2</sub>   | electrolysis with wind, 50 (kW h)/kg of H <sub>2</sub> <sup>c</sup> | 0.43 kg of CO <sub>2</sub> equiv/kg of H <sub>2</sub> |
| NG supply              | EU-27 supply mix <sup>b</sup>              | 0.011 kg of CO <sub>2</sub> equiv/MJ                    | EU-27 supply mix <sup>b</sup>                                       | 0.011 kg of CO <sub>2</sub> equiv/MJ                  |
| heat supply            | natural gas boiler <sup>b</sup>            | 0.071 kg of CO <sub>2</sub> equiv/MJ                    | power to heat ( $\eta = 95\%$ ) <sup>d</sup>                        | 0.0025 kg of CO <sub>2</sub> equiv/MJ                 |
| electricity supply     | EU-27 grid mix <sup>b</sup>                | 0.371 kg of CO <sub>2</sub> equiv/(kW h)                | EU-27 wind <sup>b</sup>                                             | 0.0088 kg of CO <sub>2</sub> equiv/(kW h)             |

<sup>a</sup>von der Assen et al.<sup>58</sup> <sup>b</sup>GaBi LCA database.<sup>65</sup> <sup>c</sup>Götz et al.<sup>66</sup> <sup>d</sup>Ling et al.<sup>67</sup>

manifold additional opportunities for chemistry to make an impact along the full life cycle of CO<sub>2</sub>-based products:

- In the *supply* stage: e.g., the development of novel materials for CO<sub>2</sub> capture,<sup>37–40</sup> efficient catalysts for hydrogen production.<sup>41–43</sup>
- In the *downstream processing* stage: e.g., the development of green solvents.<sup>44,45</sup>
- In the *distribution* stage: e.g., novel additives to improve flows in pipelines,<sup>46</sup> coating for pipelines.<sup>47,48</sup>
- In the *utilization* stage: e.g., reducing the energy demand in the use phase of products (e.g., by low rolling resistance tires), novel fuel combustion additives.<sup>49,50</sup>
- At the *end-of-life*: e.g., after treatment for combustions processes (e.g., NO<sub>x</sub>),<sup>51,52</sup> recycling technologies.<sup>53,54</sup>

If the conversion of CO<sub>2</sub> yields a molecular structure identical to that yielded by a conventional fossil-based production process, the performance of the product and its application are entirely described by the molecular structure, and the corresponding functional unit for LCA is “1 kg of chemical”. LCA studies can thus focus on the comparison of the two production pathways. The life cycles are compared on a cradle-to-gate basis (cf. Figure 1) where all life cycle stages after the factory gate are neglected since they are identical for the conventional fossil-based and CO<sub>2</sub>-based products. This scope is applied to the chemicals studied in section 2 of this review.

If transportation fuels are produced from CO<sub>2</sub>, their molecular structures may differ from those of the conventional fossil-based process yet still fulfill the same function in the use stage. In a first approximation, one may assume that all fuels are used such that their functionality is reflected by their lower heating value (LHV). Thus, the corresponding functional unit employed in this review is “1 MJ (LHV)”. To include the use phase, the system boundaries consequently span from cradle-to-grave (cf. Figure 1). This scope is applied to the fuels studied in section 3.

A key driver for CO<sub>2</sub> chemistry is the reduction of the global warming impact. Thus, an LCA study of CO<sub>2</sub> conversion should include the environmental impact category related to global warming. Related data are available in all current LCA studies on CO<sub>2</sub> conversion. This environmental impact category has different names in the literature, such as climate change, carbon footprint, or global warming impact. In this review, we will use the term global warming impact (GWI). The GWI is obtained by multiplying all emissions along the life cycle by their global warming potential (GWP). The GWP is usually measured in “kilograms of CO<sub>2</sub> equivalents” and quantifies the radiative forcing induced by an emission of a substance relative to the radiative forcing induced by 1 kg of

CO<sub>2</sub>. The radiative forcing is integrated over a time horizon of interest, typically chosen as 100 years,<sup>55</sup> which therefore serves as the time horizon in this review. While this time frame is widely applied, it is recommended to report results also for shorter periods such as 20 years to resolve potential temporal trade-offs.<sup>56</sup> Values for the global warming potential have been provided for different time horizons by the Intergovernmental Panel on Climate Change (IPCC).<sup>57</sup>

The choice to quantify climate change impacts in terms of “CO<sub>2</sub> equivalents” has led to some confusion regarding carbon accounting in CO<sub>2</sub> conversion processes. In particular, the feedstock CO<sub>2</sub> has often been treated as negative greenhouse gas (GHG) emission, and the use of 1 kg of CO<sub>2</sub> has been fully deduced from the overall global warming impact. Most CO<sub>2</sub> conversion processes require purified CO<sub>2</sub> streams, however, and the energy requirement for purification needs to be taken into account for the carbon feedstock CO<sub>2</sub>. Proper accounting often requires making methodological choices in LCA since the CO<sub>2</sub> source is usually intended to generate other products (e.g., electricity, steel, concrete, ammonia, ethylene oxide, and others). The resulting methodological choices are potentially ambiguous, but can be avoided by a system-wide perspective including both the CO<sub>2</sub> conversion process and the CO<sub>2</sub> source (for more details see ref 30). Global warming impacts for the feedstock CO<sub>2</sub> have been reported for a wide variety of CO<sub>2</sub> sources.<sup>58,59</sup> The global warming impacts correlate strongly with the purity of the CO<sub>2</sub> source, indicating that highly concentrated and easily separable streams are preferred, including, for example, concrete production, chemical processes, and biogas units. Very dilute sources such as air require large amounts of energy for separation, resulting in lower reductions of global warming impacts.

From a climate change perspective, temporary storage of carbon over the life cycle of a CO<sub>2</sub>-based product<sup>11,60</sup> may be valuable for delaying climate change. However, conventional life cycle assessment does not account for temporary storage,<sup>61</sup> and there is an intensive discussion in the community of whether (and, if yes, how) it should be incorporated. Time-corrected global warming potentials have been proposed for this purpose.<sup>55,61</sup> Due to the open discussion in the literature, current standards recommend reporting the amount and duration of carbon stored as a separate piece of information.<sup>62,63</sup> For the scope of the present review, such information is not required. For the chemicals discussed in section 2, the storage period is excluded since cradle-to-gate analysis assumes identical gate-to-grave emissions for CO<sub>2</sub>-based and fossil-based production. In simple terms, if the same chemical is produced, the same amount of carbon would be stored for the same time.

Scheme 1. Reaction Sequence and Interconversions of Organic Carbonates Exemplified for the Production of Bisphenol A-Based Polycarbonate (R = H, Me)<sup>81,82</sup>

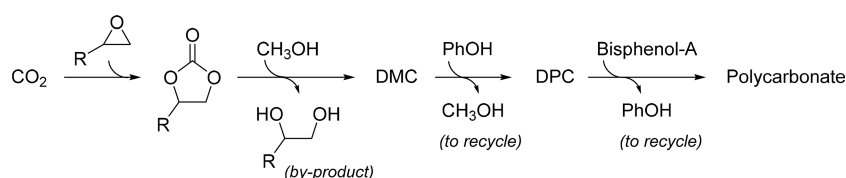


Table 2. Current Production Routes to Dimethyl Carbonate from Various Carbonylation Agents and Extension of the Process Concept to the Use of CO<sub>2</sub> as Starting Material<sup>b</sup>

| Route | Co-reagent(s)                                                                                                    | Carbonylation agent                                                                                                   | By-product                                                                 | Process concept                   |
|-------|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|-----------------------------------|
| 1     | None                                                                                                             | CO <sub>2</sub>                                                                                                       | + 2 CH <sub>3</sub> OH<br>DMC + H <sub>2</sub> O                           | Direct route                      |
| 2a    | CO <sub>2</sub> + H <sub>2</sub> → CO - H <sub>2</sub> O                                                         | CO + Cl <sub>2</sub> → COCl <sub>2</sub>                                                                              | + 2 CH <sub>3</sub> OH<br>DMC + 2 HCl (to recycle <sup>a</sup> )           | CO shift, phosgene, Bayer process |
| 2b    | CO <sub>2</sub> + H <sub>2</sub> → CO - H <sub>2</sub> O                                                         | + 1/2 O <sub>2</sub><br>+ 2 CH <sub>3</sub> OH                                                                        | DMC + H <sub>2</sub> O                                                     | CO shift, Eni process             |
| 2c    | CO <sub>2</sub> + H <sub>2</sub> → CO - H <sub>2</sub> O                                                         | 2 CH <sub>3</sub> OH<br>↓ + N <sub>2</sub> O <sub>3</sub> / - H <sub>2</sub> O<br>+ 2 CH <sub>3</sub> NO <sub>2</sub> | DMC + 2 NO (to recycle)                                                    | CO shift, Ube process             |
| 3     | CO <sub>2</sub> + R-substituted epoxide                                                                          | R-substituted cyclic carbonate                                                                                        | + 2 CH <sub>3</sub> OH<br>DMC + R-substituted ethylene glycol (by-product) | Cyclic carbonate, Asahi process   |
| 4a    | CO <sub>2</sub> + 2 NH <sub>3</sub> → H <sub>2</sub> N-C(=O)-NH <sub>2</sub> - H <sub>2</sub> O                  | + 2 CH <sub>3</sub> OH                                                                                                | DMC + 2 NH <sub>3</sub> (to recycle)                                       | Trans-esterification of urea      |
| 4b    | CO <sub>2</sub> + 2 RNH <sub>2</sub> → RHN-C(=O)-O <sup>-</sup> RNH <sub>3</sub> <sup>+</sup> - H <sub>2</sub> O | + 2 CH <sub>3</sub> OH                                                                                                | DMC + 2 RNH <sub>2</sub> (to recycle) + H <sub>2</sub> O                   | Electro-chemical energy input     |

<sup>a</sup>Hydrogen chloride is conventionally recycled to chlorine by electrolysis (−H<sub>2</sub>) or via the Deacon process over a ruthenium catalyst (+1/2O<sub>2</sub>, −H<sub>2</sub>O). <sup>b</sup>The water-removal step is highlighted in bold.

For the application of fuels discussed in section 3, the storage period is usually very short and is thus neglected.

This short discussion already highlights that methodological choices are left open by the ISO standards for the life cycle assessment of CO<sub>2</sub> conversion processes. Currently, a common and accepted framework for LCA of CO<sub>2</sub> conversion is still

lacking.<sup>64</sup> Consequently, the available LCA results on CO<sub>2</sub> conversion analyzed in this review were found to show significant variations for the same chemical product and even for the same routes. These variations are mainly due to differences in assumptions regarding the supply of feedstocks such as CO<sub>2</sub> itself or hydrogen and electricity, the system

boundaries, and the allocation of coproducts. Process data uncertainty is in particular a major issue for processes at early stages of development. The uncertainties resulting from all these assumptions need to be quantified and reported in addition to uncertainties in the used data sets.

In the present review, we therefore tried to harmonize the available LCA studies as much as possible. For this purpose, we define two reference scenarios for the most common upstream processes (Table 1). Both scenarios are based on average data for the European Union (EU-27). In the scenario 2020, only the electricity supply includes renewable sources. For the supply of materials, the fossil-based processes are considered that lead to the lowest global warming impacts. Thus, hydrogen is supplied by steam methane reforming and not by electrolysis using grid electricity. The CO<sub>2</sub> source is based on flue-gas capture from a coal-fired power plant. In the “best case” scenario, we assume the utilization of wind electricity for both heat supply and hydrogen supply by electrolysis. Furthermore, we assume the utilization of a CO<sub>2</sub> stream that is already sufficiently purified for CO<sub>2</sub> conversion. Thus, no energy for purification is required. For both scenarios, the global warming impacts are determined according to the characterization method ReCiPe (H) midpoint indicator.

## 2. CARBON DIOXIDE AS A BUILDING BLOCK FOR CHEMICAL STRUCTURES

### 2.1. Organic Carbonates

The functional group ROC(O)OR' is a key constituent of organic products comprising molecules with one carbonate unit and polycarbonates with numerous carbonate moieties. Important representatives with one carbonate unit are dimethyl carbonate, diphenyl carbonate, and cyclic carbonates. Polycarbonates are defined by a polymer backbone with repetition units of carbonate groups interspaced either solely with aliphatic moieties or with chemical entities comprising aromatic moieties. The molecular weight can be in the oligomer or polymer range, defining very different application areas. For aliphatic polycarbonates, it is therefore convenient to differentiate low to medium molecular weight oligomers with functional groups at the termini of the polymer chains from high molecular weight materials. Aromatic polycarbonates find their main application field as high molecular weight polymeric material. Presently available life cycle assessments cover the use of CO<sub>2</sub> for manufacture of dimethyl carbonate and low molecular weight aliphatic polycarbonate polyols with terminal hydroxyl groups. Thus, we will focus here on these products and closely related structure types.

**2.1.1. Dimethyl Carbonate.** *2.1.1.1. Background and Motivation.* Dimethyl carbonate is currently produced on a 90 kt/a scale mostly by phosgenation or oxidative carbonylation of methanol.<sup>68</sup> The market was estimated to be \$440 million by the end of 2016 and is expected to grow rapidly parallel to an increasing production volume.<sup>69</sup> Dimethyl carbonate has manifold potential applications in the chemical and electronics industry as well as the fuel sector.<sup>70</sup> At present, the main consumption is the captive use for the production of polycarbonates (~46 kt/a, ca. 50% of the world production).<sup>70</sup> A synthetic application is the use as a methylation agent.<sup>71–75</sup> Dimethyl carbonate is used also as a solvent in paints, coatings, and inks and as an electrolyte in lithium ion batteries (~23 kt/a, ca. 25% of the world production). Due to the high oxygen

content (53 wt %), dimethyl carbonate is also considered as a fuel additive to reduce emissions.<sup>76</sup>

Diphenyl carbonate is produced currently on a 250 kt/a scale mostly by phosgenation of phenol or transesterification of dimethyl carbonate.<sup>77</sup> Diphenyl carbonate is a key intermediate in the production of aromatic polycarbonates (Scheme 1). A new CO<sub>2</sub>-based process to produce diphenyl carbonate was recently developed by Shell.<sup>78</sup> Here, CO<sub>2</sub> is reacted with phenol using propylene oxide as a water scavenger. Propylene glycol is obtained as a byproduct. In 2011, a 500 t/a demonstration unit was opened at Singapore's petrochemical hub on Jurong Island.<sup>79,80</sup>

As for the production of dimethyl carbonate and diphenyl carbonate, there is a large captive use for cyclic carbonates in the production of aromatic polycarbonates (Scheme 1). Cyclic carbonates also find manifold applications as chemical intermediates and solvents and as a high-permittivity component of electrolytes in lithium ion batteries. Ethylene carbonate is used as a precursor to vinylene carbonate, another intermediate in polymer production, and as a plasticizer. The synthesis of cyclic carbonates is a very prolific research area also in terms of catalyst development, process options, and product diversity.<sup>83–88</sup>

**2.1.1.2. Current Status of CO<sub>2</sub> Conversion to Dimethyl Carbonate.** The utilization of CO<sub>2</sub> for introducing the carbonate group into dimethyl carbonate has received great attention for many years. Different process concepts can be envisioned (Table 2). The direct synthesis of dimethyl carbonate from CO<sub>2</sub> and methanol (route 1) suffers from equilibrium limitations. Consequently, various carbonylation agents are in use, or considered, for introducing the carbonyl group. Conceptually, many of the carbonylation agents can be derived from CO<sub>2</sub>, which places these routes also into the context of the current CO<sub>2</sub> conversion concepts. Most prominently, carbon monoxide can be considered a CO<sub>2</sub>-derived feedstock as discussed in section 2.2.

The direct conversion of CO<sub>2</sub> and methanol to dimethyl carbonate (route 1, Table 2) has been studied intensively.<sup>89,90</sup> The reaction is performed typically at 160–180 °C and 90–300 bar. Equilibrium limitations restrict the conversion to 1–5%.<sup>91</sup> Formally, the reaction involves the removal of a water molecule by condensation. Attempts to overcome the equilibrium limitations focus on the selective removal of water from the system.<sup>92</sup> To drive the reaction to completion, microwave irradiation and photochemical and electrochemical energy input have also been considered.<sup>93</sup> The mixture of dimethyl carbonate and methanol creates an azeotrope, which is broken by use of water or aniline as an entrainer.<sup>68</sup> Water is more benign, while aniline is the most effective known entrainer for the dimethyl carbonate–methanol azeotrope. Due to the significant energy demand of the separation train and large recycle streams, the direct synthesis of dimethyl carbonate is currently not an option for the commercial production of dimethyl carbonate.

The use of carbon monoxide is at the base of several alternative process routes (routes 2a–2c, Table 2), for which pilot plants have been built, or which are currently exploited for dimethyl carbonate production.<sup>68,73,76,94,95</sup> The carbon monoxide is currently supplied from fossil resources, but could be obtained potentially from CO<sub>2</sub>, when an adequate supply of renewable energy is available (section 2.2). Considering CO<sub>2</sub> as the starting material, two water molecules have to be removed as a byproduct. Reducing the oxidation state of the carbon

Table 3. Overview of LCA Studies for Dimethyl Carbonate

| reference                           | route | global warming impact <sup>a</sup> (kg of CO <sub>2</sub> equiv/<br>kg of dimethyl carbonate) | system<br>boundary | life cycle inventory/background data                          | assessment<br>method      |
|-------------------------------------|-------|-----------------------------------------------------------------------------------------------|--------------------|---------------------------------------------------------------|---------------------------|
| Aresta and Galatola <sup>112</sup>  | 2a    | 116.00                                                                                        | cradle-to-gate     | not reported                                                  | CML 2001                  |
| Monteiro et al. <sup>95</sup>       | 4a    | 29.45                                                                                         | cradle-to-gate     | WAR database <sup>115</sup>                                   | Cetesb <sup>b</sup>       |
|                                     | 3     | 0.86                                                                                          |                    |                                                               |                           |
|                                     | 4a    | 0.34                                                                                          |                    |                                                               |                           |
| Souza et al. <sup>114</sup>         | 3     | 0.77                                                                                          | gate-to-gate       | WAR database <sup>115</sup>                                   | EPAA <sup>c</sup>         |
| Kongpanna et al. <sup>113</sup>     | 2b    | 0.52                                                                                          | gate-to-gate       | thermal energy from stoichiometric CH <sub>4</sub> combustion | literature <sup>116</sup> |
|                                     | 3     | 0.45                                                                                          | gate-to-gate       |                                                               | CEQR-NY <sup>d</sup>      |
|                                     | 4a    | 2.93                                                                                          |                    |                                                               | US-EPA <sup>e</sup>       |
|                                     | 4a    | 2.93                                                                                          |                    |                                                               | IPCC <sup>f</sup>         |
| Garcia-Herrero et al. <sup>88</sup> | 2b    | 3.18                                                                                          | cradle-to-gate     | Ecoinvent                                                     | CML 2001                  |
|                                     | 4b    | 78.90                                                                                         |                    |                                                               |                           |

<sup>a</sup>Averaged values are used if more than one process design was assessed. <sup>b</sup>Companhia Ambiental do Estado de São Paulo (a Brazilian environmental agency). <sup>c</sup>Environmental Protection Authority of Australia. <sup>d</sup>City Environmental Quality Review of the City of New York. <sup>e</sup>U.S. Environmental Protection Agency. <sup>f</sup>Intergovernmental Panel on Climate Change.

center from IV in CO<sub>2</sub> to II in CO eliminates half of this water. Depending on the process route, the other half is then removed in the following CO conversion in the same way as in the conventional processes, i.e., in the recycle stream during conversion of HCl to the phosgene CO carrier (route 2a, Bayer process), from the product mixture during oxidative carbonylation (route 2b, Eni process), or from methanol during the formation of nitromethane (route 2c, Ube process).

In the phosgenation route to dimethyl carbonate, phosgene is produced by reacting carbon monoxide with chlorine. At a relatively low temperature of −5 to +30 °C, phosgene (COCl<sub>2</sub>) is then reacted with methanol. The phosgene route is progressively phased out and replaced by the oxidative carbonylation route. The phase out is motivated by the high energy demand associated with phosgene production as well as legislative restrictions imposed due to the toxicity of phosgene.<sup>68</sup> These negative aspects of phosgene-based dimethyl carbonate production go in parallel with high environmental impacts (see the discussion of life cycle assessment in the next section (section 2.1.1.3)).

In the Eni process, dimethyl carbonate is produced by oxidative carbonylation of methanol using oxygen as the oxidant. The reaction is performed typically at 70–200 °C and 5–60 bar. Conventionally, the process is based on the use of a reactor with a fixed catalyst bed. Supported transition-metal chlorides, such as CuCl, catalyze the reaction. Migration of copper and irreversible loss of chloride lead to catalyst deactivation. To alleviate this effect, the conversion per pass is normally limited to less than 20%.<sup>76</sup> The Eni route accounts for 85% of the current dimethyl carbonate production in Europe. Versalis/Lummus have developed a corresponding liquid-phase process.<sup>96</sup> Compared to the gas-phase process, higher space time yields can be achieved. This advantage is offset by higher operating pressures, more severe equipment corrosion, and a more elaborate product separation sequence.

In the Ube process, nitrogen oxides are used as the oxidant to convert methanol to nitromethane, which is then reacted with CO to dimethyl carbonate. The reaction is typically performed at 50–150 °C and up to 10 bar. Compared to the Eni process, a smaller reactor volume is required.<sup>76</sup> No equilibrium limitations are encountered, and the reaction is operated at close to

complete conversion. This route accounts for 11% of the current dimethyl carbonate production in Europe.<sup>97</sup>

Route 3 (Table 2) is based on the idea that in an upstream step a cyclic carbonate is produced by reacting CO<sub>2</sub> with the corresponding epoxide. This process was commercialized for the production of cyclic carbonate as long ago as 1950 by Huntsman Corp. The reaction is performed conventionally in the presence of ammonium halide-based catalysts. Novel aluminum complexes as catalysts enable the reaction to be performed under milder conditions.<sup>98</sup> In early 2000, dimethyl carbonate production by transesterification of ethylene carbonate (route 3, Table 2, R = H) was commercialized by Asahi.<sup>82,99</sup> The reaction is performed at 100–180 °C and 40–60 bar. Texaco has established a comparable process based on propylene carbonate (route 3, Table 2, R = Me).<sup>76</sup> Considering the overall process concept, the epoxide is used to capture the water and thereby converted to the corresponding glycol as a byproduct. The chemically bound energy in the epoxide essentially drives the reaction.<sup>11,26</sup>

Various basic metal oxide catalysts, including MgO, CaO, ZnO, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, are suitable for route 3.<sup>100</sup> Among the catalysts examined, MgO was found to be the most active and selective catalyst. Both reaction steps can be integrated in a one-pot synthesis at the expense of a lower selectivity as alcoholysis of the epoxide occurs as a side reaction. The oxidative carbonylation of less reactive polyols, generated readily from biobased feedstock, provides an alternative access to cyclic carbonates for subsequent transesterification with methanol according to route 3.<sup>101,102</sup>

The two process concepts 4a and 4b (Table 2) are based on the use of an amine in generating the carbonylation agent *prior* to carbonate formation. Route 4a involves urea as the reactive intermediate. Urea has been produced for nearly a century by reaction of CO<sub>2</sub> with ammonia mostly for use as a fertilizer.<sup>26</sup> In the context of CO<sub>2</sub> conversion, the transesterification of urea to dimethyl carbonate (DMC) is being explored.<sup>94,95,103,104</sup> Fixing the diol to an ionic liquid in the two-step transesterification of urea via the intermediate cyclic carbonate to DMC has been proposed to alleviate equilibrium limitations.<sup>105</sup> Suitable catalysts for the transesterification of urea comprise certain metal oxides.<sup>106,107</sup> The reaction is performed at 170–

200 °C and 1–30 bar. For process intensification, the reaction has been performed in a reactive rectification column.<sup>108</sup> At present, the process technology is being evaluated for commercial use by CDT Ltd., a Sumitomo Chemical Group Co.

The use of ethanolamine to capture CO<sub>2</sub> followed by conversion of the intermediate carbamate salt with methanol to dimethyl carbonate (route 4b, Table 2) has also been suggested, but is currently at a much lower technology readiness level.<sup>109</sup> The conversion of the intermediate carbamate salt to dimethyl carbonate is performed in the presence of a base (MeOK) and an ionic liquid ([BMIM]Br). Note that such ionic liquids are known as efficient catalysts in carbonate formation.<sup>92</sup> Electrochemical energy input is used to drive the reaction. Current electrochemical cells for the synthesis of dimethyl carbonate from CO<sub>2</sub> and methanol are limited to 0.7–0.9% conversion.<sup>110,111</sup> Consequently, large-volume streams are encountered to recycle unreacted methanol.

**2.1.1.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Dimethyl Carbonate.** Currently, five LCA studies have investigated the environmental impacts of CO<sub>2</sub>-based production routes for dimethyl carbonate (Table 3). Two LCA studies have analyzed the conventional chemical routes from carbon monoxide: the phosgene-based route<sup>112</sup> (route 2a in Table 2) and the oxidative carbonylation route<sup>68,113</sup> (route 2b). Conceptually, these routes can be extended to CO<sub>2</sub> as the starting material. Also the transesterification of ethylene carbonate derived from ethylene oxide and CO<sub>2</sub><sup>95,113,114</sup> (route 3), the urea transesterification<sup>95,112,113</sup> (route 4a), and the electrochemical conversion of CO<sub>2</sub> and methanol<sup>68</sup> (route 4b) have been analyzed. To the authors' knowledge, no LCA study has been reported yet for the direct synthesis route of converting CO<sub>2</sub> and methanol to dimethyl carbonate (route 1).

All LCA studies assessed the global warming impact. In addition, two studies<sup>68,112</sup> reported the acidification potential, the ozone depletion potential, the photochemical oxidant creation potential, and the eutrophication potential. The obtained results for these impact categories show the same trend as for the global warming impact. Thus, only the global warming impact is discussed in detail below.

The global warming impact for oxidative carbonylation (route 2b) reported by Garcia-Herrero et al.<sup>68</sup> equals 3.18 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate. Raw material production contributes 1.42 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate. Waste treatment and energy supply correspond to 0.13 and 1.63 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate, respectively. For the same route 2b, gate-to-gate global warming impacts were calculated also by Kongpanna et al.<sup>113</sup> These authors report a value of 0.52 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate. In comparison, the global warming impact for the overall energy supply reported by Garcia-Herrero et al.<sup>68</sup> is more than 3 times higher. The divergence probably results from differences in the process and reaction designs. However, no inventory data have been reported for the cradle-to-gate systems,<sup>68</sup> and the primary data source is no longer accessible. Thus, the reason for the large difference cannot be resolved.

Three LCA studies were devoted to transesterification of ethylene carbonate (route 3).<sup>95,113,114</sup> Two studies<sup>113,114</sup> focused on the global warming impact of gate-to-gate systems; i.e., they only took into account the global warming impact associated with the heat supply. The reported global warming impacts vary between 0.45 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate<sup>113</sup> and 0.77 kg of CO<sub>2</sub> equiv/kg of dimethyl

carbonate.<sup>114</sup> The difference originates from diverging background LCA data for heat supply and a difference of total heat supply. In particular, a higher methanol to dimethyl carbonate ratio increases the separation effort and thus results in higher global warming impacts.<sup>114</sup>

A cradle-to-gate study for transesterification of ethylene carbonate reported a global warming impact of 0.86 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate.<sup>95</sup> The value is slightly higher than the value reported by Souza et al.<sup>114</sup> and nearly twice as high as the value reported by Kongpanna et al.<sup>113</sup> The underlying process design for the cradle-to-gate system includes a 79.16% net heat recovery, resulting in a large reduction of the global warming impact for the heat supply.<sup>95</sup> In summary, the total global warming impact of ethylene carbonate transesterification largely depends on (a) the effort to separate methanol from the dimethyl carbonate azeotrope and (b) the integration of heat released in the process operations.

However, the production of ethylene oxide consumes high amounts of energy, resulting in high global warming impacts. Furthermore, ethylene oxide is highly toxic, making special precautions in process operation necessary. The large energy demand and toxicity issues associated with ethylene oxide production, thus, represent drawbacks of the ethylene carbonate route.<sup>117</sup>

For urea transesterification (route 4a), the global warming impact reported for gate-to-gate<sup>113</sup> systems exceeds the one reported for cradle-to-gate<sup>95,113</sup> systems by a factor of 8.6. The reported global warming impacts are 2.93 and 0.34 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate, respectively. For the gate-to-gate system analysis, an optimal methanol to urea ratio of 8 was found to achieve approximately 70% urea conversion at equilibrium. This conversion rate fits well with reported experimental data.<sup>113,118</sup> Thus, large methanol recycling streams are needed, resulting in a high separation effort.

In contrast, an improved two-step reactor design was found to strongly reduce the global warming impact due to a reduced separation effort.<sup>95</sup> In the first step, 100% urea conversion to methyl carbamate is assumed with a methanol to urea ratio of approximately 2. In a subsequent reactive distillation column, excess methyl carbamate is used with methanol in a ratio of about 5.5 to achieve approximately a 50% yield to dimethyl carbonate. By shifting the recycling stream from methanol to methyl carbamate, the separation effort is thus largely reduced: Methyl carbamate has a higher boiling point, and dimethyl carbonate has to be separated from smaller amounts of methanol. In conclusion, similar to those of ethylene carbonate transesterification, the chosen process design and associated separation efforts largely influence the total global warming impact for the transesterification of urea.

Aresta and Galatola<sup>112</sup> calculated the global warming impact for the urea transesterification to be 29.4 kg of CO<sub>2</sub> equiv/kg of dimethyl carbonate. The value equals 10 times the value derived for gate-to-gate systems<sup>113</sup> and 86 times the value reported for cradle-to-gate systems.<sup>95</sup> The large deviation originates from the choice of Aresta and Galatola<sup>112</sup> to supply all energy (heat and electricity) by the electricity grid mix of Europe in 2000. Thus, the results cannot be directly compared to those of the other authors.

The use of electrochemistry for the conversion of CO<sub>2</sub> and methanol to dimethyl carbonate (route 4b) was compared to oxidative carbonylation (route 2b).<sup>68</sup> Spanish photovoltaic power plants were assumed to supply electrical energy. On the basis of a process simulation, the electrochemical conversion

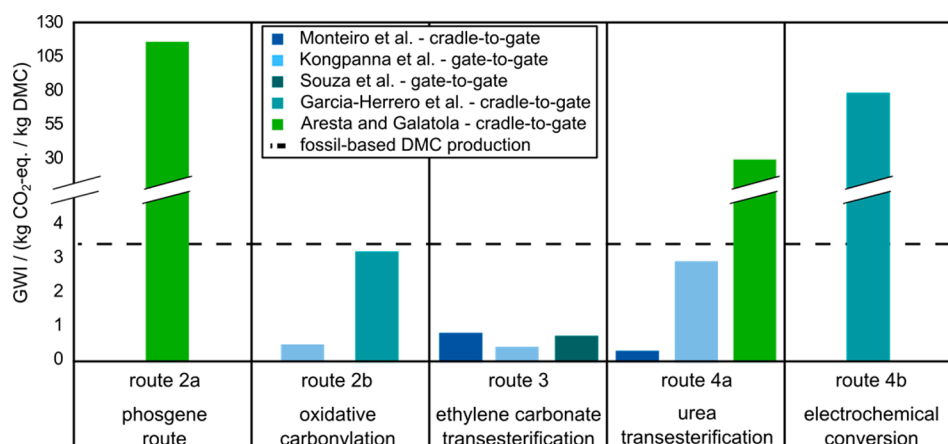


**Figure 2.** Reported global warming impacts for dimethyl carbonate (DMC) production (for details see Table 3). The global warming impacts reported by the five LCA studies vary largely due to diverging LCA methodologies, dissimilar background LCA data, and differing underlying process designs. Thus, a direct comparison should be restrained to deriving general trends.

was found to be environmentally beneficial, but only if the yield were to be increased to 20%. Current yields reported are in the range of 0.7–0.9% conversion and limited to 1–5% by equilibrium.<sup>91</sup> Thus, breakthrough improvements in the process design would be required for the electrochemical conversion to be environmentally beneficial.

Production of dimethyl carbonate via oxidative carbonylation leads to a reported global warming impact of 3.49 kg of CO<sub>2</sub> equiv/kg in LCA databases.<sup>65</sup> As can be seen from Figure 2, all reported global warming impacts for CO<sub>2</sub>-based production via transesterification to dimethyl carbonate are lower. The only exception is the very early preliminary study of Aresta and Galatola,<sup>112</sup> who assumed all energy (heat and electricity) to be supplied by the electricity grid mix in 2000. Thus, despite the differences in LCA methodology and process design, environmental benefits of the ethylene carbonate and urea transesterification route have been suggested, when compared to the production of DMC via the oxidative carbonylation route, yet these environmental benefits show a high sensitivity to the yield of dimethyl carbonate and the corresponding methanol to dimethyl carbonate ratio in the product mixture. The methanol to dimethyl carbonate ratio dictates the separation effort for azeotrope separation and methanol recycling. Consequently, the methanol to dimethyl carbonate ratio has a large impact on the total global warming impact of dimethyl carbonate production.<sup>95,113,114</sup>

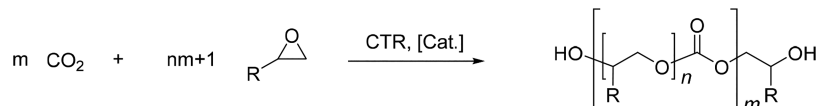
The available LCA studies differ largely in case of the chosen LCA methodology. Therefore, a comparative LCA study is desirable, using consistent methodology and data sets for all CO<sub>2</sub>-based and conventional dimethyl carbonate production routes as the foundation for their quantitative analysis.

**2.1.1.4. Further Trends and Research Topics: Direct Synthesis of Dimethyl Carbonate from CO<sub>2</sub> and Methanol.** The discussion above indicates that there are several production routes (see Table 2) available to convert CO<sub>2</sub> with suitable coreagents to organic carbonates, providing significant benefits on global warming impact and toxicity aspects as compared to the conventional route. Common to these routes to dimethyl carbonate production is that the equilibrium limitation encountered in the direct reaction of CO<sub>2</sub> with methanol (route 1) is bypassed. Despite emissions associated with production of the epoxides or the separation efforts, reported GWIs for CO<sub>2</sub>-based ethylene carbonate and

urea transesterification are lower compared to those of conventional production routes. Although the available LCAs differ in process designs and methods, an environmental benefit through introducing CO<sub>2</sub>-based production routes via ethylene carbonate and urea transesterification seems highly probable.

The direct synthesis of dimethyl carbonate from CO<sub>2</sub> and methanol remains a major challenge for kinetic and thermodynamic reasons. The search for effective catalysts continues to be an active field of research. In the development of new catalysts, the use of tin alcoholates has been extended to niobium alcoholates and molybdenum clusters as well as metallophthalocyanines and binuclear metal species. Early studies report dibutyldimethoxystannane [Bu<sub>2</sub>Sn(OMe)<sub>2</sub>] to be an active homogeneous catalyst.<sup>119</sup> Kinetic and mechanistic studies on dibutyldimethoxystannane revealed a cluster containing 10 tin atoms as a resting species.<sup>90</sup> Grafted on a polystyrene resin, the complex [Bu<sub>2</sub>Sn(OMe)<sub>2</sub>] was found to be active also when used as a heterogenized catalyst.<sup>119</sup> Likewise, the organotin catalyst can also be tethered to the surface of SBA-15.<sup>120</sup> For mesoporous tin-based catalysts, a high surface hydrophobicity and the presence of a large number of hexacoordinated Sn species and small tin oxide clusters appear to be relevant.<sup>120</sup> Such organotin-functionalized ordered mesoporous silica can be obtained by co-condensing [(MeO)<sub>2</sub>-ClSi(CH<sub>2</sub>)<sub>3</sub>SnCl<sub>3</sub>], tetraethyl orthosilicate, and 1,4-bis-(triethoxysilyl)benzene in acidic Pluronic 123 solution. Density functional theory (DFT) calculations of intermediates and transition states suggest the interaction of CO<sub>2</sub> with tin(IV) alkoxides of the type R<sub>2</sub>Sn(OCH<sub>3</sub>)<sub>2</sub> (R = alkyl, Ph, halogen) to be controlled by the entropic term.<sup>121</sup> The subsequent insertion of CO<sub>2</sub> into the Sn–OCH<sub>3</sub> bond is thermodynamically favorable. The computed free energy of activation was smallest for the substituent R being Ph groups. Alkyl groups lead to intermediate barriers, while halogen atoms provide the highest barriers. These results are in agreement with experimental results that indicate a higher turnover number for dimethyl carbonate formation, when the complex [Ph<sub>2</sub>SnO] was used as a catalyst.

Group 5 and 6 elements also make suitable catalysts. V<sub>2</sub>O<sub>5</sub> catalysts are effective for the direct and selective synthesis of dimethyl carbonate from CO<sub>2</sub> and methanol.<sup>122</sup> Upon modification with H<sub>3</sub>PO<sub>4</sub>, the crystal phase changes from orthorhombic to an orthorhombic–tetragonal double phase,

Scheme 2. CO<sub>2</sub>-Based Route to Poly(ether carbonate) Polyols<sup>a</sup>

<sup>a</sup>The molecular weight is controlled with a chain transfer reagent (CTR; in the equation, formally H<sub>2</sub>O).

resulting in an increase in the concentration of weaker acid sites. Both CO<sub>2</sub> and CH<sub>3</sub>OH are effectively activated by coordination to the catalyst surface. For nanosized monoclinic zirconia, the formation of methoxy carbonate as a key intermediate was reported.<sup>123</sup> Due to faster adsorption of CO<sub>2</sub> on zirconia compared to methanol, bidentate bicarbonate moieties (b-HCO<sub>3</sub><sup>−</sup>) are formed at the initial stage of the reaction. Increasing formation of methoxy carbonate with time suggests that methoxy carbonate is formed by the reaction between methoxy and b-HCO<sub>3</sub><sup>−</sup> groups. The reaction is thought to proceed via an electron donor–acceptor interaction between CO<sub>2</sub> and methanol. Another early study also reports pentamethoxyniobium [Nb(OMe)<sub>5</sub>]<sub>2</sub> as a homogeneous catalyst.<sup>119</sup> Also molybdenum clusters, such as Cs<sub>2</sub>Mo<sub>6</sub>Br<sub>8</sub>Br<sub>6</sub>, function as homogeneous catalysts for dimethyl carbonate formation. Supported on graphene, oxide molybdenum clusters provide suitable heterogenized catalysts.<sup>124</sup>

For metallophthalocyanines (M = Mn, Fe, Co), a hemi-carbonate moiety bonded to the central metal was found to be a key step in activating carbon dioxide and methanol.<sup>125</sup> An optimum balance of acid and base sites enhances dimethyl carbonate formation. For Mo-promoted Cu–Fe bimetal catalysts, the relative concentration of acid and base sites can be adjusted by changing the molybdenum content.<sup>126</sup> In parallel, the presence of molybdenum promoters decreases the reducibility and increases the dispersion of Cu–Fe clusters. Metal oxide binuclear MO<sub>x</sub>M species (M = Mg, Ca, Sr, Ba, with  $x = 1\text{--}4$ , depending on the cation) were studied with quantum mechanical density functional theory (DFT) calculations.<sup>127</sup> The species were considered to be immobilized in alkaline-earth-metal zeolites, mordenite and phillipsite. The calculations revealed that carbonates are formed with almost no energetic barrier. The participation of the MO<sub>x</sub>M species explains the source of the third O atom in CO<sub>3</sub> species in dehydrated zeolites.

However, the previous discussion on CO<sub>2</sub>-based routes to dimethyl carbonate shows that the full processes need to be considered, including, in particular, also the separation steps to quantify the potential environmental benefits. In this context, the small equilibrium conversions of the direct DMC formation are a major limitation that cannot be resolved by catalyst development. To drive the equilibrium-limited reaction to higher yields, a dehydrating agent is frequently used. CeO<sub>2</sub> has been shown to be an effective catalyst for a tandem reaction system for dimethyl carbonate formation from CO<sub>2</sub> and methanol and parallel benzonitrile hydration to benzamide.<sup>128</sup> This reaction system can be applied to the synthesis of other dialkyl carbonates from CO<sub>2</sub> and their corresponding alcohols. In the presence of *N,N'*-dicyclohexylcarbodiimide as a dehydration agent, copper phthalocyanine tetrasulfonamide supported on graphene oxide was found to be a good catalyst for dimethyl carbonate formation.<sup>129</sup> However, in all these concepts, the dehydration agent has to be recycled or has to find a potential commercial outlet as a coupled byproduct. The efficiency of the overall value chain for such integrated

processes seems challenging, and evaluations by techno-economic analysis and life cycle assessments would be highly welcome to evaluate their potential.

### 2.1.2. CO<sub>2</sub>-Based Routes to Polycarbonates.

**2.1.2.1. Background and Motivation.** The possibility to synthesize aliphatic polycarbonates from copolymerization of CO<sub>2</sub> and epoxides has been known for many decades.<sup>130</sup> It is possible to obtain either oligomers with terminal reactive groups or high molecular weight polycarbonates. Copolymerization in a nonalternating fashion gives rise to a poly(ether carbonate) polymer backbone with a statistic sequence of ether and carbonate linkages. Copolymerization in an alternating fashion gives rise to a polycarbonate polymer backbone with only carbonate linkages. For aromatic polycarbonates, the use of CO<sub>2</sub> as a feedstock is currently possible indirectly via intermediate formation of cyclic carbonates (Scheme 1). These processes can lead to materials for drop-in solutions in existing applications of the polymer market or provide novel materials with specific properties to be evaluated for commercial use. The economic and ecologic boundaries for drop-in solutions are more readily assessed as they can be compared to a clearly defined benchmark.

**2.1.2.2. Current Status of CO<sub>2</sub> Conversion to Poly(ether carbonate)s and Polycarbonates.** Hydroxyl-terminated aliphatic poly(ether carbonate)s with molecular weight in the oligomer range (<20000 g/mol) have recently been introduced as polymer building blocks in polyurethane manufacturing.<sup>131</sup> Such poly(ether carbonate) polyols are obtained by reaction of CO<sub>2</sub> with epoxides in the presence of double metal cyanide catalysts.<sup>132,133</sup> A chain transfer reagent (CTR) is used to control the molecular weight during production of the polyol (Scheme 2). Poly(ether carbonate) polyols are low-viscosity liquids with a glass transition temperature below 0 °C, which makes them suitable for producing polyurethanes by reacting the polyol with polyisocyanates.

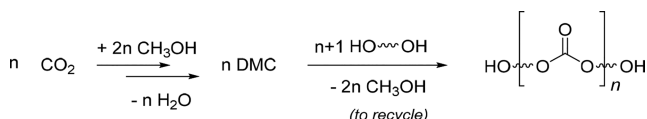
In 2016, Covestro opened a production plant for poly(ether carbonate) polyols in Dormagen, Germany, with 5000 t/a capacity.<sup>134</sup> CO<sub>2</sub> is reacted with propylene oxide in the presence of a zinc-based catalyst to make polyols. The polyols are used in the production of flexible foam polyurethanes for foam mattresses.<sup>131</sup> In the Covestro process, a roughly 20 wt % concentration of the polyol product stems from carbon dioxide that is coupled into the process from a neighboring ammonia plant.

The production of poly(ether carbonate) polyols addresses the polyol market, which is dominated by polyether and polyester polyols. Polyether polyols dominate in the manufacture of flexible foam polyurethanes. Polyester polyols find applications mostly in the production of rigid foam polyurethanes. The current polyol market is about 7.5 million t/a.<sup>135</sup> With a 20 wt % average CO<sub>2</sub> content, up to 1.6 million t/a of CO<sub>2</sub> could find potential use as a raw material. New application fields for poly(ether carbonate)s are explored, such as transparent films and elastomers,<sup>136,137</sup> which could provide

further options for the utilization of CO<sub>2</sub>-based poly(ether carbonate) polyols.

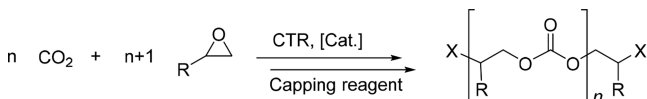
Aliphatic polycarbonate comprising a polymer backbone with an alternating sequence of carbonate moieties and comonomers and molecular weight in the oligomer range are obtained currently by transesterification of aliphatic diols with dimethyl carbonate. The reaction is driven to completion by continuously removing methanol as a byproduct (Scheme 3). Utilizing dimethyl carbonate derived from CO<sub>2</sub> (see section 2.1.1) also allows introduction of this feedstock indirectly into this value chain.

**Scheme 3. CO<sub>2</sub>-Based Route to Polycarbonate Polyols**



Aliphatic polycarbonates obtained by alternating copolymerization of CO<sub>2</sub> with epoxides (Scheme 4) have particular

**Scheme 4. CO<sub>2</sub>-Based Route to High Molecular Weight Polycarbonates by Catalytic Copolymerization of CO<sub>2</sub> and Epoxides<sup>a</sup>**



<sup>a</sup>To stabilize the polymer chain against backbiting, the terminal hydroxyl groups are converted to inert end groups X using a capping reagent.

properties which are advantageous for numerous applications. The development of catalysts with high activity and selectivity to achieve the desired molecular weights and structural regularities is studied intensively worldwide.<sup>130,138–148</sup> Mostly homogeneous catalysts are used in the copolymerization reaction.<sup>144,147,149,150</sup> Cobalt and chromium complexes with special salen, salan, or salophen ligands provide high selectivity to the polymeric product.<sup>151–155</sup> Also, bimetallic zinc catalysts are suitable.<sup>156–158</sup> For zinc catalysts, the activation of the epoxide seems to be the rate-determining step, while insertion of CO<sub>2</sub> into the growing polymer chain has been found to be facile.<sup>159,160</sup> Likewise, aluminum coordination complexes are widely used catalysts for the copolymerization of CO<sub>2</sub> with epoxides.<sup>161</sup>

Several companies are currently in the process of commercializing aliphatic polycarbonates obtained by reacting CO<sub>2</sub> with epoxides. Eonic offers polycarbonates that contain up to 50% CO<sub>2</sub> by weight.<sup>162</sup> The length and number of branches are adjusted to suit the requirements of the application. Novomer markets alternating carbonates for polymer applications and as polyol building blocks for polyurethanes.<sup>140</sup> The terminal hydroxyl groups are typically converted with a capping reagent to an inert end group to minimize the extent to which the polycarbonate degrades to cyclic carbonate by backbiting. To overcome the sensitivity of polycarbonate with a high CO<sub>2</sub> content (40–50%) to moisture, polyol intermediates and final products are stabilized with the use of additives. Recently, Novomer's technology was acquired by Saudi Aramco.<sup>163</sup> The Korean company SK Energy has built a plant for production of polycarbonate from CO<sub>2</sub> and

propylene oxide. The company has introduced colaminates with polypropylene films to equip the material with mechanical stability.<sup>164</sup> The German chemical company BASF has been exploring the copolymerization of CO<sub>2</sub> and cyclohexene oxide to a polycarbonate with a glass transition temperature of around 80 °C for blending with polylactide.<sup>165</sup>

Aromatic polycarbonates have a large market as high-performance thermoplastics. Bisphenol A-based polycarbonate was commercialized in the early 1960s and is now the second largest engineering thermoplastic. It has a unique property profile combining optical transparency with toughness and high impact strength. The tendency to yellow upon prolonged exposure to UV light has been overcome by the use of UV stabilizers. The global demand for aromatic polycarbonate in 2011 was around 3.6 million t/a, growing at a rate of 4–5% per annum.<sup>80</sup> The production volume is estimated to reach 6.3 million t/a by 2020.<sup>166</sup>

CO<sub>2</sub>-based aromatic polycarbonate production via the Asahi process involves a transesterification train to transfer the carbonate moiety contained in ethylene carbonate via dimethyl carbonate and diphenyl carbonate to bisphenol A polycarbonate (Scheme 1).<sup>82,167</sup> This transesterification train avoids the formation of azeotropes and the alkylation of bisphenol A. The alkylation occurs as a prominent side reaction with dimethyl carbonate. Therefore, dimethyl carbonate is conventionally reacted with phenol first to diphenyl carbonate. Novel catalysts include cerium-based binary and ternary oxides.<sup>168</sup> Diphenyl carbonate is then used in the polymerization with bisphenol A (Scheme 1). In comparison, the sulfur analogues, dithiocarbonates, can be reacted directly with bisphenol A.<sup>169</sup> Targeting at skirting the use of ethylene oxide, Asahi Kasei has developed a process to make the dialkyl carbonate precursor directly from CO<sub>2</sub> and alcohol.<sup>170</sup> Asahi Kasei has announced the startup of a pilot plant with 100 kt/a capacity at the Mizushima site in Kurashiki, Japan, in 2017.

**2.1.2.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Aliphatic Poly(ether carbonate).** LCA studies of polymers from CO<sub>2</sub> are currently available for the copolymerization of CO<sub>2</sub> and epoxides to poly(ether carbonate) polyols<sup>117,171</sup> and the polymerization of CO<sub>2</sub>-based formaldehyde to poly-(oxymethylene) polyols.<sup>171–173</sup> The CO<sub>2</sub>-based poly-(oxymethylene) polyols use formaldehyde produced by the oxidation of CO<sub>2</sub>-based methanol. Thus, the decisive step is the production of methanol from CO<sub>2</sub> and H<sub>2</sub> rather than the downstream processing to poly(oxymethylene) polyols. Therefore, the results of the LCA studies assessing poly-(oxymethylene) polyols are discussed in the methanol section (section 2.4).

Von der Assen and Bardow<sup>117</sup> assessed the benefits of directly including CO<sub>2</sub> in poly(ether carbonate) polyols by copolymerization with propylene oxide. The authors used industrial data to assess both the capture of CO<sub>2</sub> from an industrial lignite-fired power plant and the utilization of CO<sub>2</sub> in poly(ether carbonate) polyols. The utilization process represents a pilot plant operated in industry. CO<sub>2</sub> capture from lignite power plants involves also the production of electricity. Thus, the LCA assessed the combined functional unit of 1 kg of polyol and 0.36 kW h of electricity. The electricity amount represents the electricity produced to supply CO<sub>2</sub> required for 30 wt % inside the polymer backbone. The CO<sub>2</sub>-based polyols are compared to fossil-based polyether polyols, consisting of 15 wt % ethylene oxide and 85 wt % propylene oxide.

It was found that the change of environmental impacts due to CO<sub>2</sub> utilization for poly(ether carbonate) polyols originates from two effects:

- (1) CO<sub>2</sub> capture reduces the global warming impact, but slightly increases fossil resource depletion.
- (2) Substitution of energy-intensive reactants, e.g., ethylene and propylene oxide, reduces both the global warming impact and fossil resource depletion.

The slight increase in fossil resource depletion for CO<sub>2</sub> capture is due to the corresponding energy demand. Nevertheless, the effect is outweighed by the substitution effect of energy-intensive reactants, leading to an overall reduction of fossil resource depletion. For a polyol with 30 wt % CO<sub>2</sub>, the reductions for the global warming impact and fossil resource depletion are 25% and 22%, respectively. To avoid problem shifting between different environmental impact categories, <sup>30,117</sup> a comparative analysis of further environmental impacts of CO<sub>2</sub>-based polyols was included. The results showed that reductions are achieved in all nine impact categories that were considered (Figure 3).<sup>117</sup> Thus, CO<sub>2</sub>-based polyols demonstrate that the motivation for using CO<sub>2</sub> as a feedstock can go far beyond reducing the global warming impact.

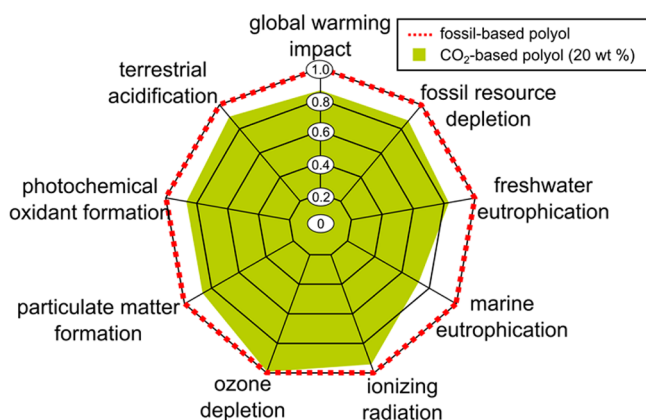


**Figure 3.** Environmental impacts of CO<sub>2</sub>-based polyols compared to fossil-based polyols according to von der Assen and Bardow.<sup>117</sup> The values are related to the fossil-based production of 1 kg of fossil-based polyol. The CO<sub>2</sub>-based polyols offer environmental impact reductions in all nine impact categories.

The study further pointed out the importance of distinguishing between the amount of CO<sub>2</sub> utilized (e.g., the concentration (wt %) inside the polymer backbone) and the CO<sub>2</sub> emissions avoided.<sup>117</sup> For this purpose, the global warming impact reduction was related to the amount of CO<sub>2</sub> utilized (see Figure 4).

For all cases, the amount of avoided CO<sub>2</sub> emissions is significantly higher than the amount of utilized CO<sub>2</sub>. The reference polyol consists of 15 wt % ethylene oxide and 85 wt % propylene oxide. At the beginning, only ethylene oxide is substituted by CO<sub>2</sub>. For a CO<sub>2</sub> content of 10 wt %, the global warming impact reduction is consequently limited. At higher CO<sub>2</sub> content, the increasing substitution of propylene oxide leads to more pronounced global warming impact reductions. This pronounced beneficial effect is based on the nearly twice as high global warming impact of propylene oxide compared to ethylene oxide. Thus, by utilizing 1 kg of CO<sub>2</sub> to produce a poly(ether carbonate) polyol with 30 wt % CO<sub>2</sub>, up to 3 kg of CO<sub>2</sub> equiv emissions can be avoided.

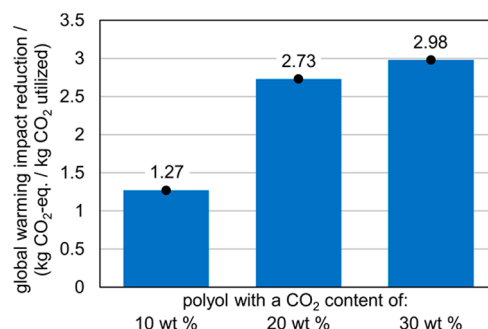


**Figure 4.** Global warming impact reduction (kg of CO<sub>2</sub> equiv/kg of utilized CO<sub>2</sub>). The amount of avoided greenhouse gas emissions (1.27–2.98 kg of CO<sub>2</sub> equiv) is higher than the amount CO<sub>2</sub> utilized, due to the substitution of energy-intensive reactants. If 30 wt % CO<sub>2</sub> is included inside the polymer polyol backbone, up to 3 kg of CO<sub>2</sub> equiv emissions can be avoided for every 1 kg of CO<sub>2</sub> utilized. Adapted with permission from ref 117. Copyright Royal Society of Chemistry.

Another LCA study<sup>171</sup> analyzes further opportunities for CO<sub>2</sub> utilization in the supply chain of polyol and polyurethane production. The authors determined optimal pathways and quantified, e.g., the maximum possible amount of utilized CO<sub>2</sub> in the supply chain and the maximum reduction of environmental benefits. The relation between the amount of utilized CO<sub>2</sub> and the environmental benefits is shown to depend strongly on clean hydrogen production. If formaldehyde-based units are also considered, further reduction in GHG emissions can be achieved.

In summary, the conducted LCA for poly(ether carbonate) polyols underlines that the substitution of energy-intensive resources by CO<sub>2</sub> offers a promising pathway to reduce global warming impacts and fossil resource depletion. Future research seems attractive to identify pathways for direct incorporation of CO<sub>2</sub> into new polymers to substitute energy-intensive reactants.

**2.1.2.4. Further Trends and Research Topics: Expanding the Polymer Architecture for New Applications.** The quantitative data presented above demonstrate that CO<sub>2</sub> utilization for poly(ether carbonate) polyols reduces the global warming impact compared to that for conventional polyols even beyond the amount of CO<sub>2</sub> incorporated. Nevertheless, the CO<sub>2</sub>-based polyols are no “carbon sink” over the full life cycle. Clearly, however, they enable a more carbon-efficient production of polyols, reducing at the same time other environmental impact categories significantly. Thus, the substitution of energy-intensive resources by CO<sub>2</sub> offers a promising pathway to reduce the environmental footprint of the chemical industry.

Congruous with the beneficial CO<sub>2</sub> footprint, poly(ether carbonate) polyols and polycarbonates produced with CO<sub>2</sub> as the feedstock are currently being commercialized for industrial applications, such as polyurethanes for flexible foam mattresses<sup>131</sup> and automotive seats.<sup>174</sup> The optimal content of CO<sub>2</sub> in the polymer is thereby a design parameter to balance between economy, ecology, and desired properties for the application. A high content of CO<sub>2</sub>, being an inexpensive feedstock, provides economic advantages. It will also maximize the carbon footprint reduction. However, increasing the CO<sub>2</sub> content toward the maximum content leads to drawbacks on the application side. The glass transition temperatures of alternating CO<sub>2</sub>–propylene oxide copolymers gets close to room temperature, leading to softening of the material

properties. Furthermore, alternating copolymers have a high propensity of polymer degradation by backbiting of open chain ends.

Many recent studies concern new synthetic approaches to poly(ether carbonate)s and polycarbonates with specific structural features. The regioselectivity of the ring opening of terminal epoxides is strongly influenced by the nature of the epoxide, whereby styrene oxide differs from aliphatic epoxides as the ring opening occurs predominantly at the methine C<sub>α</sub>–O bond due to electron delocalization into the phenyl group.<sup>175</sup> Recently, the use of chiral mononuclear and dinuclear cobalt(III) catalysts for the stereospecific copolymerization of CO<sub>2</sub> and epoxides has been reported.<sup>139</sup> Isotactic copolymers of CO<sub>2</sub> with *meso*-epoxides are semicrystalline with melting points in the range of 180–260 °C. In contrast, only some of the isotactic copolymers obtained with terminal epoxides were found to be crystalline. Another line of research concerns the introduction of further comonomers, such as cyclic anhydrides, lactones, and lactides, into the polymer backbone (Figure 5).<sup>176</sup>

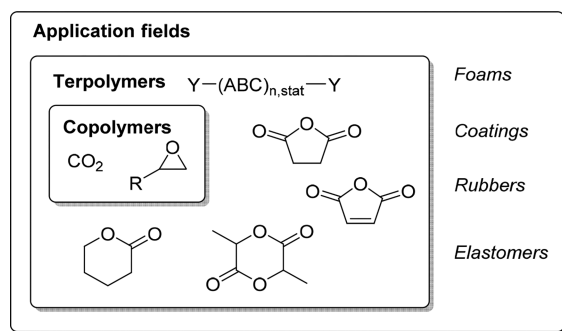


**Figure 5.** Examples for comonomers known to be suitable for the terpolymerization with CO<sub>2</sub> and epoxides and application fields for CO<sub>2</sub>-based materials.

Many of these comonomers can be obtained from sustainable resources. Use as comonomers thus reduces the environmental impact of the materials as a further part of the epoxides to be substituted as raw material. Particularly interesting is the option to introduce additional functions such as alkene moieties,<sup>136,177</sup> which gives rise to manifold new possibilities in polymer chemistry. Consequently, it is anticipated that aliphatic poly(ether carbonate) polyols and polycarbonates will find diverse applications in new fields such as elastomers, rubbers, and coatings.<sup>137</sup>

Sulfur atoms can also be introduced into the polymer chain through use of carbonyl sulfide (COS) or carbonyl disulfide (CS<sub>2</sub>), which are heterocumulenes structurally analogous to CO<sub>2</sub>. The sulfur-containing polymers are obtained in a manner analogous to the corresponding CO<sub>2</sub>–epoxide copolymerization.<sup>178,179</sup> Zinc–cobalt double metal cyanide complexes and homogeneous [Cr(salen)X] complexes are suitable catalysts. Using [Cr(salen)X] in combination with onium salts for the copolymerization of COS with propylene oxide, copolymers with >99% monothiocarbonate units and a high tail-to-head content of up to 99% were obtained.<sup>179</sup> A particularity of the COS–epoxide copolymerization is the occurrence of oxygen–sulfur exchange reactions, which leads to formation of carbonate and dithiocarbonate units along the polymer backbone. The sulfur-containing copolymers give highly transparent materials with excellent optical properties, such as a high refractive index and Abbe number. Polymers with an

ABA triblock structure containing “hard” semicrystalline poly(ethylene monothiocarbonate) (A) and the “soft” amorphous poly(propylene monothiocarbonate) (B) moieties have been proposed for thermoplastic elastomers.<sup>180</sup> The copolymer is obtained by the copolymerization of COS and achiral ethylene oxide. The alternating poly(ethylene monothiocarbonate) copolymer has a melting temperature of 128 °C, with a melting enthalpy of 75.4 J/g. A redox-responsive poly(vinyl cyclohexenecarbonate) with a detachable disulfide bond backbone has been obtained with a [Co(salen)/TFA]/[bis(triphenylphosphine)iminium] binary catalyst.<sup>181</sup>

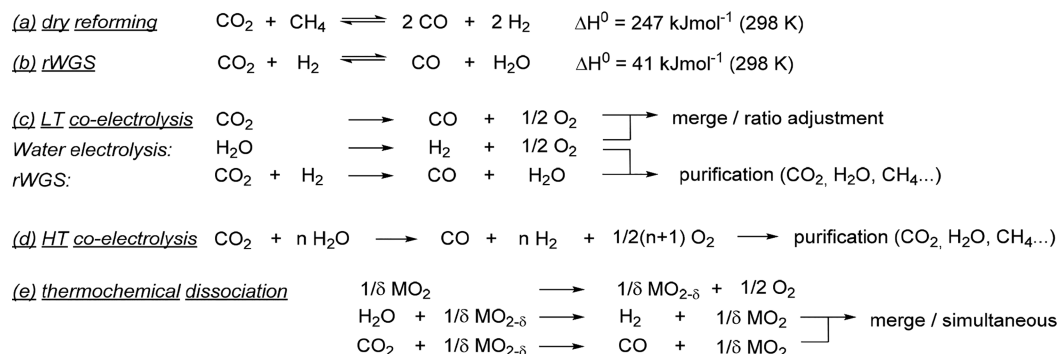
Epichlorohydrin has also been introduced into the polymer backbone. The reaction with CO<sub>2</sub> is catalyzed by zinc glutarate as a heterogeneous catalyst.<sup>182</sup> The CO<sub>2</sub>–epichlorohydrin copolymer exhibits a glass transition temperature of 44 °C. The alternating copolymerization of CO<sub>2</sub> with biorenewable limonene dioxide can be catalyzed with a zinc β-diiminate complex.<sup>183</sup> Only the more reactive epoxide group is being converted to provide a linear polycarbonate. The polymer is characterized by a relatively high glass transition temperature of up to 135 °C, consistent with the steric bulk of the chemical entities along the polymer backbone. The pendent methoxy-irane groups can be modified by thiols or carboxylic acids without destruction of the main chain. Another review concerns poly(ester carbonates) obtained by the copolymerization of CO<sub>2</sub>, epoxides, and cyclic anhydrides. Chemical modification, including terpolymerization, block copolymerization, graft copolymerization, chain extension, cross-linking, and end-capping, has been used to regulate the chain structure of poly(propylene carbonate) (PPC) and adjust its properties.<sup>184</sup>

In summary, the incorporation of CO<sub>2</sub> into the industrial production of polymers has been successfully achieved for low molecular weight poly(ether carbonate) polyols as substitutes for the structurally closely related polyether polyols in polyurethane production. The significant environmental benefits resulting from this replacement strategy are clearly documented. The basic chemistry behind this process is the ring-opening copolymerization of epoxides and CO<sub>2</sub>, which opens manifold opportunities to generate advanced materials that utilize CO<sub>2</sub> as a feedstock. Catalyst development and synthetic strategies based on mechanistic insights are the key elements to drive innovation in this research area. As these materials are novel chemical structures, their environmental assessment would have to be compared to the specific application for which they are intended, where polymers of very different molecular structures are probably in use today. Such studies would be highly welcome for emerging application areas to identify opportunities for sustainable products and challenges for the production routes.

## 2.2. Synthesis Gas

**2.2.1. Background and Motivation.** Synthesis gas (also denoted as syngas) comprises a mixture of carbon monoxide and hydrogen, often also containing carbon dioxide, and derives its name from its utilization as an intermediate for the synthesis of hydrogen, ammonia, methanol, and various synthetic hydrocarbon-based fuels. Industrially, syngas is commonly produced via Pt-catalyzed partial oxidation of methane, Ni-catalyzed steam reforming of methane and light hydrocarbons, or gasification of heavy hydrocarbons and coal as carbon feedstock. The different fossil raw materials and routes lead to synthesis gas with variable compositions and purities. However, defined ratios of carbon monoxide and hydrogen are needed for

**Scheme 5. Synthesis Gas Production Pathways from CO<sub>2</sub> via (a) Dry Reforming of Methane (DRM), (b) Reverse Water–Gas Shift (rWGS) Reaction, (c) Low-Temperature (LT) and (d) High-Temperature (HT) Coelectrolysis, and (e) Solar-Driven Thermochemical Dissociation of CO<sub>2</sub> and H<sub>2</sub>O**



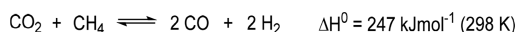
further valorization as defined by the stoichiometry of the reactions. For instance, a ratio of H<sub>2</sub> to CO of 2:1 is ideal for methanol synthesis or hydrocarbon production via the Fischer–Tropsch process, whereas a 1:1 ratio corresponds to the stoichiometry of hydroformylation. If required, the H<sub>2</sub> to CO ratio in syngas can be adjusted via the water–gas shift equilibrium interconverting CO and water with CO<sub>2</sub> and H<sub>2</sub>. Furthermore, syngas is also the major source for pure hydrogen and carbon monoxide for chemical processes.

At present, renewable raw materials gain increasing interest motivated by the aim of defossilization of the energy, transportation, and chemical sectors. One way of introducing renewable raw materials is the gasification of biomass.<sup>185–187</sup> Alternatively, CO<sub>2</sub> is available as a most abundant carbon source and has thus also become an attractive carbon feedstock for the production of synthesis gas. Among other technologies, dry reforming of methane (DRM)<sup>188–190</sup> and the reverse water–gas shift (rWGS) reaction<sup>191</sup> have received considerable attention in recent years. In addition, solar-driven thermochemical dissociation reaction<sup>192–194,194</sup> of CO<sub>2</sub> and water as well as low- or high-temperature coelectrolysis (LT or HT coelectrolysis)<sup>195,196</sup> could gain importance for the production of syngas in the transition to a renewable and thus fluctuating energy supply.

The following section focuses on these synthesis gas production pathways from CO<sub>2</sub> (Scheme 5) to discuss the available insight into the potential for environmental impact reduction and to survey technological benefits and challenges.

**2.2.2. Current Status of CO<sub>2</sub> Conversion to Synthesis Gas.** **2.2.2.1. Dry Reforming of Methane.** Syngas can be produced from CO<sub>2</sub> by dry reforming of methane (DRM) (Scheme 6). Methane is the major constituent of natural gas. In

**Scheme 6. Dry Reforming of Methane (DRM) with CO<sub>2</sub> To Form Synthesis Gas**

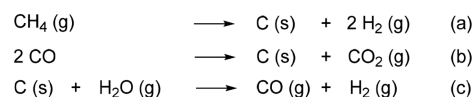


addition, further sources of methane come into consideration to decrease the depletion of fossil resources. For example, the emission of methane from landfills into the atmosphere is estimated to be 35 Mt of CH<sub>4</sub>/year.<sup>197</sup> As the landfill gas is produced naturally and could thus be considered “renewable”, the direct reaction with CO<sub>2</sub> by DRM to obtain synthesis gas could be advantageous from the defossilization perspective. However, the syngas produced has a H<sub>2</sub>/CO ratio of 1:1, and

thus, the ratio has to be adjusted to the ratio needed for follow-up processing. In addition, the DRM is a strongly endothermic reaction requiring temperatures in the range of 750 °C, where heterogeneous catalysts are available to convert CH<sub>4</sub> and CO<sub>2</sub> effectively.<sup>198,199</sup> As for many other catalytic processes, noble metals play a predominant role due to their high activity and selectivity, but suffer from being costly and of limited abundance. Early transition metals such as nickel represent a cost-effective alternative, even though coke resistance is still a major issue for these systems. In general, Ru, Rh, Ir, and Ni are considered to be among the most active catalysts.<sup>200</sup>

The major challenge for DRM is the formation and deposition of carbon on the catalyst, thus leading to deactivation.<sup>201,202</sup> Furthermore, CH<sub>4</sub> derived from landfills or fossil resources contains high amounts of impurities, such as sulfur gases, causing catalyst poisoning and deactivation.<sup>189</sup> Thus, the DRM reaction demands catalysts which are stable under harsh reaction conditions. Methane decomposition (Scheme 7a) and the Boudouard reaction (Scheme 7b) are

**Scheme 7. Methane Decomposition (a), Boudouard Reaction (b), and Surface Carbon Oxidation with Water (c)**



the main reasons for carbon formation on the catalyst surface. A low ratio of hydrogen to carbon in DRM promotes the coke formation and deposition even further. Increasing the H<sub>2</sub>O/CH<sub>4</sub> (Scheme 7c) and CO<sub>2</sub>/CH<sub>4</sub> feed gas ratios and lowering the reaction temperature can help to prevent the formation of surface carbon species.

In comparison to nickel, noble metals show a reduced tendency for carbon formation and are thus more resistant. Rostrup-Nielsen and Bak Hansen monitored the tendency for carbon formation at 500–650 °C and 1 bar and found the order Ni > Pd >> Ir > Pt > Ru ≈ Rh.<sup>200</sup> For Ni catalysts, it was shown that coking of the active sites follows the whisker carbon formation mechanism.<sup>203,204</sup> The nucleation takes place on the step sites of the Ni crystals. A carbon layer is formed, enabling the formation of carbon nanotubes from the nickel particles.<sup>205</sup> Formation of the whiskers and the accompanying mechanical stress lead to breakage of the catalyst pellets, thus resulting in an increased pressure drop. Large Ni particles above a critical particle size of 10 nm tend to accelerate the carbon formation

process.<sup>199,205–207</sup> A further decrease in the carbon formation tendency was observed upon passivation of the catalyst with sulfur.<sup>200</sup> In general, carbon formation can be influenced by various characteristics of the catalyst, including the choice of the active species, crystallite size, and promoters as well as passivating agents. To enable the application of low-cost nickel in DRM, several investigations study bulk and supported metal catalysts, promoters, and catalyst preparation techniques, attempting to derive structure–activity correlations (e.g., in terms of specific surface areas, porosity, or acid/base properties) for those catalyst systems.<sup>190,208–213</sup>

Regarding catalyst supports, metal oxides with strongly basic sites have been reported to inhibit carbon deposition.<sup>214</sup> Furthermore, they enhance CO<sub>2</sub> activation since CO<sub>2</sub> adsorbs more readily on the basic sites, and binding energies to metal oxides are generally higher compared to those to sole metal surfaces.<sup>215</sup> In this regard, metal–support interactions play an important role, as the dissociation of CO<sub>2</sub> is believed to proceed via a hydrogen-spillover-like mechanism at the interface of metal particles to the support material.<sup>216</sup> The oxygen species produced from CO<sub>2</sub> dissociation is needed for the oxidation of CH<sub>4</sub> to CH<sub>3</sub>O species on the active metal sites, which will then undergo further decomposition reactions to form carbon monoxide and hydrogen.<sup>214</sup> To provide oxygen vacancies, suitable metal oxides have been investigated, such as TiO<sub>2</sub>, MgO, CeO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, and especially Al<sub>2</sub>O<sub>3</sub>, in various modifications.<sup>199</sup> For the latter, the CO<sub>2</sub> adsorption capacity is rather moderate, but can be enhanced by addition of alkaline-earth-metal oxides, e.g., MgO or CaO, to decrease carbon formation and deposition and thus enhance catalytic activity.<sup>217</sup>

To improve the coke resistance of DRM catalysts even further, the active phase could be introduced into a well-defined structure, enabling migration of homogeneously dispersed active species into the surface upon reduction and thus enhancing metal–support interactions as well as thermal stability.<sup>218</sup> This can be achieved by incorporation of Ni species within spinel structures, mixed metal oxides of the formula AB<sub>2</sub>O<sub>4</sub>, with A and B being divalent and trivalent metal cations. The synergy of the two homogeneously dispersed catalytically active cations within the material structure makes them very attractive as heterogeneous catalysts.<sup>219,220</sup> MgAl<sub>2</sub>O<sub>4</sub> is most commonly used as a support for DRM, whereby Ni is incorporated via coprecipitation. With approximately 90% CO<sub>2</sub> conversion observed at a reactant feed ratio CH<sub>4</sub>/CO<sub>2</sub> = 1 (flow rate 30 mL min<sup>−1</sup>, 0.02 g of catalyst), such a NiMgAl<sub>2</sub>O<sub>4</sub> catalyst is a more active and stable catalyst when compared to Ni supported solely on γ-Al<sub>2</sub>O<sub>3</sub> and MgO–γ-Al<sub>2</sub>O<sub>3</sub>.<sup>221</sup> The superior activity and carbon resistance are attributed to the strong interaction between Ni and MgAl<sub>2</sub>O<sub>4</sub>, enhancing the control over sintering. The formation of a MgAl<sub>2</sub>O<sub>4</sub> spinel layer suppresses the formation of NiAl<sub>2</sub>O<sub>4</sub>, considered to be the phase responsible for reduced efficiency and coke resistance of the DRM catalyst. CeO<sub>2</sub> and ZrO<sub>2</sub> are able to enhance the performance of Ni/MgAl<sub>2</sub>O<sub>4</sub> even further, preventing carbon formation due to strong metal–support interactions.<sup>222</sup> Also, bimetallic catalysts of Ni/Co at 1:1 or 1:2 ratios have been reported to show superior activity and stability upon formation of Ni–Co spinels.<sup>223</sup> The hydrogen produced at highly active cobalt sites enables the reduction of the nickel sites under the reaction conditions, while nickel is believed to inhibit carbon deposition on the cobalt sites.

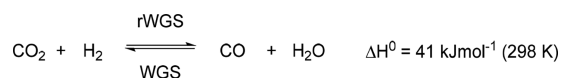
The same effect can be achieved with perovskites, mixed metal oxides of the formula ABO<sub>3</sub>, with A and B representing two metal cations. In initial studies, LaNiO<sub>3</sub> was used as a catalyst precursor for DRM.<sup>224</sup> Upon reduction of the precursor, Ni<sup>0</sup> species supported on La<sub>2</sub>O<sub>3</sub> were formed as the active catalyst, yielding full conversion of CH<sub>4</sub> and 92% conversion of CO<sub>2</sub> at 800 °C (flow rate 20 mL min<sup>−1</sup>, 0.05 g of catalyst). The authors proposed the partial reoxidation of La<sub>2</sub>O<sub>3</sub> and Ni<sup>0</sup> by CO<sub>2</sub> followed by a simultaneous back-reduction by CH<sub>4</sub>. The stability and selectivity are strongly influenced by the A site cations, as observed by a study involving perovskites of the Ln<sub>1−x</sub>Ca<sub>x</sub>Ru<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> type (Ln = La, Sm, Nd) as precursors for Ru<sub>0.8</sub>Ni<sub>0.2</sub>/CaO and/or La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Nd<sub>2</sub>O<sub>3</sub>.<sup>225,226</sup> LaRu<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> was found to be the best performing catalyst, converting 89% and 72% of CH<sub>4</sub> and CO<sub>2</sub> at a CO selectivity of ca. 90% after 150 h.

Furthermore, several promoters (e.g., gold) can be used to block low-valency coordination sites, further reducing whisker carbon formation.<sup>227,228</sup> Nevertheless, blocking the low coordination sites might inhibit the most active sites for the DRM reaction, therefore decreasing the activity of the catalyst. Modification with potassium salts is used to promote steam adsorption, in this way suppressing carbon formation via gasification of carbon deposits on the catalyst surface.<sup>229</sup>

Kinetic investigations revealed that, under operation conditions relevant to DRM, the reverse water–gas shift (rWGS) reaction is partially equilibrated.<sup>214,230,231</sup> In this regard, DRM can be considered to be a combination of both rWGS and steam reforming of methane.<sup>198,232</sup> The reverse water–gas shift reaction itself represents a convenient method to produce synthesis gas as discussed in the next section.

**2.2.2.2. Reverse Water–Gas Shift.** The water–gas shift (WGS) reaction (Scheme 8) is operated on a large technical

**Scheme 8. (Reverse) Water–Gas Shift (rWGS) Reaction between CO<sub>2</sub> and Hydrogen as Well as CO and Water**



scale to adjust the ratio of CO, H<sub>2</sub>, and CO<sub>2</sub> in synthesis gas used in the production of hydrogen, Haber–Bosch ammonia, methanol, and hydrocarbons. WGS was first discovered by Carl Bosch and Wilhelm Wild in 1914 in their attempt to produce H<sub>2</sub> from steam and CO over an iron oxide catalyst.<sup>233</sup> Even though thermodynamically less favored than the direct hydrogenation of CO<sub>2</sub>, the reverse water–gas shift (rWGS) reaction gained increasing interest during the past several decades. rWGS is considered a potential key step in the production of methane<sup>234</sup> and Fischer–Tropsch products<sup>235</sup> from CO<sub>2</sub>. In this regard, rWGS products are also envisaged in space exploration, as, for example, the atmospheric concentration of CO<sub>2</sub> on Mars is approximately 95% and H<sub>2</sub> is readily available as a byproduct of oxygen generation.<sup>236,237</sup> More importantly in an earthly context, the rWGS reaction is an attractive pathway to utilize H<sub>2</sub> from renewable energies with CO<sub>2</sub> to provide CO as a C1-synthon for the production of methanol (see section 2.4) and thus takes a central role in the combination of CO<sub>2</sub> conversion with renewable energy.

The rWGS reaction can be catalyzed with heterogeneous catalysts at temperatures of around 200–600 °C<sup>238–241</sup> or even with molecular catalysts under relatively mild conditions.<sup>242–244</sup> The most common heterogeneous catalyst systems are based

on copper, such as Cu–Ni or Cu–Zn/Al<sub>2</sub>O<sub>3</sub>,<sup>245–248</sup> or supported ceria.<sup>249–251</sup> Several novel catalysts have been reported, even though comparison of the different systems is often challenging due to varying experimental conditions as well as incomplete information on the reaction rates, conversions, or yields.<sup>191</sup> As for dry reforming of methane, both noble- and non-noble-metal catalysts can be applied for the rWGS reaction. Noble metals, such as supported platinum at 500 °C, most often provide higher conversions, whereas catalysts based on non-noble metals, such as Cu, are preferred due to cost-efficiency and abundance.<sup>248</sup> Furthermore, Pt is prone to poisoning with CO and the formation of carbon deposits.<sup>252</sup>

Pt supported on ceria was shown to be a suitable catalyst for CO<sub>2</sub> conversion at low temperatures between 100 and 300 °C.<sup>253</sup> For Pt supported on Al<sub>2</sub>O<sub>3</sub>, a redox mechanism was postulated, in which O atoms formed from CO<sub>2</sub> dissociation refill vacant Al<sub>2</sub>O<sub>3</sub> surface sites or recombine with adsorbed H atoms.<sup>254</sup> Rhodium is predominantly used as a molecular catalyst for CO<sub>2</sub> hydrogenation.<sup>7</sup> Furthermore, Rh supported on several supports such as MgO, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, or TiO<sub>2</sub> resulted in high selectivity to methane and methanol at temperatures between 100 and 300 °C at H<sub>2</sub>/CO<sub>2</sub> feed ratios of 3:1.<sup>255</sup> The selectivity to CO is strongly dependent on the catalyst loading and dispersion of the metal on the surface of the support.<sup>256</sup> At high Rh loadings, large nanoparticles are formed, tending to hydrogenate CO<sub>2</sub> to CH<sub>4</sub> and thus suppressing CO selectivity. In accordance with that, Rh/SiO<sub>2</sub> shows higher selectivity to CO when increasing amounts of surface hydroxyl groups surround the supported Rh particles, as the formation of rhodium carbonyl clusters is preferred over hydride species on the surface.<sup>257</sup> Addition of lithium as a promoter led to an increase of selectivity to CO against CH<sub>4</sub> but also decreased CO<sub>2</sub> conversions for a Rh–Y-zeolite system.<sup>258</sup> While In<sub>2</sub>O<sub>3</sub> as a support is known to inhibit the conversion and selectivity toward CO,<sup>259</sup> bimetallic In–Pd/SiO<sub>2</sub> catalysts enable 100% selectivity toward carbon monoxide.<sup>260</sup> This effect is attributed to weaker CO adsorption on the bimetallic system as predicted from DFT studies, suppressing hydrogenation of CO to CH<sub>4</sub>. Nevertheless, while promoting the selectivity toward CO, addition of indium lowers the activity when compared to the parent Pd/SiO<sub>2</sub>.

In addition to their lower price, Cu-based catalysts achieve good performances at relatively low temperatures,<sup>239</sup> while no (or only little) CH<sub>4</sub> is produced during rWGS.<sup>241,261,262</sup> Nevertheless, high H<sub>2</sub>/CO<sub>2</sub> feed ratios are needed to perform the unfavorable CO<sub>2</sub> dissociation on Cu catalysts.<sup>263–265</sup> To achieve enhanced CO<sub>2</sub> conversions, high Cu dispersion on supporting materials is favorable, as was shown for Cu/SiO<sub>2</sub><sup>248</sup> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.<sup>246</sup> Furthermore, promoters can improve both catalyst activity and stability. Upon addition of iron to a Cu/SiO<sub>2</sub> system, sintering of the Cu nanoparticles was prevented, thus enabling long-term stability and activity.<sup>263,266</sup> With addition of potassium, the amount of surface active sites for adsorption and decomposition of formates was increased, which led to an increase of catalytic activity.<sup>267</sup> In contrast to Pt-based catalysts, formates were proposed to be the main reaction intermediates in the rWGS mechanism on Cu nanoparticles.<sup>238,241,267</sup> However, steady-state isotopic transient kinetic analysis (SSITKA) coupled with diffuse reflectance FT-IR spectroscopy (DRIFTS) has also been interpreted to indicate that formates and carbonyl intermediates play only a minor role for the rWGS reaction.<sup>268</sup>

Since the rWGS reaction is thermodynamically less favored when compared to the direct hydrogenation of CO<sub>2</sub>, the latter was considered to be a potential industrial candidate for the synthesis of methanol.<sup>269</sup> However, in the CAMERE process for carbon dioxide hydrogenation to form methanol, the overall methanol yield is increased when CO<sub>2</sub> is converted to CO via rWGS before methanol is formed over a Cu/ZnO/ZrO<sub>2</sub>/Ga<sub>2</sub>O<sub>3</sub> catalyst.<sup>270–272</sup> A comprehensive evaluation of the direct vs the indirect route to form methanol from CO<sub>2</sub> and H<sub>2</sub> is given in section 2.4.

**2.2.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Synthesis Gas.** Synthesis gas is an important intermediate in the chemical industry but is usually not sold or marketed directly as a final product. Due to this reason, no LCA is available in the literature that analyzes solely the production of syngas (mixture of H<sub>2</sub> and CO) from CO<sub>2</sub>. However, several LCA studies and technoeconomic assessments are available that analyze processes using CO<sub>2</sub>-based syngas as the feedstock, e.g., CO<sub>2</sub>-based methanol via syngas,<sup>273–276</sup> CO<sub>2</sub>-based dimethyl ether,<sup>277</sup> and CO<sub>2</sub>-based fuels via Fischer–Tropsch synthesis.<sup>278–280</sup> These studies are reviewed in the sections of this paper which focus on the corresponding final products. In the present section, we review one LCA study<sup>281</sup> that analyzed the supply of individual CO and H<sub>2</sub> streams from CO<sub>2</sub>-based syngas and attempt to derive general conclusions for different syngas routes. The supply of pure CO from CO<sub>2</sub>-based syngas is also considered by the same authors in a further LCA study<sup>282</sup> that focuses on the comparison of different CO<sub>2</sub>-based products (formic acid, CO, methanol, and methane). However, this later LCA study<sup>282</sup> is not considered in this section, because the results are presented per kilogram of hydrogen used (input-based functional unit). If the results are recalculated per output, the results are identical to those of the earlier LCA study.<sup>281</sup>

The LCA compares the two processes reverse water–gas shift (rWGS) and dry reforming of methane (DRM) to produce pure CO and hydrogen as individual products (0.216 kg of H<sub>2</sub>/kg of CO).<sup>281</sup> The results can be transferred to syngas supply (molar ratio H<sub>2</sub>/CO = 3) since the only difference is the electricity demand for the purification of products. This electricity demand is almost equal for rWGS and DRM, because they require a similar raw gas treatment. A molar ratio H<sub>2</sub>/CO = 3 was chosen, because both products are coproduced by fossil-based steam methane reforming in approximately the same ratio, which was considered as the benchmark process. As the rWGS process itself does not deliver hydrogen as a product, hydrogen is supplied by an electrolysis unit in the LCA study. The DRM process generates both CO and hydrogen that can be separated and isolated. However, to achieve a molar ratio H<sub>2</sub>/CO = 3, additional hydrogen supply is also required from an electrolysis unit.

In Figure 6, the global warming impacts of both rWGS and DRM are compared to those of the fossil-based production of CO and H<sub>2</sub>. The global warming impacts are recalculated from the LCA study<sup>281</sup> by considering the scenarios presented in Table 1. The process data of the rWGS and DRM processes are derived from process simulations assuming equilibrium conversion. For the rWGS process, about 60% CO<sub>2</sub> and 50% hydrogen are converted per pass. For the overall process, a conversion of 100% is obtained by recycling the unreacted reactants to the reactor. The CO yield of the overall process is over 99%. These data are based on the CAMERE process, for which a CO<sub>2</sub> conversion of 60% per pass is reported at 600 °C

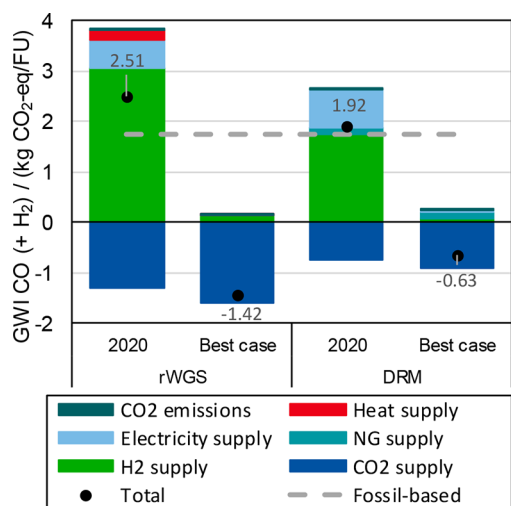


**Figure 6.** Global warming impact (GWI) of two CO<sub>2</sub>-based pathways for CO (+ H<sub>2</sub>) production (cradle-to-gate): reverse water–gas shift (rWGS; Scheme 5b) and dry reforming of methane (DRM; Scheme 5a). The results are presented for 1 kg of CO and 0.216 kg of H<sub>2</sub> (functional unit, FU). For each pathway, a scenario for 2020 and a best-case scenario are considered (Table 1) on the basis of the LCA data by Sternberg and Bardow.<sup>281</sup> The CO<sub>2</sub>-based processes are compared to the fossil-based steam methane reforming (dashed line).

using a zinc aluminate-based catalyst in a tubular catalytic reactor (see also section 2.4).<sup>272</sup> The DRM process is assumed to achieve a CO<sub>2</sub> conversion of about 85% per pass and 100% for the overall process. The yields for CO and hydrogen are about 97% and 90%, respectively. These data were chosen on the basis of a CO<sub>2</sub> conversion of about 90% as reported for reaction in a tubular reactor over a Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst at 750 °C.<sup>283</sup> It should be noted, however, that currently investigated catalysts are often operated at lower conversion rates to avoid coke formation (see section 2.2.4, Further Trends and Research Topics).

In the scenario 2020, the DRM process has a lower global warming impact than the rWGS process, which is primarily due to the lower hydrogen demand. Both DRM and rWGS have higher global warming impacts than the fossil-based process (1.74 kg of CO<sub>2</sub> equiv/FU) in this case, but lead to a very significant reduction in the best-case scenario. With increasing defossilization of the electricity generation, the rWGS process has lower global warming impacts than the DRM process, because the global warming impact of hydrogen supply is very low compared to that of the scenario 2020. The credit for CO<sub>2</sub> supply determines which process achieves the lowest global warming impacts under these conditions. The rWGS process

demands more CO<sub>2</sub> than the DRM process, because CO<sub>2</sub> is the only carbon source of the rWGS process, while the DRM process uses methane and CO<sub>2</sub> as carbon sources.

The DRM and rWGS processes have also higher fossil depletion impacts than the fossil-based process if hydrogen is supplied by steam methane reforming.<sup>281</sup> If hydrogen is supplied by an electrolysis unit using renewable electricity, the DRM and rWGS processes achieve lower fossil depletion impacts than the fossil-based process. For the case where CO<sub>2</sub> is obtained from capture at a coal-fired power plant, 12 further environmental impact categories were analyzed in the LCA study.<sup>281</sup> In this case, the DRM and rWGS processes are estimated to lead to higher environmental impacts than the fossil-based process in almost all impact categories even if the environmental impact of electricity supply is not considered. Only the DRM process achieves a lower photochemical oxidant formation than the fossil-based process. The environmental impacts are estimated to be higher due to the construction of the electrolysis unit and the supply of CO<sub>2</sub> from a coal-fired power plant. Thus, the impacts caused by the CO<sub>2</sub> supply can be decreased through the utilization of alternative CO<sub>2</sub> sources. Furthermore, the impact caused by the construction of the electrolyzer should only be considered as indicative because currently only very few LCA data sets are available for the construction of electrolysis units. Still, increasing the material and energy efficiencies of electrolyzers seems highly desirable from an environmental point of view. The example further shows that the analysis of further environmental impact categories is crucial to avoid problem shifting between reducing global warming impacts and other environmental categories.

#### 2.2.4. Further Trends and Research Topics: Catalyst Design, Robust Processes, and Alternative Energy Inputs.

**2.2.4.1. Catalyst Design and Piloting Activities for Dry Reforming and Reverse Water–Gas Shift.** The LCA studies discussed above reveal that the dry reforming of methane and the reverse water–gas shift reaction show good potential to reduce global warming impacts if renewable energy can be applied to the processes. In particular, one can identify different scenarios where either DRM or rWGS would be the preferred option: DRM enables CO<sub>2</sub> utilization without large amounts of additional hydrogen supply, which could be promising if renewable hydrogen is limited; in contrast, if hydrogen can be supplied with a very low carbon footprint, the rWGS reaction achieves the lowest global warming impacts. For rWGS to be advantageous, electricity would have to be supplied with global warming impacts of less than 0.05 kg of CO<sub>2</sub> equiv/(kW h) based on current electrolyzer efficiencies. These impacts correspond to current electricity from photovoltaics. The LCA studies also highlighted that—even with renewable

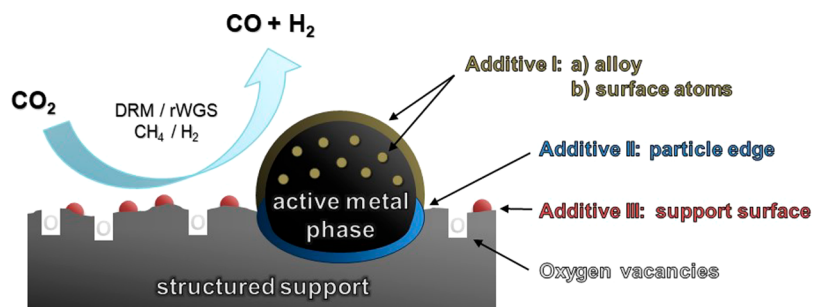


**Figure 7.** Catalyst optimization strategies envisaged for heterogeneous DRM and rWGS catalysts.

electricity as an input—improving electrolyzer technologies and selecting suitable CO<sub>2</sub> sources are crucial to avoid increasing other environmental impacts. Both DRM and rWGS reactions have reached high technology readiness levels, but the development of economic, efficient, and stable catalysts remains a major challenge for commercialization (Figure 7).

For dry reforming, especially the coke resistance of cost-efficient and abundant Ni catalysts will play a major role.<sup>190</sup> To enhance the stability of Ni-based catalysts by preventing Ni particle detachment from the support material, Pegios et al. investigated a reversed system, based on etched Ni foams incorporated in aluminum oxide, deposited by a dip-coating procedure.<sup>284</sup> The Ni foams, potentially further modified with MgO and SiO<sub>2</sub> promoters, still enabled high accessibility of the active metal surface. An ALSB/MgO@Ni catalyst, prepared via dip coating in aluminum tri-*sec*-butylate colloidal suspension, showed the highest activity, although deactivation via coke deposition and destruction of the morphology of the catalyst could not be fully prevented.

Another method to enhance the catalytic activity and coke resistance of Ni catalysts involves structuring of the support of the active phase. For example, perovskite-type catalysts could be further improved by structuring of the mixed metal oxide support. One example is the formation of Pd supported on LaCr<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3-δ</sub> nanowires, enhancing the exposure of active sites in comparison to that of the bulk materials, thus yielding higher turnover frequencies of 6.04 s<sup>-1</sup> for CH<sub>4</sub> at remarkable stability at 750 °C after 12 h on stream.<sup>285</sup> Another promising method to further enhance activity and coke resistance might be the incorporation of the active phase within a porous structure. In this regard, the pore system of mesostructured materials with high thermal resistance, such as mesoporous silica (e.g., SBA- or KIT-type materials), is finding attention.<sup>286</sup>

The increased specific surface area enhances both the dispersion and the accessibility of the active sites, while mass transfer limitations are overcome by the high porosity of the support. Due to the high thermal stability, sintering and agglomeration of the active sites are prevented. The first attempts at structuring bimetallic Ni–Co catalysts via impregnation on a mesoporous silica material of the INT-MM1 type led to lower conversions compared to that of a benchmark LaCo<sub>0.4</sub>Ni<sub>0.6</sub>O<sub>3</sub> perovskite catalyst.<sup>287</sup> However, both catalysts were stable for up to 100 h on stream. Furthermore, 12 wt % Ni on Ce-modified SBA-15 materials was investigated in terms of the Ce/Si ratio, with a Ce/Si molar ratio of 0.04 yielding the highest activity and stability.<sup>288</sup> Cerium was found to promote the dispersion of the Ni species within the support material, thus resulting in smaller particle sizes, while the pore walls of the SBA-15 support prevented agglomeration of the active species. Within a further study, it was found that 5 wt % Ni and 6 wt % Ce within SBA-15 were most active when Ce was impregnated prior to Ni as it tends to block the pores and thus prevents access to the catalytically active Ni phase.<sup>289</sup>

As an alternative to SBA-15 materials, Liu et al. investigated the potential of Ni-loaded KIT-6 ordered mesoporous SiO<sub>2</sub>.<sup>290</sup> The extremely small Ni particles resulted in high catalytic activity and very good carbon formation resistance. In a comparative study, La<sub>2</sub>NiO<sub>4</sub>/KIT-6 catalysts showed even better stability than La<sub>2</sub>NiO<sub>4</sub>/SBA-15 as a result of the unique cubic structure enhancing diffusion of reactant and product molecules in the course of the reaction.<sup>291</sup> The ordered mesoporous silica SBA-15 can also act as a hard template for

the structuring of perovskites.<sup>292</sup> After removal of the template, the perovskites with high specific surface areas of 150 m<sup>2</sup> g<sup>-1</sup> were reduced to form the active LaNiO<sub>3</sub> catalyst under partial loss of specific surface area ( $S_{\text{BET}}(\text{LaNiO}_3) = 50 \text{ m}^2 \text{ g}^{-1}$ ). A 90% conversion was reached with these mesoporous catalysts, while no coke formation could be observed. The stabilization of Ni particles and improved activity were attributed to the structural properties of the catalyst.

Since 2015, Linde AG has tested the production of synthesis gas via dry reforming on a pilot plant scale over Ni and Co catalysts at 800–1000 °C and 20 bar.<sup>293</sup> Novel catalysts for this pilot plant are developed in collaboration of Linde, the Karlsruhe Institute of Technology (KIT), BASF, HTE, and Dechema, and traces of steam are applied to reduce coking of the catalyst. The study also includes the assessment of the reintegration of CO<sub>2</sub> from industrial waste streams into the carbon cycle if the produced synthesis gas is used for valuable downstream production of base chemicals or fuels, such as dimethyl ether (DME). The production of the latter offers both improved energy balances and lower CO<sub>2</sub> emissions. Linde states that the energy efficiency of this process is significantly higher compared to that of the conventional reforming. If successful, commercialization of the so-called Dryref process at a reference plant for a Linde customer is planned for 2017.

For rWGS processes, numerous piloting and demonstration units are operating as integral parts of activities toward methanation, methanol production, or Fischer–Tropsch synthesis. Representative examples are discussed in the corresponding sections. Future research on catalyst design is directed toward advanced methodologies to enhance metal–support interfaces, oxygen vacancies within the support material, and support surface properties. In comparison to the dry reforming of methane, rWGS is only slightly endothermic, thus requiring lower temperatures to achieve high conversion. The CO<sub>2</sub> conversion is also favored by an excess of hydrogen, following the Le Chatelier principle.<sup>294</sup> A membrane reactor to separate the products has been used to achieve almost 100% CO<sub>2</sub> conversion, corresponding to approximately 5 times the equilibrium concentrations.<sup>295</sup> Furthermore, to achieve high CO selectivity, very low residence times are necessary.<sup>296</sup> Another option to further shift the reaction equilibrium and increase reaction rates is the application of an electric field to catalytically activate the reaction. In this manner, applying 3.0 mA to a 1 wt % Pt/10 mol % La–ZrO<sub>2</sub> catalyst resulted in the same outcome as if the reaction temperature was increased by 100 °C, with CO being the sole carbonaceous product.<sup>294</sup>

Among homogeneous catalyst systems, the triruthenium dodecacarbonyl precursor [Ru<sub>3</sub>(CO)<sub>12</sub>] introduced by Laine et al.<sup>296</sup> for the WGS reaction has been investigated extensively for the rWGS technology by Tominaga and Sasaki.<sup>244,297–299</sup> In the presence of iodide, suppressing formation of metallic ruthenium, they reported the hydrogenation of carbon dioxide to methane via carbon monoxide and methanol, in which [H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>12</sub>]<sup>2-</sup> was suggested to be the active species within a metal carboxylate reaction pathway. The mononuclear complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] can convert CO<sub>2</sub> and H<sub>2</sub> to CO in the presence of ethylene oxide, forming ethylene carbonate with the CO<sub>2</sub> and subsequently being hydrogenated to yield CO and ethylene glycol.<sup>300</sup> Further improvements could be achieved with [PPN][RuCl<sub>3</sub>(CO)<sub>3</sub>] in the presence of [PPN]Cl, resulting in a turnover number (TON) of 96 at 180 °C.<sup>242</sup> These catalytic systems become very attractive when the formation of CO is directly coupled to a subsequent

conversion with the same catalyst, e.g., if used for carbonylation reactions.<sup>3</sup> In this manner, storage and transportation of toxic carbon monoxide could be avoided by the use of CO<sub>2</sub> and thus be provided in situ for the chemical transformation via the rWGS reaction. This principle has been demonstrated or inferred for several reactions, including hydroformylation,<sup>301,302</sup> hydroaminomethylation,<sup>303</sup> hydroxycarbonylation,<sup>304,305</sup> and alkoxycarbonylation.<sup>306</sup> These reactions have been covered and discussed in a recent review in detail.<sup>1</sup> If these molecular systems could be integrated into a heterogeneous support, the catalysts might benefit from easy product separation and facile processing. An example for the immobilization of a molecular WGS shift catalyst was reported by Werner et al., supporting a RuCl<sub>3</sub> catalyst within a supported ionic liquid on different alumina phases.<sup>307</sup> When using boehmite as a support, the catalytic system even outperformed the commercial Cu-based catalyst under mild conditions.<sup>308,309</sup>

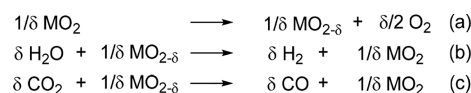
For heterogeneous catalysts, variation of active sites, support materials, and promoters plays a crucial role in catalyst design. In addition, also the different methods to support the active phase can strongly influence the activity and stability. This was shown for a Ni/CeO<sub>2</sub> system, in which both the oxygen vacancy sites and the dispersion of surface Ni species affected the catalyst activity strongly.<sup>249,310,311</sup> The mesoporous catalyst obtained via the template-assisted coprecipitation method showed higher stability compared to those obtained via the conventional coprecipitation methods while suppressing the formation of CH<sub>4</sub>.<sup>249</sup> Furthermore, the incorporation of the active Ni<sup>2+</sup> sites within the CeO<sub>2</sub> lattice produces a large number of oxygen vacancies, thus enhancing the reducibility of the surface CeO<sub>2</sub>.

Regarding support materials, among many different metal oxides, such as TiO<sub>2</sub>, MgO, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZnO,<sup>255,312</sup> lanthanide oxides were tested as novel support materials.<sup>313</sup> Among these, ceria was identified as the most suitable support as the activity followed the order CeO<sub>2</sub> > PrO<sub>2</sub> > La<sub>2</sub>O<sub>3</sub>. This effect has been attributed mostly to the high oxygen mobility within CeO<sub>2</sub>.<sup>253,268,314</sup> As the oxygen mobility of the oxide support increases at higher temperatures, CeO<sub>2</sub> shows almost 100% selectivity toward CO at higher temperatures of 550 °C.<sup>315</sup> For a Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, it was found that CO<sub>2</sub> can reoxidize the oxygen vacancies, while Pd facilitates the reduction of ceria.<sup>313</sup> Within a Pt/CeO<sub>2</sub> system, it is believed that, similar to the described mechanisms for DRM, CO<sub>2</sub> is believed to adsorb at a CeO<sub>2</sub> vacancy site near a platinum/ceria interface<sup>268</sup> or a platinum step.<sup>316</sup> Likewise, an oxygen species produced from CO<sub>2</sub> dissociation refills a vacant site, and CO is desorbed, possibly after migration to the Pt surface. Hence, CO<sub>2</sub> dissociation depends on the oxidation state of the CeO<sub>2</sub> support.<sup>253</sup> This interesting concept utilizing the redox properties of CeO<sub>2</sub> is also investigated within the so-called intensified rWGS reaction of CO<sub>2</sub>. In this approach, the metal oxide support becomes an oxygen carrier, which is first reduced via hydrogen and then oxidized via CO<sub>2</sub> during CO formation.<sup>317–319</sup> Since H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub> flows are separated, the methanation reaction can be suppressed, while product separation is facilitated, driving the equilibrium toward the desired product side. Furthermore, no excess of hydrogen is necessary for this approach, as stoichiometric reactions occur at the metal oxides. From experimental screenings combined with thermodynamic modeling, Fe-based transition-metal oxides showed the best CO<sub>2</sub> capacity at a wide range of temperatures for dry and steam reforming reactions.<sup>320,321</sup> Coherent with

that, the highest rates for the intensified rWGS reaction were observed for Fe-containing systems, showing the highest CO formation. At high temperatures and containing a high iron loading, a Fe<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> mixture resulted in the highest CO formation rates. This effect can be attributed to the high oxygen mobility within ceria, as discussed priorly.<sup>322</sup> As remarked by Daza and Kuhn, interestingly, Fe outperforms Cu in the intensified process, even though Cu is a widely applied catalyst for both the reverse and the conventional water–gas shift reaction.<sup>191</sup> The concept of oxygen mobility within metal oxides is the basic concept also for another interesting technology for the production of synthesis gas, the so-called (solar-driven) thermochemical dissociation of CO<sub>2</sub> and H<sub>2</sub>O discussed in the following section.

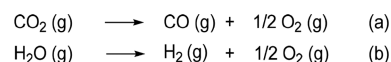
**2.2.4.2. Solar-Driven Thermochemical Dissociation of CO<sub>2</sub> and H<sub>2</sub>O.** The solar thermal dissociation of CO<sub>2</sub> and water involves their reduction to CO and hydrogen via two-step thermochemical cycles over the oxygen vacancies of a metal oxide providing high oxygen mobility.<sup>323–329</sup> Several oxides, such as CeO<sub>2</sub>, Er<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3–δ</sub>, and perovskite La<sub>0.6</sub>Sr<sub>0.4</sub>Cr<sub>1–x</sub>Co<sub>x</sub>O<sub>3–δ</sub>, as well as combinations with various dopants (e.g., Zr, Sr, or Mn) have been reported for this technology.<sup>330–334</sup> Furthermore, “volatile” ZnO/Zn<sup>335–338</sup> as well as other nonvolatile Fe<sub>3</sub>O<sub>4</sub>/FeO<sup>337–339</sup> redox systems have been investigated intensively. Among this variety of metal oxides, ceria stands out due to its rapid oxygen mobility<sup>340</sup> and stability over a broad range of oxidation states.<sup>341,342</sup> The general cycle of the thermochemical water or CO<sub>2</sub> splitting over non-stoichiometric oxides can be represented by the equations in Scheme 9.

#### Scheme 9. Thermochemical Cycle of Water and CO<sub>2</sub> Splitting over Nonstoichiometric Oxides



In the first endothermic step, the metal oxide is reduced to a nonstoichiometric state (Scheme 9a). This involves temperatures above 1000 °C or long time periods of several hours at lower temperatures to activate the metal oxides and form oxygen vacancy sites. Within the second exothermic step, ceria is then reoxidized via dissociation of water (Scheme 9b) or CO<sub>2</sub> (Scheme 9c) to hydrogen or CO over the metal oxide vacancy sites.<sup>343,344</sup> In this manner, O<sub>2</sub> and either hydrogen or CO evolve separately. Since ceria can be recycled, the net reactions can be summarized as given in Scheme 10.

#### Scheme 10. Net equation for Thermochemical Splitting of CO<sub>2</sub> (a) and Water (b)



Since the first reduction step is carried out with solar reactors containing the redox material directly exposed to high-flux solar irradiation,<sup>327,331,345–347</sup> low optical thickness is required to allow volumetric radiative absorption as well as uniform heating. For the reoxidation, high specific surface areas are beneficial to enhance the reaction kinetics.<sup>348</sup> To achieve this goal, porous structures containing voids in the range of millimeters that exhibit high specific surface areas but still

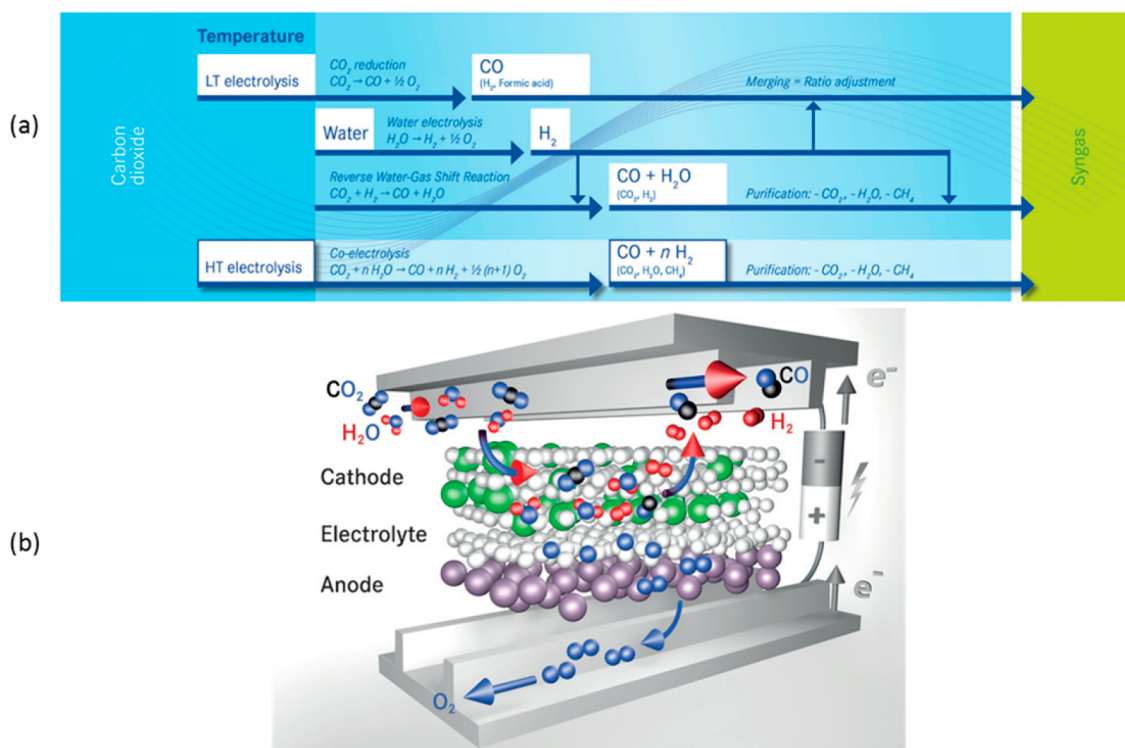


**Figure 8.** (a) Schematic representation of reaction steps during LT and HT coelectrolysis and (b) principle of CO<sub>2</sub> and H<sub>2</sub>O coelectrolysis. Reprinted with permission from ref 196. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA.

enable radiation penetration and volumetric absorption have been the focus of research. In this regard, ceria reticulated porous ceramic (RPC) structures have been developed, containing void sizes on two different scales.<sup>349</sup> Due to voids in the millimeter range, these materials are capable of volumetric radiative absorption during the reduction step. On the other hand, voids in the micrometer range allow for high specific surface areas, increasing the reaction rates during oxidation by a factor of 10.

Simultaneous splitting of water and CO<sub>2</sub> to obtain synthesis gas was shown experimentally for consecutive cycles.<sup>350</sup> The H<sub>2</sub>/CO molar ratio ranging from 0.25 to 2.34 is dependent on the H<sub>2</sub>O/CO<sub>2</sub> cofeeding ratio, in this study ranging from 0.8 to 7.7. Stable and constant syngas compositions could be achieved for 10 consecutive runs performed over an 8 h reaction time. So far, no attempt to optimize the solar reactor for maximum efficiency was conducted.<sup>331</sup> However, thermodynamic analysis indicates solar-to-fuel energy conversion efficiencies of 20% (without heat recovery) or exceeding 30% by recovery of heat of the hot products.<sup>351</sup>

The major drawback of this technology is the high temperature crucial for the endothermic activation of the metal oxide. Solar concentrators may be used to focus solar radiation and provide the high operational heat input. However, specialized and costly gear as well as additional equipment becomes inevitable.<sup>191</sup> Furthermore, the use of solar concentrators for heat input would be fully dependent on fluctuating solar radiation, limiting the technology area of operation strongly to a specific infrastructure and location. Nevertheless, techno-economic analysis studies are available that anticipate a methanol price competitive with other renewable-resource-based alternatives for the production of methanol via solar thermochemical dissociation of water and CO<sub>2</sub> with energy

conversion efficiencies of 20% combined with an overall efficiency of 7.1% from solar to methanol.<sup>275</sup>

**2.2.5. Coelectrolysis.** Electrochemistry can be considered an essential technology for efficient energy conversion systems allowing direct transformation of electrical into chemical energy.<sup>352</sup> Coelectrolysis, the simultaneous splitting of water and conversion of carbon dioxide, is a promising upcoming technology to produce synthesis gas from nonfossil resources (Figure 8). It can be carried out in two separate steps at low temperature (LT coelectrolysis) or in one integrated system at high temperature (HT coelectrolysis).<sup>196</sup> LT coelectrolysis comprises the direct reduction of CO<sub>2</sub> to CO, while hydrogen needs to be produced from an independent source and merged with CO to obtain synthesis gas. Within a scenario using renewable energy to produce synthesis gas, water splitting would be a suitable method for the hydrogen production side. A drawback of this technology would be the need for two separate processes to produce both components, hence leading to higher energy consumption and two different reactors to operate.<sup>353–357</sup> In this regard, HT coelectrolysis may offer potential for cost reductions and efficiency improvements, as it combines both the CO<sub>2</sub> reduction and steam electrolysis in one process step.<sup>358</sup> The typical setups and types of electrolyzers put into practice for water (steam), carbon dioxide, and coelectrolysis have been covered in recent publications and are not discussed within this review.<sup>195,196</sup> It is believed that H<sub>2</sub>/CO ratios ranging from 1:1 to 3:1 become accessible by varying the chosen parameters, such as temperature, current density, and materials, among others, even though the authors state that this is yet to be demonstrated, since product distributions as a function of operation parameters have not been the focus of research so far.<sup>196</sup> The resulting synthesis gas can be further processed into chemicals and fuels, e.g., via the Fischer–Tropsch process. In principle, this opens the possibility to

chemically store the energy for generating power with the same electrochemical device operating as a solid oxide fuel cell in the reverse mode.<sup>359</sup>

Solid oxide cells (SOCs) for electrolysis of steam and CO<sub>2</sub> were first proposed in 1981, where the major interest was to produce oxygen for applications in submarines and space.<sup>353</sup> The reversible operation of a tubular 8 mol % yttrium oxide-stabilized zirconium oxide (8YSZ) SOC was demonstrated for humidified CO/CO<sub>2</sub> mixtures. Most recent publications on HT coelectrolysis are directed to cells<sup>356,357,360–367</sup> and stacks<sup>355,368–372</sup> established in solid oxide fuel cell (SOFC) applications. Especially Ni/8YSZ–8YSZ–LSM/8YSZ–LSM (LSM = strontium-doped lanthanum manganite composite) systems have been extensively studied regarding various fuel feed compositions.<sup>356</sup>

Impurities such as sulfur contaminants can segregate and hinder electrochemical reaction, and purification of the feed gases is recommended.<sup>354,357,373</sup> Furthermore, delamination of the oxygen electrode at the electrode–electrolyte interface can occur due to the high partial pressure of oxygen, causing pore and thereupon crack formation.<sup>374,375</sup> The cracks will cause a decrease in conductivity of the electrolyte and thus an increase in the cell voltage. With increasing expansion of the cracks, delamination of the electrode from the electrolyte is promoted. Another degradation of the cell voltage results from coarsening of Ni particles in the fuel electrode as the numbers of reactive sites and electronic conductivity pathways are reduced.<sup>374,376</sup> At last, carbon deposition at high operating voltages can have a negative effect on the electrochemical performance of the cell.<sup>377,378</sup>

So far, only few research studies have focused on alternative materials to minimize degradation of the setup.<sup>379–385</sup> A perovskite of the (La<sub>0.75</sub>Sr<sub>0.25</sub>)<sub>0.97</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3–δ</sub> (LSCM) type is attractive due to its high persistence toward an oxidizing atmosphere.<sup>379–381</sup> Therefore, it can be used both for the fuel and for the oxygen electrode, without the need for a reducing atmosphere at the fuel electrode side. Another promising setup is a symmetric cell consisting of an Sr<sub>2</sub>Fe<sub>1.5</sub>Mo<sub>0.5</sub>O<sub>6</sub> + Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> electrode and an LSGM electrolyte.<sup>384</sup> For this cell, an ASR (area-specific resistance) approaching the values for LSM + 8YSZ–8YSZ–Ni + 8YSZ cells has been reported. In this regard, future research will be directed toward development of novel setups and materials in terms of enhancing performance and long-term stability even further. As stated before, it is also yet to be demonstrated how product distributions can be influenced depending on the operation parameters.<sup>196</sup>

In summary, syngas is a very attractive platform that can be accessed from CO<sub>2</sub> with various technologies. An interesting perspective of this strategy is the potential for utilization of established technologies and existing infrastructures for syngas conversion. However, this is an advantage and limitation at the same time. The resulting potential benefits are concentrated entirely on the energy source and energetic efficiency of the conversion technology for this single step in the value chain. As we will see in the following sections, additional opportunities arise if the CO<sub>2</sub> conversion leads to the desired products directly.

### 2.3. Carboxylic Acids and Carboxylation Reactions

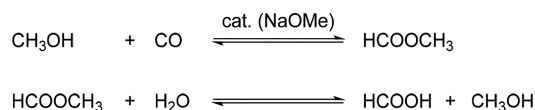
#### 2.3.1. Formic Acid. 2.3.1.1. Background and Motivation.

Formic acid was industrially produced as a commodity chemical with a production rate of 720000 t/a in 2013.<sup>386</sup> Today, the

largest volume application of formic acid is silage preservation.<sup>14,387</sup> Furthermore, formic acid is used in the leather and textile industry and rubber industry, for steel pickling and wood pulping, and for the synthesis of organic chemicals (around 10%), such as pharmaceuticals and crop protection products.<sup>1,14,387</sup> BASF is the world market leader, with an annual production capacity of 305000 t,<sup>388</sup> followed by BP and Eastman.<sup>389</sup>

The most commonly used production process of formic acid is the formal carbonylation of water in a two-step process via methyl formate (Scheme 11).<sup>387</sup> The liquid-phase carbon-

**Scheme 11. Production of Formic Acid from CO and Water via Methyl Formate**

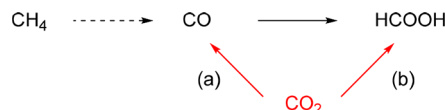


ylation of methanol with CO is carried out in the presence of a base catalyst, for example, sodium or potassium methoxide (NaOCH<sub>3</sub> or KOCH<sub>3</sub>). Typical reaction conditions are 80 °C, 45 bar of pressure, and 2.5 wt % sodium methoxide catalyst. Under these conditions, conversions of 30% for methanol and 95% for CO are achievable. Recycling of the unconverted methanol results in a nearly quantitative conversion of methanol to methyl formate. In the second step, methyl formate is hydrolyzed to formic acid and methanol. In this process, formic acid itself acts as a hydrolysis catalyst (autocatalysis). However, the hydrolysis equilibrium is relatively unfavorable and requires a large excess of water. Consequently, the energy requirements to remove the water are a critical factor. The CO used in the process is obtained from fossil resources, tracing the value chain, for example, back to methane as the carbon source.

##### 2.3.1.2. Current Status of CO<sub>2</sub> Conversion to Formic Acid.

In principle, there are two possibilities for the integration of CO<sub>2</sub> into the synthesis of formic acid: (a) generation of CO from CO<sub>2</sub> followed by the commercial carbonylation process and (b) direct hydrogenation of CO<sub>2</sub> to form formic acid (Scheme 12).

**Scheme 12. Possible Pathways for the Integration of CO<sub>2</sub> into the Synthesis of Formic Acid**



Similar to the current commercial scale hydrolysis step, thermodynamic limits of the direct hydrogenation of CO<sub>2</sub> result in challenges for the downstream processing to isolate the product. Whereas a wide variety of efficient catalytic systems are available, only few processing schemes have been developed to address this challenge.<sup>1</sup> An interesting process for the direct synthesis of formic acid from CO<sub>2</sub> was patented and reported by Schaub and Paciello from BASF in 2010/2011.<sup>390–392</sup> The BASF process was tested on a pilot scale. The developed process can be divided into three parts: (1) hydrogenation, (2) catalyst extraction, and (3) product separation (Figure 9). First, CO<sub>2</sub> is hydrogenated in the presence of NHex<sub>3</sub> and high-boiling diols, resulting in the

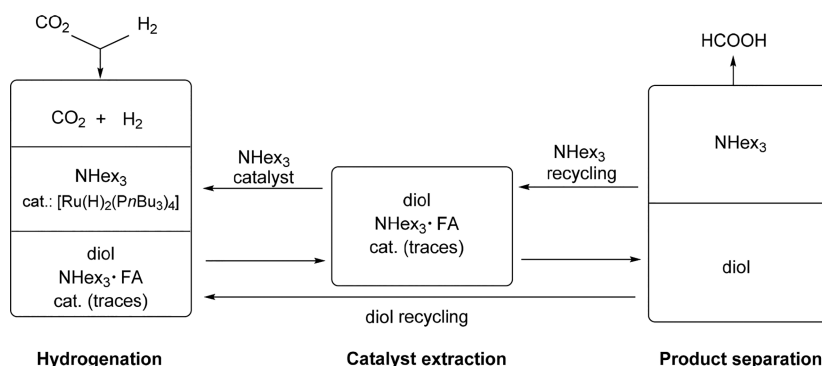


**Figure 9.** Process concept of the hydrogenation of CO<sub>2</sub> to formic acid in the presence of NHex<sub>3</sub> and diol, presented by BASF.<sup>391,392</sup>

formation of the corresponding amine adduct. FA–NHex<sub>3</sub> adducts are soluble in polar solvents such as diols, which leads to the formation of a biphasic system with the nonpolar amine NHex<sub>3</sub>. The catalyst [Ru(H)<sub>2</sub>(PnBu<sub>3</sub>)<sub>4</sub>] is preferably dissolved in the nonpolar amine phase. After reaction, the phases are separated, and the amine/catalyst phase is reused for hydrogenation. The product phase still contains traces of catalysts that are extracted with NHex<sub>3</sub> and recycled to the hydrogenation step. In the last step, diol, amine, and formic acid are separated from the product phase by distillation. Complete catalyst separation before distillation is necessary since otherwise decomposition of formic acid to CO<sub>2</sub> and H<sub>2</sub> occurs. The diol is reused for the hydrogenation and the amine for the extraction of the catalyst in the second step. Further investigations by BASF indicated that the use of low-boiling solvents, such as methanol, ethanol, and/or water instead of the diol results in higher yields of the formic acid/amine adduct.<sup>393</sup> Furthermore, it was shown that adding CO to the mixture before distillation deactivates the catalyst and previous extraction is not required. The catalyst could be reactivated under the reaction conditions in the hydrogenation reactor.

Recently, another piloting activity to validate a CO<sub>2</sub>-based formic acid process has been initiated by the company Reactwell.<sup>394,395</sup> Their study is based on a process developed by the Leitner group<sup>396,397</sup> in 2012 which allows the continuous hydrogenation of CO<sub>2</sub> to pure formic acid in a biphasic system (Figure 10). In this concept, CO<sub>2</sub> is used under supercritical conditions as the mobile phase and combined with an ionic liquid (IL) as the stationary phase containing the ruthenium catalyst and the nonvolatile base. Under these conditions, the supercritical phase carries both reagents efficiently into the IL phase where CO<sub>2</sub> is hydrogenated to formic acid, which is in situ extracted and carried out of the reactor. Thermodynamically, the solvation of formic acid in the scCO<sub>2</sub> (sc = supercritical) phase can be regarded as the driving force. Overall, this reaction system integrates the reaction and the separation in a single process unit. Under laboratory conditions, total turnover numbers remained limited due to high catalyst loadings, but excellent stable performance was achieved under continuous-flow conditions over 200 h.

**2.3.1.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Formic Acid.** The direct hydrogenation of CO<sub>2</sub> to formic acid (Scheme 12b) has been evaluated in a recent LCA study,<sup>282</sup> wherein two process simulations were analyzed from the literature.<sup>398,399</sup> Both process simulations are based on data from patents of the previously described BASF process (Figure 9).<sup>391,392</sup> The two process simulations vary in (a) the choice of batch experiments from patents, (b) predicted thermodynamics

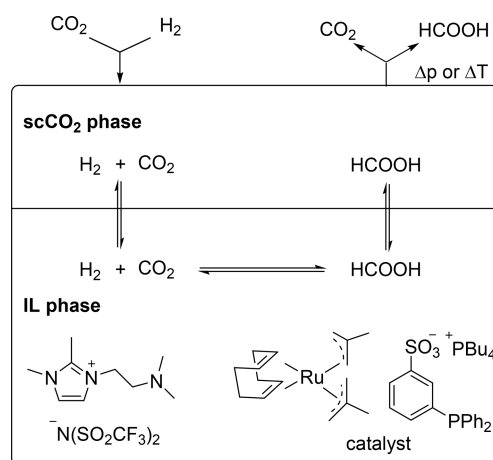


**Figure 10.** Process scheme of a fully integrated process for the ruthenium-catalyzed continuous-flow hydrogenation of CO<sub>2</sub> to pure formic acid by using a stationary IL phase and an scCO<sub>2</sub> mobile phase.<sup>397</sup>

for dissolved hydrogen, and (c) product separation. These differences lead to different conversions of hydrogen in the overall process (see Table 4).

For the CO<sub>2</sub>-based production of CO followed by the commercial carbonylation to formic acid (Scheme 12a), an LCA study is so far missing. However, process data for CO<sub>2</sub>-based production of CO via rWGS can be derived from the study discussed in section 2.2.<sup>281</sup> On the basis of these data, the CO<sub>2</sub>-based production of CO for the commercial carbonylation process is also considered in our discussion.

In Figure 11, the results for the global warming impact of the CO<sub>2</sub>-based processes are benchmarked to the commercial fossil route to formic acid. For the CO<sub>2</sub>-based processes, the process data were used from Sternberg et al.<sup>282</sup> using the scenarios presented in Table 1. For the fossil-based formic acid process, steam reforming of methane was used for CO production in the commercial carbonylation to formic acid (Scheme 11). Since steam reforming coproduces CO and hydrogen, the global warming impact of the fossil route has a range which depends on the credit assigned for the coproduced hydrogen: If the coproduced hydrogen replaces the hydrogen supply by steam methane reforming in other chemical processes (credit: 10.6 kg of CO<sub>2</sub> equiv/kg of H<sub>2</sub>), the global warming impact of the fossil-based process is 1.1 kg of CO<sub>2</sub> equiv/kg of HCOOH. If the coproduced hydrogen is used for heating purposes and replaces the heat supply by natural gas (credit: 7.4 kg of CO<sub>2</sub>

Table 4. Process Details for Process Concepts Considering Direct Hydrogenation of CO<sub>2</sub> to Formic Acid

| reference                          | conversion rates (%)                                                                                         | reaction conditions | catalyst                       | comment                                                                                   |
|------------------------------------|--------------------------------------------------------------------------------------------------------------|---------------------|--------------------------------|-------------------------------------------------------------------------------------------|
| Pérez-Fortes et al. <sup>399</sup> | process: H <sub>2</sub> , 62; CO <sub>2</sub> , 96<br><br>reactor: H <sub>2</sub> , 19; CO <sub>2</sub> , 81 | 105 bar, 93 °C      | ruthenium- and phosphine-based | purity of HCOOH, 85 wt %<br><br>conversions based on data from patents <sup>391,392</sup> |
| Jens et al. <sup>398</sup>         | process: H <sub>2</sub> , about 97; CO <sub>2</sub> , about 97                                               | 94 bar, 50 °C       | not considered                 | purity of HCOOH, 99 mol %<br>conversions based on data from patents <sup>391,392</sup>    |

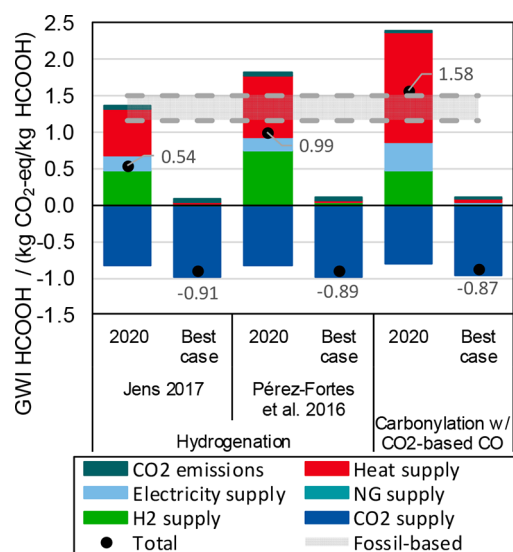


**Figure 11.** Global warming impact (GWI) for CO<sub>2</sub>-based formic acid production as compared to the current industrial benchmark (cradle-to-gate). Two different pathways are shown: hydrogenation of CO<sub>2</sub> (Scheme 12b) and carbonylation with CO<sub>2</sub>-based CO (Scheme 12a). For the direct hydrogenation, two process concepts from the literature are shown (Jens<sup>398</sup> and Pérez-Fortes et al.<sup>399</sup>). For each process, a scenario for 2020 and a best-case scenario are considered (Table 1). Furthermore, the CO<sub>2</sub>-based processes are compared to the fossil-based process (Scheme 11, range of dashed lines). For the fossil-based process, a range is shown, because steam methane reforming coproduces hydrogen: the upper bound applies if hydrogen is used thermally and the lower bound applies if hydrogen is used chemically.

equiv/kg of H<sub>2</sub>), the global warming impact of the fossil-based process is 1.5 kg of CO<sub>2</sub> equiv/kg of HCOOH.

In the scenario 2020, the global warming impact of CO<sub>2</sub>-based formic acid ranges from 0.54 to 1.58 kg of CO<sub>2</sub> equiv/kg of HCOOH. In the best-case scenario, the global warming impacts are in fact negative for all considered processes (−0.91 to −0.87 kg of CO<sub>2</sub> equiv/kg of HCOOH) since CO<sub>2</sub> is consumed and all other impacts are low. The lowest global warming impact is found for the process concept discussed by Jens.<sup>398</sup> The global warming impact of the process concept from Pérez-Fortes et al.<sup>399</sup> is higher due to a lower H<sub>2</sub> conversion and thus higher H<sub>2</sub> losses (see Table 4). The higher H<sub>2</sub> demand has a particularly negative effect in the scenario 2020. Remarkably, both process concepts for direct hydrogenation achieve lower global warming impacts than the fossil-based process even for the scenario 2020. This is associated mainly with the high energy demand for the methyl formate hydrolysis step of the fossil-based process. The energy-intensive distillation process of the formic acid/water mixture with a large excess of water is circumvented in the direct hydrogenation of CO<sub>2</sub> by the extraction process. Although the

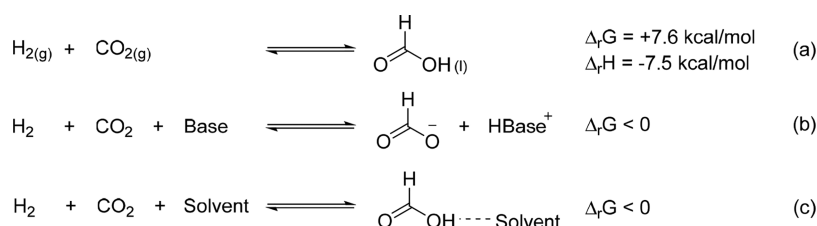
formic acid/amine mixture also requires thermal cleavage, the overall energy requirements are still favorable.

In total, the fossil-based process requires about 19.25 MJ of heat/kg of formic acid, while the direct hydrogenation of CO<sub>2</sub> to formic acid requires 9–12 MJ of heat/kg of formic acid.<sup>282</sup> This indicates that the heat demand of the direct hydrogenation of CO<sub>2</sub> is lower than for the fossil-based process, even though the chemical transformation is of course thermodynamically more favorable for the carbonylation of water. However, the correct basis for comparison of the life cycles must comprise the complete chain of transformations from methane in the fossil route. In this case, an improvement results from the lower overall process heat demand for the CO<sub>2</sub>-based route, which is mainly caused by purification processes constituting a major contribution to the total global warming impacts in both cases. Consequently, the utilization of CO<sub>2</sub>-based CO for the commercial carbonylation process (Scheme 12a) has the highest global warming impact in the scenario 2020, because the energy-intensive purification of the commercial formic acid process is not avoided. The utilization of CO<sub>2</sub>-based CO for commercial carbonylation would therefore require the input of renewable energy (best-case scenario) to achieve lower global warming impacts than the fossil-based process. In contrast, the direct hydrogenation of CO<sub>2</sub> provides a “shortcut” to the desired product that overcompensates the thermodynamic difference in the final reaction step.

In addition to reducing the global warming impacts, the hydrogenation of CO<sub>2</sub> to formic acid has the potential to also reduce fossil depletion impacts compared to the fossil-based formic acid production.<sup>282</sup> If hydrogen is supplied by steam methane reforming, the CO<sub>2</sub> source has to be considered as a decisive factor: If CO<sub>2</sub> is taken from emissions of concentrated sources, the fossil depletion impact is reduced. If CO<sub>2</sub> is supplied from air, the fossil depletion impact is not reduced due to the higher energy demand for air capture.

**2.3.1.4. Further Trends and Research Topics: Downstream and Upstream Integration of the Catalytic Conversion into the Value Chain.** The LCA studies show that the direct hydrogenation of CO<sub>2</sub> to formic acid is an attractive potential pathway to integrate CO<sub>2</sub> into the value chain. Remarkably, this synthesis can reduce the carbon footprint and the fossil resource depletion for HCOOH production compared to the conventional route even in a fossil-based scenario. Obviously, the benefit would further increase if nonfossil hydrogen can be utilized on the basis of renewable energy. The largest improvements result if the integration of CO<sub>2</sub> into the final product is achieved most directly. Thus, the potential benefits depend most strongly on the employed feedstock and the energy demand of the separation steps. Technology developments focusing on the development of largely integrated process concepts appear therefore most promising.

**Scheme 13. Influence of Basic Additives and Reaction Media on the Thermodynamics of the Hydrogenation of CO<sub>2</sub> to Formic Acid (Gibbs Free Energy  $\Delta_r G$  and Enthalpy  $\Delta_r H$ )<sup>402</sup>**



The available results thus show that the upstream and downstream integrations are important factors to leverage the potential and to maximize the benefits from CO<sub>2</sub>-based formic acid production. In this context, the thermodynamics of the direct hydrogenation of CO<sub>2</sub> to formic acid define a natural limit. The gas-phase reaction of CO<sub>2</sub> and H<sub>2</sub> is strongly endergonic because of the strong and unfavorable entropic contribution (Scheme 13a). The thermodynamics can be rendered favorable by the presence of basic additives and/or by the choice of the reaction solvent.<sup>400,401</sup> The presence of a basic additive, such as ammonia or amines, leads to an exothermic protonation of the base caused by formic acid and an exergonic reaction (Scheme 13b). An exergonic reaction can be achieved by solvation effects using water or other strongly hydrogen bonding solvents (Scheme 13c). The aim for process design is to minimize any extra energy requirements resulting from these stabilizing effects during the workup to reduce the “additional penalty” to the overall energy balance.

In the past several decades, a large number of catalysts with remarkable activities even under mild reaction conditions have been developed for the hydrogenation of CO<sub>2</sub> to formic acid, and the subject has been reviewed extensively.<sup>1,7,9,10,400,403–407</sup> In the following sections, we therefore focus on recent developments of downstream processes to recycle the catalysts and to separate the pure formic acid from the reaction mixture as well as on systems that allow upstream integration with possible CO<sub>2</sub> sources in the value chain.

In attempts to simplify the downstream separation, efforts have been made to avoid the formation of base adducts in the synthesis of formic acid with CO<sub>2</sub> and H<sub>2</sub>. Shifting the reaction equilibrium by choice of the reaction solvent reduces the number of components in the product mixture. In early studies, dimethyl sulfoxide (DMSO) and water were identified as favorable solvents for the hydrogenation of CO<sub>2</sub> to formic acid.<sup>408,409</sup> The formation of free formic acid was observed in DMSO with the most active ruthenium catalyst [ $\{\text{Rh}(\text{cod})(\mu\text{-H})\}_4$ ]/dppb available at the time. However, the concentration (0.034 mol L<sup>−1</sup> after 6.5 h) was orders of magnitude lower in comparison to that of the reactions in the presence of a base. In 2014, Moret et al.<sup>410</sup> reported the first catalyst which could generate high formic acid concentrations in the absence of a base. Using the catalyst  $[\text{RuCl}_2(\text{PTA})_4]$  (PTA = 1,3,5-triaza-7-phosphaadamantane) in DMSO resulted in a final formic acid concentration of 1.9 mol L<sup>−1</sup> corresponding to a TON of up to 700 in 120 h under optimized conditions (60 °C, 100 bar, CO<sub>2</sub>/H<sub>2</sub> ratio of 1:1). Moreover, the recycling of the catalyst was demonstrated whereby an active Ru species was obtained as a dry powder upon removal of all volatiles under vacuum. The basic thermodynamic data for stabilization of HCOOH by solvation in DMSO mixtures were also confirmed experimentally.<sup>411</sup>

Rohmann et al.<sup>402</sup> reported that the ruthenium-based catalyst  $[\text{Ru}(\text{Acridophos})(\text{PPh}_3)(\text{Cl})(\text{PhCO}_2)]$  allowed a combination of high activity and productivity in DMSO as a stabilizing solvent. Under optimized conditions (60 °C, 80 bar of H<sub>2</sub>, 40 bar of CO<sub>2</sub>, 16 h), TONs and turnover frequencies (TOFs) of up to 4200 and 260 h<sup>−1</sup> were obtained in a mixture of DMSO and water (95:5, v/v), but still at relatively low HCOOH concentration. Detailed DFT calculations revealed the molecular basis for the stabilizing effect of DMSO as a solvent and helped to identify the proton concentration as one of the limiting factors for catalyst productivity. On the basis of these insights, a further optimization was achieved by adding substoichiometric amounts of an acetate buffer to the reaction solution, resulting in an average TOF of 1019 h<sup>−1</sup> and a formic acid concentration of 1.27 mol L<sup>−1</sup>.

According to basic thermodynamic data, water should also be a potentially suitable medium for base-free hydrogenation of CO<sub>2</sub>. In 2016, Li and co-workers<sup>412</sup> described a very active iridium-based catalyst for the synthesis of formic acid in water and in the absence of base. At 80 °C and elevated pressure (50 bar, CO<sub>2</sub>/H<sub>2</sub> ratio of 1:1), a TOF of 13000 h<sup>−1</sup> was achieved in 5 h, albeit at a relatively low formic acid concentration of 0.27 mol L<sup>−1</sup>. Ionic liquids have also been reported as base-free reaction media. Yasaka et al.<sup>413</sup> reported in their study on the decomposition of formic acid that the equilibrium can be shifted to the formic acid side if the reaction is conducted in the ionic liquid 1,3-dipropyl-2-methylimidazolium formate. The group of Leitner<sup>397</sup> showed that the use of 1-propyl-2,3-dimethylimidazolium formate as the solvent for the hydrogenation of CO<sub>2</sub> results in high TONs (1968) and TOFs (295 h<sup>−1</sup>) and a high corresponding formic acid concentration of 3.94 mol L<sup>−1</sup>.

Although the use of solvation reduces the number of components by making the base obsolete, the effect of the strong interactions between formic acid and the reaction medium for the compensation of the unfavorable entropic contribution on downstream processes cannot be assessed easily. It remains to be validated how the pure formic acid can be isolated from reaction mixtures where strong interactions such as hydrogen bonds between the solvent and solute are critical for its stabilization.

If distillation of the product mixture is envisaged to isolate the product, it is mandatory to remove any catalytically active species before because the decomposition reaction of formic acid is generally thermodynamically favored at reduced pressure and increased temperatures in any reaction mixture. The separation of the catalyst before downstream processing can be achieved efficiently if a phase boundary between the active component and the product is introduced. One possibility to achieve such a phase boundary is the immobilization of the organometallic catalyst on solid supports. In recent years, several immobilized catalysts have been developed for the

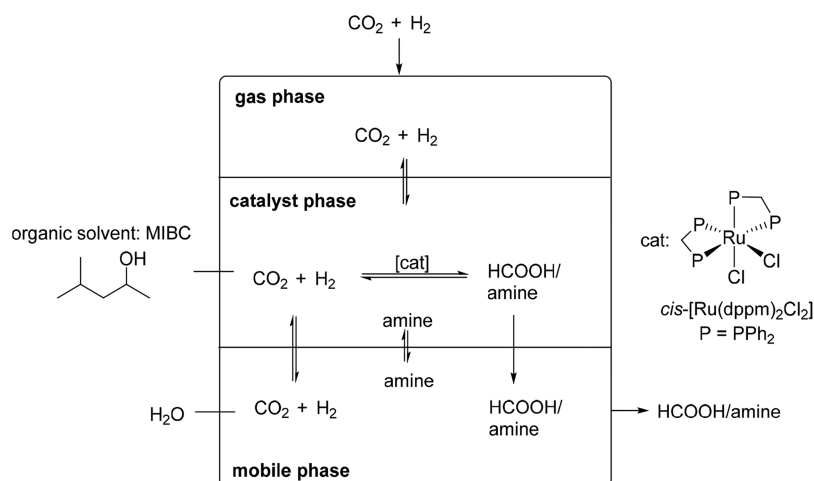


**Figure 12.** Process scheme of the hydrogenation of  $\text{CO}_2$  to formic acid in a biphasic system, comprising mono- and diethanolamines as used in  $\text{CO}_2$  scrubbing processes.<sup>430</sup>

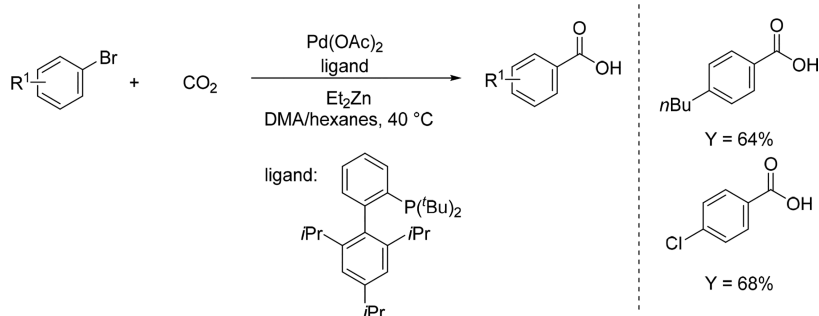
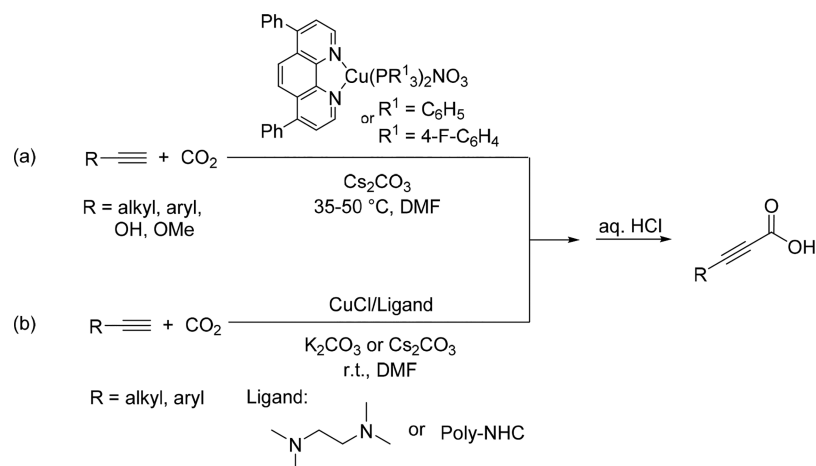
hydrogenation of  $\text{CO}_2$  to formic acid. Zhang et al.<sup>414,415</sup> used a ruthenium phosphine catalyst immobilized on amino-functionalized silica and achieved high TOFs of up to  $1384 \text{ h}^{-1}$  in  $\text{EtOH}/\text{NEt}_3/\text{scCO}_2$  ( $80^\circ\text{C}$ , 40 bar of  $\text{H}_2$ , 120 bar of  $\text{CO}_2$ ). Similar results were obtained by Ying-Min et al.<sup>416</sup> in 2005. In 2013, Hicks and co-workers<sup>417</sup> developed an iridium-based catalyst supported on SBA-15. Using  $\text{IrCl}_3$  immobilized by coordination to an iminophosphine ligand which was covalently bound to the support, TOFs of up to  $1200 \text{ h}^{-1}$  were achieved in  $\text{H}_2\text{O}/\text{NEt}_3$  ( $120^\circ\text{C}$ , total pressure 40 bar). The catalyst was recycled 10 times by filtration, and only slight deactivation was observed. The use of a solid-supported ruthenium catalyst in water combined with an ionic liquid containing a tertiary amino group as a nonvolatile base for the synthesis of formic acid was reported by the group of Han.<sup>418</sup> After the reaction, the solid catalyst was separated by filtration, water was evaporated at  $110^\circ\text{C}$ , and formic acid was isolated by passing a  $\text{N}_2$  stream over the IL solution at  $130^\circ\text{C}$ . Under optimized conditions ( $70^\circ\text{C}$ , 180 bar of total pressure), a TOF of  $103 \text{ h}^{-1}$  was achieved, and the catalyst was reused four times. Furthermore, phosphorus-based porous polymers loaded with Ru complexes exhibit high activity and selectivity in the base-free decomposition of formic acid to  $\text{CO}_2$  and  $\text{H}_2$ .<sup>419</sup> On the basis of microscopic reversibility, these materials could also be interesting for the synthesis of formic acid.

Another approach to integrated catalyst separation is multiphase catalysis, where the catalyst resides in an immiscible liquid phase. Already in 1989, BP Chemicals described a biphasic reaction system for the hydrogenation of  $\text{CO}_2$  to formic acid using aliphatic or aromatic hydrocarbons as the catalyst phase and alcohols or water as the product phase for formic acid adducts with trialkylamines (usually  $\text{NEt}_3$ ).<sup>420,421</sup> The catalyst solution was reused three times, but only low TONs (150–190) were achieved. In 2003, Behr et al.<sup>422</sup> demonstrated the in situ extraction of formic acid in a biphasic system. Formic acid was extracted from the aqueous solution containing the water-soluble catalyst  $\text{RuCl}_3/\text{TPPTS}$  (triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) by using *N,N*-dibutylformamide as a solvent. Due to the catalyst loss of 6–9 wt % after the first extraction, a back-extraction of the organic product phase with water was necessary.

Whereas the amine is often perceived as a possible problematic component in the downstream processing, it may

provide a potential link for the upstream integration with  $\text{CO}_2$  sources. Aqueous amine solutions are used on a commercial scale as  $\text{CO}_2$ -scrubbing media. Combining this technology with the hydrogenation of  $\text{CO}_2$  to formic acid would provide an attractive strategy if the same solution can be utilized for both parts of the overall process. This would avoid the energy-intensive and costly separation of  $\text{CO}_2$  from the scrubbing solution by converting it directly into a potentially valuable chemical. The hydrogenation of  $\text{CO}_2$  to formate in aqueous amine solutions was first demonstrated in 1993.<sup>423</sup> Using water-soluble rhodium catalysts (Wilkinson-type), formic acid concentrations up to  $3.63 \text{ mol L}^{-1}$  and TONs up to 3439 were achieved under mild conditions (40 bar,  $\text{CO}_2/\text{H}_2$  ratio of 1:1, room temperature,  $\text{HNMe}_2$ ). The possibility to use aqueous solutions comprising ethanolamines, which are used in commercial scale  $\text{CO}_2$ -scrubbing processes, was also demonstrated.<sup>424</sup> Also, other catalyst systems have been reported for the hydrogenation of  $\text{CO}_2$  in aqueous solutions in the presence of amines or inorganic bases.<sup>425–427</sup> However, the use of water-soluble catalysts in aqueous media results in challenging catalyst separation processes as described above.

In an attempt to combine  $\text{CO}_2$  capture and conversion, the Hicks group combined the catalyst system based on  $\text{IrCl}_3$  with iminophosphine ligands with poly(ethylenimine) (PEI) as the support.<sup>428</sup>  $\text{CO}_2$  capture for these materials was demonstrated by dry  $\text{CO}_2$  capture experiments using thermogravimetric analysis, while the catalytic activity was tested using the material in  $\text{water}/\text{NEt}_3$  as the reaction medium ( $\text{TOF} = 248 \text{ h}^{-1}$ ,  $120^\circ\text{C}$ , 20 bar of  $\text{CO}_2$ , 20 bar of  $\text{H}_2$ ). However, the combination of  $\text{CO}_2$  capture and subsequent  $\text{CO}_2$  hydrogenation was not demonstrated in this study. In 2016, Olah, Parkash, and co-workers<sup>429</sup> proposed a concept which combines  $\text{CO}_2$  capture by amines in aqueous media and its subsequent conversion to formate. The used amines, for instance, tetramethylguanidine (TMG) or diazabicyclo[2.2.2]octane (DABCO), served dual purposes of capturing  $\text{CO}_2$  on the one hand and stabilizing the formate product on the other hand. High yields of up to 95% of the formate product were obtained under mild reaction conditions (50 bar of  $\text{H}_2$ ,  $55^\circ\text{C}$ ) in the presence of Ru- and Fe-based pincer complexes in water. Furthermore, the recyclability of the catalyst was demonstrated in a biphasic system comprising water and 2-methyltetrahydrofuran. By

Scheme 14. Pd-Catalyzed Carboxylations of Aryl Bromides with CO<sub>2</sub><sup>442</sup>Scheme 15. Cu-Catalyzed Carboxylation of Terminal Alkynes with CO<sub>2</sub><sup>447,448</sup>

reusing the organic catalyst layer five times (50 bar of H<sub>2</sub>, 55 °C, 5 h), an overall TON > 7000 for formate was achieved.

In 2017, the group of Leitner<sup>430</sup> investigated biphasic systems to produce formate–amine adducts by CO<sub>2</sub> hydrogenation using aqueous solutions of amines of identical molecular structure and at similar conditions compared to those applied in commercial scale CO<sub>2</sub> scrubbing. The biphasic system consists of hydrophobic solvents as the catalyst immobilization phase and water as the product extraction phase (Figure 12). It was shown that the amines partition between the two phases depending on their structure, whereas all formate–amine adducts were nearly quantitatively extracted into the aqueous phase. The combination of methyl isobutyl carbiol (MIBC) and aqueous ethanolamine solutions led to the most practical and productive system. Using *cis*-[Ru(dppm)<sub>2</sub>-Cl<sub>2</sub>] as a prototypical catalyst, the conversion of CO<sub>2</sub>-saturated (overpressure 5–10 bar) aqueous solutions of monoethanolamine (MEA) into the corresponding formate adduct was demonstrated in a semicontinuous process. An average TOF up to 14 × 10<sup>3</sup> h<sup>−1</sup> and a total TON of 150000 over 11 cycles were achieved.

In conclusion, a large number of catalysts with remarkable activities exist for the direct hydrogenation of CO<sub>2</sub> to formic acid. Additionally, in recent years, many innovative approaches have been developed with the aim to develop simplified downstream processes. The combination of the conversion step with CO<sub>2</sub>-scrubbing processes is a promising approach to integrate formate production also upstream in the value chain. The application of these concepts to actually isolate formic acid or its derivatives as actual target products has yet to be validated. Conceptual studies by LCA on the energy require-

ments to identify the most promising strategies would be very valuable in this context.

**2.3.2. Carboxylation Reactions.** **2.3.2.1. Background and Motivation.** In view of the analysis for formic acid production and considering the remarkable progress with catalytic systems that catalyze the formal addition of the H–H molecule to CO<sub>2</sub>, it seems attractive to consider analogous processes for the synthesis of carboxylic acids via C–H bond activation.<sup>401</sup> Carboxylic acids are mostly produced by oxidation or carbonylation reactions.<sup>389</sup> However, the direct C–H carboxylation is challenging and remains a “dream reaction” especially for nonactivated sp<sup>2</sup> and sp<sup>3</sup> bonds because of thermodynamic and kinetic constraints.<sup>431,432</sup> A key step in any potential catalytic cycle would be the insertion of CO<sub>2</sub> into a metal–carbon bond of the active species. For rhodium alkyl complexes, it has been shown that this step largely correlates with the nucleophilicity of the alkyl group and hence with the electron deficiency of the metal center.<sup>432</sup> Consequently, this must be balanced with the electronic requirements for the C–H bond cleavage and the liberation of the acid from the carboxylate intermediate.<sup>433</sup> Although all these individual steps are known to be feasible in other catalytic cycles, their combination for effective carboxylation remains as yet elusive for nonactivated systems. Significant progress has been made, however, for other strategies to synthesize carboxylic acids and their derivatives from CO<sub>2</sub>, and recent developments are highlighted next.

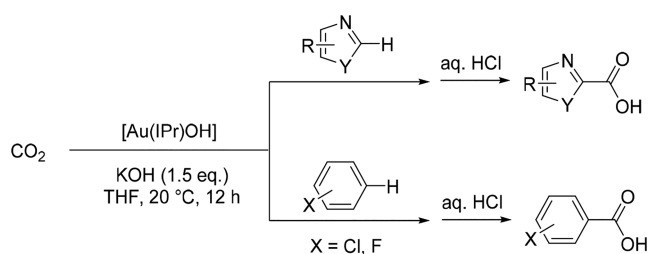
**2.3.2.2. Recent Trends in Catalytic Carboxylation Based on CO<sub>2</sub> Conversion.** The classical synthesis of carboxylic acids from CO<sub>2</sub> involves the stoichiometric conversion of a C–X (X = halogen) bond to a Grignard reagent followed by

carboxylation and subsequent acidic workup. Catalytic reactions with such activated substrates<sup>434</sup> containing C–Zn<sup>435</sup> and C–B<sup>436,437</sup> bonds or even directly from C–X bonds (X = Cl,<sup>438–440</sup> Br,<sup>439,441,442</sup> I<sup>443</sup>) or C–O bonds<sup>444,445</sup> have greatly expanded the synthetic potential of this general approach. For example, the group of Martín<sup>442</sup> reported palladium-catalyzed direct carboxylation of aryl bromides with carbon dioxide, allowing unprecedented functional group tolerance. A variety of aryl bromides were carboxylated in moderate to good yields (40–72%) in the presence of the palladium catalyst and 2 equiv of Et<sub>2</sub>Zn at ambient temperatures (40 °C) (Scheme 14). Most recently, they demonstrated the catalytic carboxylation of sp<sup>3</sup> C–X bonds, whereby the judicious choice of the Ni catalyst directed the resulting carboxylic acid function always to the terminus of the alkane chain irrespective of the initial position of the C–X group.<sup>446</sup>

The carboxylation of C–H acidic sp<sup>1</sup> and sp<sup>2</sup> bonds can be achieved in a catalytic manner directly, whereby the corresponding carboxylate salts are produced as primary products in the presence of suitable bases. Scheme 15 illustrates this for typical protocols. For example, Goossen et al.<sup>447</sup> reported the insertion of CO<sub>2</sub> into the C–H bond of terminal alkynes (Scheme 15a). The use of a copper catalyst and CsCO<sub>3</sub> (2 equiv) as a base at 35–50 °C in DMF resulted in high yields of up to 99% for a variety of terminal alkynes. After acidic workup, the isolation of free propiolic acid was demonstrated. In the same year, Yu et al.<sup>448</sup> achieved high yields for various propiolic acids by carboxylation of terminal alkynes in the presence of a copper complex and K<sub>2</sub>CO<sub>3</sub> (for arylalkynes) or Cs<sub>2</sub>CO<sub>3</sub> (for alkylalkynes) as a base at ambient conditions (Scheme 15b). In addition, silver catalysts have been investigated for the carboxylation of terminal alkynes. Similar to the Cu systems, good results were obtained in the presence of Cs<sub>2</sub>CO<sub>3</sub> as a base.<sup>449,450</sup>

In 2002, Olah et al.<sup>451</sup> demonstrated the carboxylation of arene C–H bonds using a Al<sub>2</sub>Cl<sub>6</sub>/Al system as the mediator at temperatures of 20–80 °C. A variety of substituted benzenes were carboxylated, yielding the corresponding carboxylic acids in moderate to excellent yields (25–92%) after acidic workup. More recently, the catalytic carboxylation of sufficiently C–H acidic (hetero)arenes has seen significant progress.<sup>452</sup> In 2010, Boogaerts and Nolan<sup>453</sup> described the gold-catalyzed carboxylation of a range of substrates. In the presence of the gold catalyst [Au(IPr)OH] (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) and a stoichiometric amount of base (KOH), good to excellent yields (69–96%) of the corresponding carboxylic acids were obtained after acidic workup (Scheme 16). The high basicity of the N-heterocyclic carbene (NHC) gold complex was identified as crucial for the successful

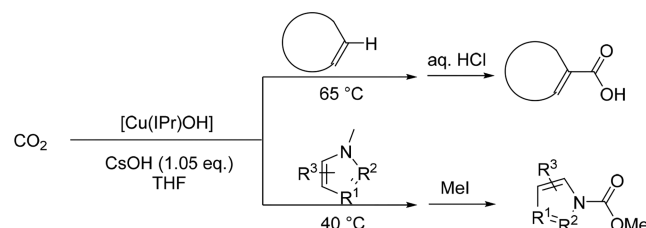
**Scheme 16. Au-Catalyzed Carboxylation of (Hetero)arenes with CO<sub>2</sub>**<sup>453</sup>



carboxylation, and high activities were observed even at ambient temperature (20 °C).

Furthermore, Cazin, Nolan, and co-workers<sup>454</sup> demonstrated the direct carboxylation of N–H and C–H bonds using [Cu(IPr)(OH)] and CsOH as the stoichiometric base (Scheme 17). Starting from a variety of substrates, including oligo-

**Scheme 17. Carboxylation of N–H and C–H Bonds Using [Cu(IPr)OH] and CsOH**<sup>454</sup>



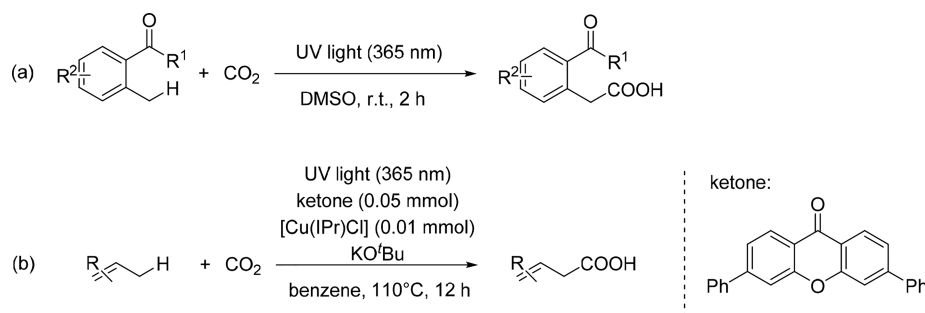
fluoroarenes, as well as benzoxazole, oxazole, and benzothiazole, good to excellent yields (77–93%) were achieved. As an alternative to the acidic workup, conversion to the corresponding esters by reaction with alkyl halides is also possible. This was also used by Zhang et al.<sup>455</sup> in the carboxylation of acidic benzoxazole and its derivatives to the corresponding ester derivatives with the isolated complex [Cu(IPr)Cl] or the in situ generated NHC/complex and KO<sup>t</sup>Bu as a base and *n*-hexyl iodide. In 2016, Fenner et al.<sup>456</sup> demonstrated that the carboxylation of heteroarenes can be achieved even under transition-metal-free conditions. The reaction was mediated by KO<sup>t</sup>Bu alone, and moderate to good yields were achieved at 100 °C for the corresponding ester derivatives.

The group of Iwasawa followed a different strategy using the principle of directed C–H bond activation to initiate the carboxylation process.<sup>457</sup> In 2014, they extended the application of the catalytic system consisting of a rhodium complex and stoichiometric amounts of Al reagents to simple arenes. TONs of up to 48 were achieved for mixtures of regioisomers depending on the substitution pattern of the starting material.

A particularly interesting target molecule for the formal carboxylation of alkenes is the synthesis of acrylic acid from ethylene and CO<sub>2</sub>.<sup>458,459</sup> The stoichiometric coupling of the two reagents at a Ni center followed by protolytic liberation of the product was described by the group of Hoberg already in 1987.<sup>460</sup> In a systematic development, Lejkowski et al.<sup>461</sup> in 2012 showed the possibility of repeated use of the Ni catalyst, and a TON of approximately 10 was observed. In 2014, the same group demonstrated the nickel-catalyzed direct carboxylation of alkenes in the presence of a base.<sup>462</sup> For the corresponding acrylic acid salt, a TON of 107 was obtained. Additionally, for a wide range of carboxylic acid salts, TONs of up to 116 were achieved at 100 °C. In the same year, the group of Vogt demonstrated for the first time the catalytic conversion of CO<sub>2</sub> and ethene to sodium acrylate with TONs of up to 21 in the presence of a homogeneous nickel catalyst, LiI as a cocatalyst, NEt<sub>3</sub>, and NaOH.<sup>463</sup>

An interesting approach for the direct carboxylation of C–H bonds was reported by Murakami and co-workers<sup>464</sup> in 2015. The group showed the carboxylation of *o*-alkenylphenyl ketones with CO<sub>2</sub> by exploiting UV light or even solar light as the driving force (Scheme 18a). Using this method, high yields of up to 91% were obtained for the corresponding benzylic carboxylic acids. In further work, the group

**Scheme 18.** Carboxylation of *o*-Alkenylphenyl Ketones (a) and Allylic CH Bonds of Simple Alkenes (b) with CO<sub>2</sub> under UV Light Irradiation<sup>464,465</sup>



demonstrated the carboxylation of allylic C–H bonds of simple alkenes with CO<sub>2</sub> (Scheme 18b).<sup>465</sup> In the presence of a substoichiometric amount of a ketone and a catalytic amount of a copper complex, good to excellent yields were achieved for the carboxylated products under UV irradiation at 110 °C.

The above examples provide new synthetic protocols for the generation of carboxylic acid groups incorporating CO<sub>2</sub> into aromatic or unsaturated molecules of different complexities. Whereas this toolbox is expanding rapidly, the synthesis of saturated carboxylic acids is less explored. Examples include Pd-, Ni-, Fe-, or Rh-catalyzed coupling reactions between CO<sub>2</sub> and alkenes,<sup>466–468</sup> dienes,<sup>469</sup> allenes,<sup>470</sup> and alkynes<sup>471–473</sup> in the presence of superstoichiometric amounts of organometallic reducing agents such as ZnR<sub>2</sub>, AlR<sub>3</sub>, Grignard reagents, and silanes. However, the use of such high-energy reagents and the stoichiometric formation of inorganic waste impose major limitations in an environmental assessment, although detailed LCA studies are currently not available.

Consequently, the formal “hydrocarboxylation” reaction has recently found increasing interest. Its potential is not limited to carboxylic acids, as aldehydes, alcohols, or even methyl groups may result as the final functional group under the reducing conditions.<sup>1,3</sup> The examples discussed herein are restricted to cases where the acids or esters are isolated as the products.

The reaction of simple olefins, CO<sub>2</sub>, and H<sub>2</sub> could provide an attractive approach toward saturated carboxylic acids. This reaction is exergonic, due to the energy released from the saturation of the double bond as an additional driving force.<sup>432</sup> In 2013, Ostapowicz et al.<sup>304</sup> developed an effective catalyst system inspired by the work of Simonato et al.<sup>474</sup> for the direct formation of carboxylic acids from nonactivated olefins, CO<sub>2</sub>, and H<sub>2</sub> (Scheme 19a). For various alkenes, high conversion and

selectivity were obtained using the catalytic system [{RhCl(CO)<sub>2</sub>}]<sub>2</sub>/PPh<sub>3</sub> in the presence of methyl iodide (promotor) and *p*-toluenesulfonic acid (*p*-TsOH) at 180 °C in acidic acid. The regioselectivities of the conversion of internal and terminal olefins were similar to those observed in hydroformylation reactions. Investigations concerning the reaction mechanism including isotopic labeling suggest that a combination of rhodium-catalyzed rWGS (formation of CO) and hydroxycarbonylation cycles were responsible for the formal hydrocarboxylation.

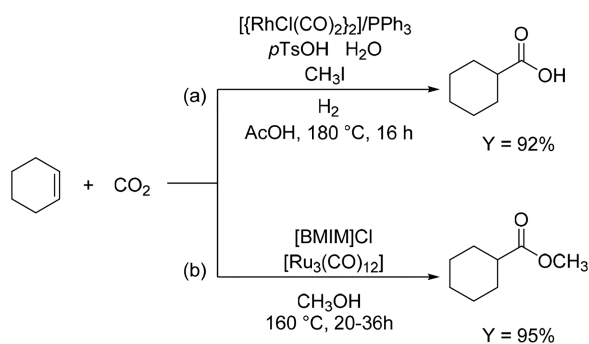
In 2014, the Beller group<sup>306</sup> used the rWGS catalyst system [Ru<sub>3</sub>(CO)<sub>12</sub>]/[BMIM]Cl for the direct conversion of olefins, CO<sub>2</sub>, and alcohol to carboxylic acid esters (Scheme 19b). For a variety of olefins and alcohols, yields of the corresponding carboxylic acid esters in the range of 41–95% were obtained. In this process, CO<sub>2</sub> is reduced by the alcohol (hydrogen borrowing<sup>475</sup>) and no external hydrogen is needed. Isotopic labeling experiments showed that the CO formed this way subsequently affects the alkoxy carbonylation reaction of the olefin and the alcohol.

In 2016, Gehrtz et al.<sup>476</sup> reported the indirect utilization of CO<sub>2</sub> by using *N*-formylsaccarin as a CO transfer reagent for the Pd-catalyzed alkoxy carbonylation of different styrene derivatives and olefins. Under mild reaction conditions, yields of up to 97% were achieved for the corresponding carboxylic acid esters. The used carbonylation catalyst is based on a Pd<sup>0</sup> precursor, a bidentate phosphine ligand, and a moderately strong acid. The latter enables a high regioselective transformation of styrene derivatives to the corresponding branched esters.

Furthermore, there are a few examples for the conversion of alcohols into carboxylic acids using CO<sub>2</sub> and H<sub>2</sub>. Ostapowicz et al.<sup>304</sup> demonstrated that, besides olefins, also alcohols can be used as substrates for the formation of carboxylic acids using the catalytic system [{RhCl(CO)<sub>2</sub>}]<sub>2</sub>/PPh<sub>3</sub>. Different alcohols were converted efficiently to the corresponding carboxylic acids with a product distribution almost identical to that of the comparable substituted alkenes. Even for this transformation a combination of rhodium-catalyzed rWGS and hydroxycarbonylation cycles were proposed to be responsible for the formal hydrocarboxylation.

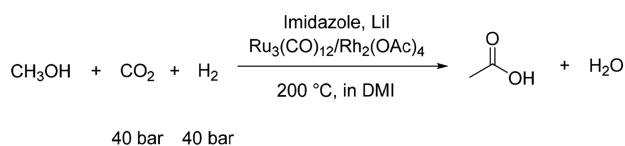
A particularly attractive target would be the formation of acetic acid, which is produced by carbonylation of methanol in about 5 million t/year production capacity. In 1995, the catalytic carboxylation of alkyl iodides, including methyl iodide, was reported by Fukuoka et al. in the presence of homogeneous Ru/Co or Ni/Co bimetallic catalysts.<sup>477</sup> Starting from methyl iodide, the formation of acetic acid was observed with a TON of 17 using a mixture of [Ru<sub>3</sub>(CO)<sub>12</sub>] and [Co<sub>2</sub>(CO)<sub>8</sub>] with

**Scheme 19.** (a) Catalytic Hydrocarboxylation of Olefins Using CO<sub>2</sub> and H<sub>2</sub> and (b) Alkoxy carbonylation of Olefins Using CO<sub>2</sub> and Alcohols<sup>304,306</sup>



CO<sub>2</sub> and H<sub>2</sub> at 150 °C and 80 bar (CO<sub>2</sub>/H<sub>2</sub> ratio of 1:3). Methane and CO were detected as side products with maximum TONs of 50 and 58. In 2016, the group of Han<sup>478</sup> reported the hydrocarboxylation of methanol with CO<sub>2</sub> and H<sub>2</sub> to acetic acid using a Ru–Rh bimetallic catalyst, imidazole as the ligand, and LiI as the promoter in 1,3-dimethyl-2-imidazolidinone (DMI) as the solvent (40 bar of CO<sub>2</sub>, 40 bar of H<sub>2</sub>, 200 °C) (Scheme 20). Under optimized reaction

**Scheme 20. Synthesis of Acetic Acid via Methanol Hydrocarboxylation with CO<sub>2</sub> and H<sub>2</sub>**<sup>478</sup>



conditions, yields of up to 77% were achieved for acetic acid. Furthermore, the recyclability of the catalyst was demonstrated, and the catalyst was used five times, resulting in a TON of 1022. The experimental data were consistent with a mechanistic proposal involving CO<sub>2</sub> rather than CO as reactive and indicated that the ligand imidazole plays a key role in the high catalytic activity, stability, and selectivity of the catalyst.

It is conspicuous that many of the hydrocarboxylation reactions proceed via CO as the reactive species. Consequently, either a two-step process (CO<sub>2</sub> is first converted to CO), or an integrated process is conceivable for the use of CO<sub>2</sub>. On the basis of the results of the LCA studies on CO<sub>2</sub>-based syngas production and on formic acid production discussed above, an integrated process probably has the higher potential. A detailed process analysis and LCA study would be highly desirable to provide guidelines for future research efforts. Moreover, LCA studies are required to assess the potential of the hydrocarboxylation in comparison to the existing processes for the synthesis of carboxylic acids and their derivatives, such as hydroformylation/oxidation.

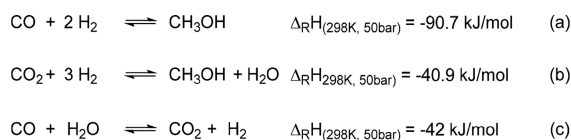
## 2.4. Methanol and Methylation Reactions

### 2.4.1. Methanol. 2.4.1.1. Background and Motivation.

With a current global demand of around 70 million metric tons in 2015,<sup>479</sup> methanol is one of the most important bulk chemicals for the chemical industry. Important applications of methanol are the production of formaldehyde, methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and acetic acid. Methanol can also be viewed as an alternative starting point for parts of the petrochemical value chain, for example, via methanol-to-olefin (MTO) processes. Its application in the mobility sector can be envisaged through its direct use, the use of derivatives such as dimethyl ether (DME) or oxymethylene ethers (see section 3.4), or conversion to hydrocarbon fuels via methanol-to-gasoline processes.<sup>1,270</sup>

Today, almost all methanol produced is synthesized from syngas (Scheme 21a), which can be obtained from virtually any carbon feedstock through gasification processes (see section

**Scheme 21. Production of Methanol from Synthesis Gas**<sup>480</sup>

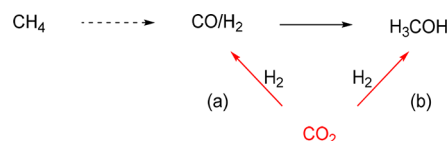


2.2). Natural gas is currently the feedstock to define the lowest carbon footprint for world-scale industrial methanol production, whereby steam reforming or partial oxidation can be used for syngas generation. The syngas to methanol conversion takes place industrially in the presence of heterogeneous catalysts (copper/zinc/aluminum oxides) at elevated pressures (50–250 bar) and temperatures (200–350 °C) and is highly exothermic.<sup>270,480</sup> Therefore, the major challenge is the removal of the excess heat to shift the equilibrium toward the products, to control selectivity, and to avoid catalyst sintering. In the case of hydrogen-rich syngas mixtures, CO<sub>2</sub> is added to balance the C/H ratio as CO<sub>2</sub> consumes more hydrogen than CO (Scheme 21b).<sup>480</sup> Using this reaction pathway, it is estimated that several million tons of CO<sub>2</sub> are converted into methanol each year.<sup>26,480</sup> The water–gas shift reaction connects these two reactions and is also catalyzed by typical heterogeneous methanol catalysts under the reaction conditions (Scheme 21c).

### 2.4.1.2. Current Status of CO<sub>2</sub> Conversion to Methanol.

Just like for formic acid, there are two possibilities to integrate CO<sub>2</sub> into the synthesis of methanol: (a) CO<sub>2</sub> conversion to CO (rWGS) and subsequent hydrogenation of CO and (b) the direct hydrogenation of CO<sub>2</sub> (Scheme 22). Both pathways have

**Scheme 22. Catalytic Routes for the Synthesis of Methanol from Natural Gas or from CO<sub>2</sub>**



been proposed to occur during the industrial processes using CO<sub>2</sub>-containing syngas. Similarly, both pathways have to be considered for utilization of CO<sub>2</sub> as the primary feedstock.

To date, several processes have been developed for the conversion of CO<sub>2</sub> to methanol on a pilot scale. Lurgi demonstrated the production of methanol from CO<sub>2</sub> and H<sub>2</sub> in a pilot plant in 1994.<sup>270,481,482</sup> Using a Cu/Zn/Al catalyst from Süd-Chemie (now Clariant), methanol was obtained with conversions of 35–45% per pass and high selectivity at 260 °C and 60 bar of pressure. A slight decrease in the activity of the catalyst is observed at about the same rate as for methanol catalysts which are used commercially. In 1996, the NIRE and RITE institutes in Japan demonstrated the hydrogenation of CO<sub>2</sub> on a 50 kg/day laboratory pilot scale.<sup>483–486</sup> This process operates at elevated pressures (30–50 bar) and temperatures (200–270 °C) using a multicomponent catalyst (Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) and achieves high selectivity to methanol (99.7%). Furthermore, the purity of crude methanol produced in this process is 99.9%, even higher than the purity of crude methanol from syngas in a present-day commercial plant. In 2009, Mitsui Chemicals opened another pilot plant with a capacity of 100 t/year that uses this Cu catalyst.<sup>487</sup> The Korean Institute of Science and Technologies developed the CAMERE process, which produces methanol in two steps using CO<sub>2</sub> and H<sub>2</sub>.<sup>271,272</sup> In the first reactor, CO<sub>2</sub> and H<sub>2</sub> are converted to CO by the reverse water–gas shift reaction using a zinc aluminate-based catalyst. To obtain a reasonable CO<sub>2</sub> conversion (>60%), temperatures higher than 600 °C are necessary. After the removal of water, the CO/CO<sub>2</sub>/H<sub>2</sub> gas mixture is transferred to the second reactor, in which a Cu/ZnO/ZrO<sub>2</sub>/Ga<sub>2</sub>O<sub>3</sub> catalyst is used for the synthesis of methanol. Gallium is used to promote the stability and activity of the catalyst. Interestingly, the

Table 5. Overview of Available LCA Studies on CO<sub>2</sub>-Based Methanol<sup>a</sup>

| reference                                                                               | CO <sub>2</sub> source                                                   | H <sub>2</sub> source                                                    | metrics <sup>b</sup>          |
|-----------------------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|-------------------------------|
| Direct Hydrogenation (Scheme 22b)                                                       |                                                                          |                                                                          |                               |
| (1) Pérez-Fortes et al. <sup>493</sup>                                                  | not considered                                                           | alkaline electrolyzer                                                    | net CO <sub>2</sub> used      |
| (2) Sternberg et al. <sup>282</sup>                                                     | no explicit source considered; range of environmental impacts considered | steam methane reforming                                                  | GW, FD                        |
| (2, i) Kiss et al. <sup>495</sup>                                                       |                                                                          |                                                                          |                               |
| (2, ii) Rihko-Struckmann et al. <sup>496</sup>                                          |                                                                          |                                                                          |                               |
| (2, iii) Van-Dal and Bouallou <sup>497</sup>                                            |                                                                          |                                                                          |                               |
| (3) Hoppe et al. <sup>173</sup>                                                         | air, biogas, cement plant, lignite-fired power plant, waste incineration | electrolyzer using wind electricity                                      | GW, RMI, TMI                  |
| Rihko-Struckmann et al. <sup>496</sup>                                                  |                                                                          |                                                                          |                               |
| (4) Matzen and Demirel <sup>494</sup>                                                   | ethanol fermentation                                                     | electrolyzer using wind electricity                                      | GW, AP; POF, PM, HT           |
| (5) Aresta et al. <sup>492</sup>                                                        | power plant                                                              | electrolyzer using photovoltaic and nuclear electricity                  | single indicator <sup>c</sup> |
| (6) Kalbani et al. <sup>276</sup>                                                       | power plant                                                              | alkaline electrolyzer using wind, photovoltaic, NG, and coal electricity | GW                            |
| Conversion of Syngas from HT Coelectrolysis (Schemes 5d and 22a)                        |                                                                          |                                                                          |                               |
| (6) Kalbani et al. <sup>276</sup>                                                       | power plant                                                              | alkaline electrolyzer using wind, photovoltaic, NG, and coal electricity | GW                            |
| Conversion of Syngas from Solar-Driven Thermochemical Dissociation (Schemes 5e and 22a) |                                                                          |                                                                          |                               |
| (7) Kim et al. <sup>275</sup>                                                           | not considered                                                           | WGS with solar-based CO                                                  | GW, AP, PCI                   |

<sup>a</sup>For LCA studies that are based on process concepts from the literature, the corresponding reference is mentioned in italics. The differences between the process concepts for direct hydrogenation are presented in Table 6. <sup>b</sup>GW = global warming impact, FD = fossil depletion impact, RMI = raw material input, TMI = total material input, AP = acidification potential, POF = photochemical oxidant formation, HT = human toxicity, and PCI = primary comparative indicator, nonrenewable. <sup>c</sup>The single indicator is a weighted sum of the greenhouse effect, ozone layer depletion, acidification, nitrification, and photochemical oxidant formation.

Table 6. Details for Process Concepts for the Direct Hydrogenation of CO<sub>2</sub> to Methanol Used in LCA Studies (See Table 5)

| reference                              | conversion rates (%)                                                                                              | reaction conditions | catalyst                              | comment                                                                        |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------------|---------------------|---------------------------------------|--------------------------------------------------------------------------------|
| Pérez-Fortes et al. <sup>493</sup>     | process: H <sub>2</sub> , about 95; CO <sub>2</sub> , 93.85<br>per pass: CO <sub>2</sub> , 21.97                  | 76 bar, 210 °C      | Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> | kinetics: Vanden Bussche and Froment <sup>498</sup>                            |
| Rihko-Struckmann et al. <sup>496</sup> | process: H <sub>2</sub> , about 96; CO <sub>2</sub> , 96.8                                                        | 50 bar, 220 °C      | not considered                        | equilibrium conversion                                                         |
| Van-Dal and Bouallou <sup>497</sup>    | process: H <sub>2</sub> , 92.8; CO <sub>2</sub> , 93.4                                                            | 78 bar, 210 °C      | Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> | kinetics: Vanden Bussche and Froment <sup>498</sup>                            |
| Kiss et al. <sup>495</sup>             | process: H <sub>2</sub> , 99.9; CO <sub>2</sub> , 100<br>per pass: H <sub>2</sub> , 18.17; CO <sub>2</sub> , 17.2 | 50 bar, 250 °C      | Cu/Zn/Al/Zr                           | kinetics: An et al. <sup>499</sup>                                             |
| Hoppe et al. <sup>173</sup>            | process: H <sub>2</sub> , 100; CO <sub>2</sub> , 100                                                              | 50 bar, 220 °C      | not considered                        | energy demands from Rihko-Struckmann et al. <sup>496</sup> but 100% conversion |
| Aresta et al. <sup>492</sup>           |                                                                                                                   | 50 bar, 250 °C      | Cu/ZnO                                | data based on a small-scale test plant                                         |
| Matzen and Demirel <sup>494</sup>      |                                                                                                                   | 50 bar, 235 °C      | Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> | kinetics: Weiduan et al. <sup>500</sup>                                        |
| Kalbani et al. <sup>276</sup>          |                                                                                                                   |                     | Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> | kinetics: Vanden Bussche and Froment <sup>498</sup>                            |

CAMERE process is described as having higher efficiency (higher methanol yields, lower operating costs) in comparison to the direct route.<sup>270</sup> The capacity of the pilot plant using the CAMERE process in Korea is about 100 kg of methanol/day.

The first commercial CO<sub>2</sub>-to-methanol plant has been operated in Iceland by CRI (Carbon Recycling International) since 2011.<sup>488</sup> The process uses industrial CO<sub>2</sub> streams and hydrogen, which is generated by the electrolysis of water. The carbon balance benefits greatly from the readily available local geothermal energy sources to operate the process and to produce electricity for the electrolysis. With a production capacity of 5 million L (ca. 4000 t)/year, the “George Olah Renewable Methanol plant” produces the equivalent of about 2.5% of the fuel demand in Iceland. Recently, an initiative to validate the integration of this technology with CO<sub>2</sub> capture from a coal-fired power plant was started in Lünen,

Germany.<sup>489</sup> Also, the OTTO-R platform established at the Technical University of Freiberg envisages to synthesize methanol from CO<sub>2</sub>, water, and renewable electricity, and to integrate it with the production of gasoline via methanol-to-gasoline technology.<sup>490,491</sup> Similar to a number of other demonstration activities worldwide, these studies focus mainly on the evaluation of technology options. The Iceland example and the LCA studies discussed below indicate, however, that the incorporation of specific infrastructures and logistics has a major influence on the overall carbon balance of these value chains.

**2.4.1.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Methanol.** The direct catalytic hydrogenation of CO<sub>2</sub> (Scheme 22b) to methanol has been the subject of a number of LCA studies.<sup>173,276,282,492–494</sup> Also, the production via CO<sub>2</sub>-based syngas (Scheme 22a) has been investigated in full LCAs with

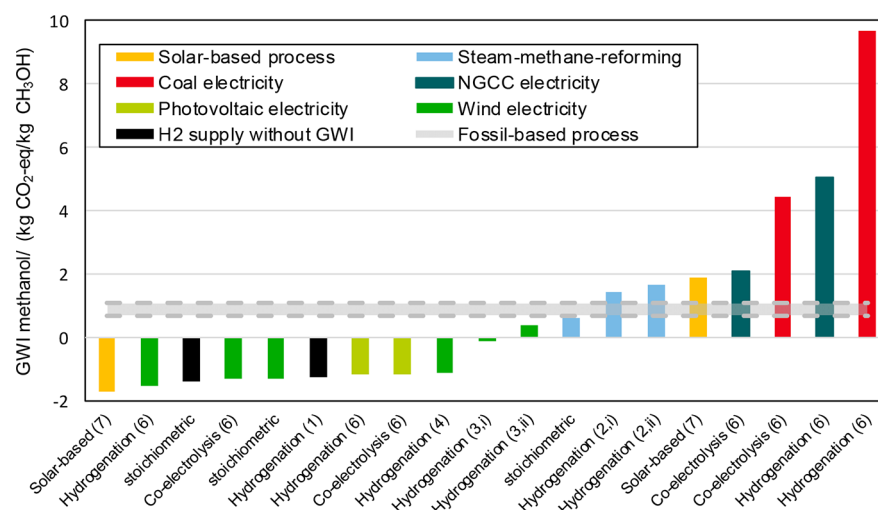


**Figure 13.** Global warming impact (GWI) for CO<sub>2</sub>-based methanol production from cradle-to-gate reported in the literature. Three different pathways are considered: syngas from solar-driven thermochemical dissociation processes (solar-based), syngas from high-temperature coelectrolysis (coelectrolysis), and direct hydrogenation of CO<sub>2</sub> (hydrogenation). For processes based on direct hydrogenation and syngas from coelectrolysis, the hydrogen sources are represented by different colors. CO<sub>2</sub>-based methanol is benchmarked to fossil-based methanol. The range of global warming impacts for CO<sub>2</sub>-based methanol results from diverging assumptions of CO<sub>2</sub> and H<sub>2</sub> sources as well as from underlying process data for CO<sub>2</sub> conversion to methanol (for details see Table 1). Key: (1) Pérez-Fortes et al.,<sup>493</sup> (2,i) Sternberg et al.,<sup>282</sup> with process concept from Kiss et al.,<sup>495</sup> (2,ii) Sternberg et al.,<sup>282</sup> with process concept from Rihko-Struckmann et al.,<sup>496</sup> (3,i) Hoppe et al.,<sup>173</sup> with CO<sub>2</sub> supply from waste incineration, (3,ii) Hoppe et al.,<sup>173</sup> with CO<sub>2</sub> supply from air capture, (4) Matzen and Demirel,<sup>494</sup> (6) Kalbani et al.,<sup>276</sup> (7) Kim et al.<sup>275</sup>

syngas derived either from high-temperature (HT) coelectrolysis (Scheme 5d)<sup>276</sup> or from solar-driven thermochemical dissociation (Scheme 5e).<sup>275</sup>

For the methanol production on the basis of syngas from reverse water–gas shift (Scheme 5b), the available technological assessments<sup>272,274</sup> cannot be directly compared to the studies using LCA methodology. We therefore first summarize the global warming impacts for the LCA studies outlined in Tables 5 and 6, followed by their detailed analysis on the basis of harmonized scenarios. The results will be put into perspective with the available technological data for the rWGS-based process, as this is implemented in the CAMERE process, which has the highest technology readiness level among the conversion options of CO<sub>2</sub>-based syngas to methanol (see section 2.2).

In Figure 13, the reported global warming impacts of CO<sub>2</sub>-based methanol are summarized for the available LCA studies. As a limiting case, the stoichiometric conversion of CO<sub>2</sub> to methanol is also considered assuming 100% conversion without any further energy demand. The global warming impacts for CO<sub>2</sub>-based methanol range widely: from −1.7 to +9.7 kg of CO<sub>2</sub> equiv/kg of methanol. The lowest global warming impact is reported for the solar-driven thermochemical process using solar heat. Note that this process has even lower global warming impacts than the limiting stoichiometric case using hydrogen without global warming impacts, which indicates that additional credits must have been given for coproducts (e.g., heat) even though this has not been reported. The conversion of syngas from high-temperature coelectrolysis to methanol has global warming impacts in the range from −1.4 to +4.3 kg of CO<sub>2</sub> equiv/kg of methanol. The direct hydrogenation of CO<sub>2</sub> has global warming impacts from −1.6 to +9.7 kg of CO<sub>2</sub> equiv/kg of methanol. The lowest global warming impacts are achieved if hydrogen is supplied by water electrolysis using wind electricity; the highest global warming impacts occur if hydrogen is supplied by water electrolysis using coal electricity.

The reported global warming impacts in Figure 13 allow some qualitative conclusions to be drawn regarding the supply of feedstock and energies. In general, CO<sub>2</sub>-based methanol reduces global warming impacts compared to fossil-based methanol if renewable electricity is used for the water electrolysis or coelectrolysis. If fossil-based electricity is employed for electrolysis or if hydrogen is supplied by steam methane reforming, the global warming impact of CO<sub>2</sub>-based processes is higher than that of fossil-based processes. However, a more quantitative comparison between the different CO<sub>2</sub>-based process pathways is not possible due to different assumptions regarding the supply processes. We therefore harmonized the LCA studies according to the scenarios shown in Table 1.

**2.4.1.3.1. Harmonized LCA Results for Direct Hydrogenation.** The harmonized global warming impacts for direct hydrogenation are shown in Figure 14, and the conversion of CO<sub>2</sub>-based syngas to methanol is analyzed separately in Figure 15.

In the five process concepts considered for CO<sub>2</sub> hydrogenation, the reaction temperatures range from 210 to 250 °C and the reaction pressures range from 50 to 75 bar (Table 6).<sup>173,493,495–497</sup> Most process concepts consider a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, which is the commercial catalyst for current fossil-based methanol processes, and single-pass conversion of 20% CO<sub>2</sub> has been specified.<sup>493,495</sup> The raw gas is first cooled and flashed to separate the gaseous compounds (CO, CO<sub>2</sub>, and hydrogen) from condensable compounds (methanol and water). Subsequently, the gaseous compounds are recycled to the reactor. Methanol is separated from the water in a distillation column. On the basis of this process configuration, a CO<sub>2</sub> conversion of up to 96% can be achieved. The remaining CO/CO<sub>2</sub> is dissolved in the methanol–water mixture and cannot be recovered. To increase the CO<sub>2</sub> conversion, Kiss et al.<sup>495</sup> consider an additional stripping unit. Here, the hydrogen feed (saturated with water) is contacted with the methanol–water mixture to recover unconverted CO/CO<sub>2</sub>. In this step,

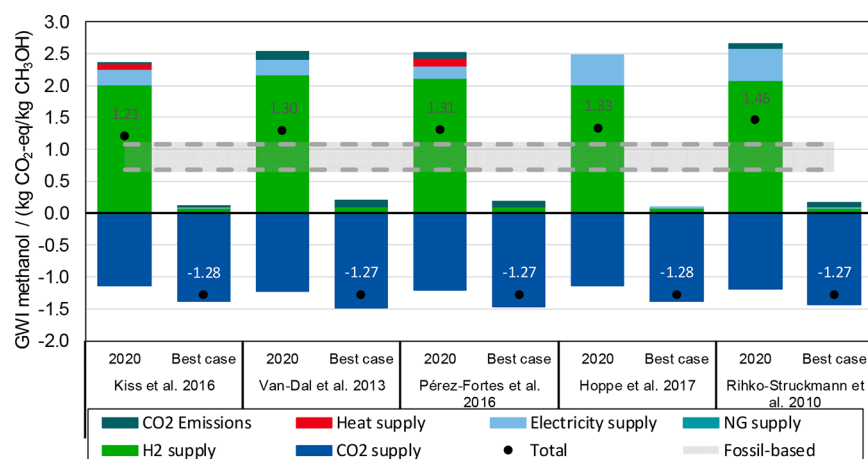


**Figure 14.** Global warming impact (GWI) for the direct hydrogenation (Scheme 22b) of CO<sub>2</sub> to methanol (cradle-to-gate). The five process concepts are presented in Table 6. For each process concept, a scenario for 2020 and a best-case scenario are considered (Table 1). Furthermore, the CO<sub>2</sub>-based processes are compared to fossil-based methanol processes (range between dashed lines). The range results from different fossil-based processes.

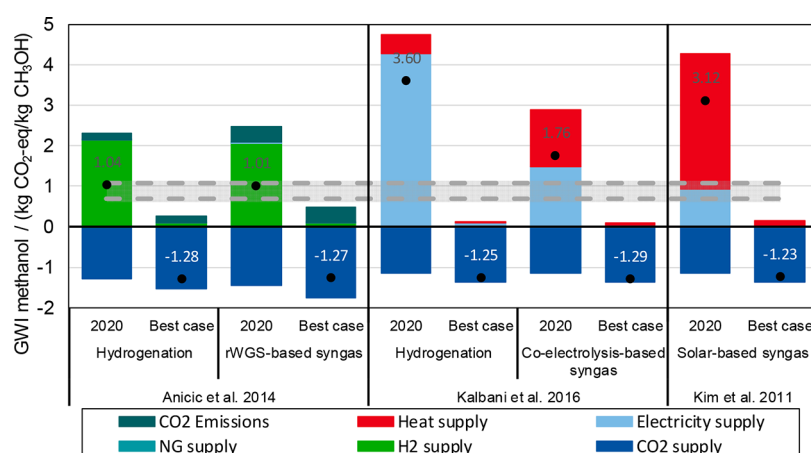


**Figure 15.** Global warming impacts (GWIs) for three pathways for CO<sub>2</sub>-based methanol production (cradle-to-gate) based on conversion of syngas: rWGS (rWGS-based syngas),<sup>274</sup> high-temperature coelectrolysis (coelectrolysis-based syngas),<sup>276</sup> and solar-driven thermochemical dissociation (solar-based syngas).<sup>275</sup> For rWGS- and coelectrolysis-based syngas, the comparison to direct hydrogenation is shown. Note that sound comparisons are only possible between processes from the same reference. For each process, a scenario for 2020 and a best-case scenario are considered (Table 1). Furthermore, the CO<sub>2</sub>-based processes are compared to the fossil-based methanol processes (range between dashed lines).

the water is also removed from the hydrogen feed. In this case, almost 100% of CO<sub>2</sub> can be converted.

The use of consistent LCA scenarios in Figure 14 significantly reduces the range of global warming impacts for direct hydrogenation of CO<sub>2</sub>, indicating that the large variations seen in Figure 13 are indeed mainly due to the differences in the assumed supply processes. The harmonized data allow quantification of the global warming impacts relative to the current fossil value chain to methanol (0.68–1.08 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH). In the scenario 2020, all CO<sub>2</sub>-based direct hydrogenation processes have higher global warming impacts ranging from 1.21 to 1.44 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH. In the best-case scenario, all CO<sub>2</sub>-based processes have significantly lower and even negative global warming impacts of −1.28 to −1.27 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH.

The lowest global warming impacts are found for the process from Kiss et al.,<sup>495</sup> because this process has the highest conversion of hydrogen and CO<sub>2</sub> (99.9%) (see Table 6) and the lowest electricity demand. The electricity demand is low due to the relatively low pressure for the reaction (50 bar) and

the direct utilization of wet hydrogen as a feed, which is dried efficiently in the stripping unit as described above. The second lowest global warming impacts are found for the processes reported by Van-Dal et al.<sup>497</sup> and Pérez-Fortes et al.,<sup>493</sup> with lower CO<sub>2</sub> and hydrogen conversions between 93% and 95%. The electricity demand is also higher than in the process by Kiss et al.,<sup>495</sup> because of a higher reaction pressure (80 bar) and conventional separation processes. The process presented by Rihko-Struckmann et al.<sup>496</sup> has the highest global warming impact, which is mainly caused by the high recycle ratio to achieve a high conversion of CO<sub>2</sub> and hydrogen.

**2.4.1.3.2. Harmonized LCA Results for CO<sub>2</sub> to Syngas to Methanol.** The global warming impacts for process options via syngas are summarized in Figure 15 and compared to that of direct hydrogenation, where possible.

The global warming impact for the rWGS route as implemented in the CAMERE process can be estimated from a recent technoeconomic assessment.<sup>274</sup> The process data are derived by process simulation considering a reaction temperature of 800 °C and a reaction pressure of 16 bar for the rWGS

reaction. In the rWGS reaction, a CO<sub>2</sub> conversion of about 60% per pass is determined over a ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. The authors state that the direct hydrogenation is thermodynamically more efficient, because it avoids the high-temperature rWGS reaction.<sup>274</sup> At the same time, the hydrogen demand is 4.7% higher for the direct hydrogenation because the rWGS-based process uses 1.5 mol % methane as a cofeedstock. As a result, the global warming impacts for both processes are very similar to values of −1.28 and −1.27 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH, respectively, and no a priori preference for either option can be deduced.

A very similar situation results for syngas produced by high-temperature coelectrolysis and its comparison to direct hydrogenation employing a low-temperature water electrolysis to produce hydrogen.<sup>276</sup> The high-temperature coelectrolysis process in the study was operated at 800 °C, and a utilization efficiency of 70% is assumed for steam and CO<sub>2</sub>. For the conversion of syngas to methanol, the commercial process is assumed. The coelectrolysis process has a 65% lower electricity demand than the direct hydrogenation, while the heat demand of the coelectrolysis process is 3 times higher than for the direct hydrogenation. The total energy demand (electricity + heat) of the coelectrolysis process is about 30% lower. However, it remains unclear whether the benefit of the high-temperature coelectrolysis results mainly from the utilization of a coelectrolysis or a high-temperature electrolysis. To answer this question, further comparison of high-temperature water electrolysis to low-temperature coelectrolysis is required. In the best-case scenario, the syngas route has a global warming impact of −1.29 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH. Although this is slightly lower than the one determined for direct hydrogenation, the difference is not significant enough to draw a general conclusion.

For syngas from solar-driven thermochemical dissociation, a technoeconomic assessment is available that additionally determines global warming impacts.<sup>275</sup> In this process, the CO<sub>2</sub> is first converted to CO in a so-called counter-rotating receiver/reactor/recuperator (CR5). The CR5 is based on a two-step iron oxide cycle. The authors assume that about 25% of CO<sub>2</sub> is converted to CO. Subsequently, a fraction of the CO is used to produce hydrogen via water–gas shift reaction. Finally, the CO and hydrogen are converted to methanol. The water–gas shift reaction causes a very high heat demand that has to be supplied by renewable energies. The results of the study do not include the energy that is directly supplied by solar irradiation. In the best-case scenario, a global warming impact of −1.23 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH is estimated from these data.

In summary, the currently available data suggest that the production of methanol from CO<sub>2</sub> and renewable energy would be associated with a negative global warming impact in the range of −1.2 to −1.3 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH as compared to +0.7 to +1.1 kg of CO<sub>2</sub> equiv/kg of CH<sub>3</sub>OH in today's fossil value chain. Considering only the carbon footprint, the combination of syngas generation and conventional synthesis and the direct hydrogenation appear to be equally suited to capture this potential. Obviously, other factors such as the number of unit operations and the complexity of processing units are additional factors that will affect more detailed analysis of economic and ecological impacts. As current trends for syngas production are discussed in section 2.2, we will focus on the direct hydrogenation of CO<sub>2</sub> in the remainder of this section.

**2.4.1.4. Further Trends and Research Topics: Efficient and Robust Catalysts To Cope with Pure CO<sub>2</sub> or CO<sub>2</sub>-Rich Feedstock Streams.** The LCA studies show that the global warming impacts for direct hydrogenation of CO<sub>2</sub> to methanol are dominated by the hydrogen supply. Thus, high conversion and selectivity are important to make best use of the hydrogen resource. At the same time, this would reduce the effort for downstream separations. Further improvements of the catalytic systems are therefore desirable. In addition, these systems need to operate over extended periods of time-on-stream, accounting also for potential fluctuations in energy or raw material supply if coupled to renewable resources. Consequently, the search of both efficient and robust catalyst systems is a key element for future developments.

The conversion of CO<sub>2</sub> and H<sub>2</sub> into methanol using heterogeneous catalysts is already part of the industrial methanol production process in which CO<sub>2</sub> is added to balance the C/H ratio in syngas mixtures. However, commercially used standard catalysts based on Cu/ZnO are not suitable for the direct hydrogenation of CO<sub>2</sub> to methanol because these catalysts exhibit a tendency to deactivate at higher CO<sub>2</sub> partial pressures.<sup>270</sup> This effect can be attributed to the formation of water during the reaction starting from CO<sub>2</sub> and not to CO<sub>2</sub> itself. The active sites of the catalysts can be inhibited in the presence of water even in the absence of CO<sub>2</sub> or in the presence of excess CO<sub>2</sub>.

Understanding the detailed function of heterogeneous catalysts based on Cu and Zn as their active components and variations to increase their tolerance for CO<sub>2</sub>-rich feedstocks have been intensively studied in recent years. An overview of these catalysts and modification options is given in various reviews.<sup>270,406</sup> Especially commercial Cu/ZnO catalysts modified by metal oxides such as Ga<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> show a higher stability.<sup>501,502</sup> Toyir et al.<sup>503</sup> suggested that the promoting effect of Ga<sub>2</sub>O<sub>3</sub> is related to the particle size. Small particles favor the formation of an intermediate state of copper between Cu<sup>0</sup> and Cu<sup>2+</sup> on the surface. Using the effective and very stable catalyst Cu/ZnO/Ga<sub>2</sub>O<sub>3</sub> supported on hydrophobic silica to produce methanol from CO<sub>2</sub> resulted in high selectivity (>99%) at temperatures of 250–270 °C.<sup>504,505</sup> Behrens et al.<sup>506,507</sup> investigated the role of the catalyst material Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in the hydrogenation of CO<sub>2</sub> and CO. In their study, they demonstrated that undistorted pure Cu is quite inactive in the synthesis of methanol. Higher activity was generated by the presence of steps at the Cu surface, which can be stabilized by bulk defects (e.g., stacking faults or twin boundaries terminating at the surface). This effect of steps at the Cu surface for the synthesis of methanol was attributed to stronger binding of the intermediates on stepped sites and lower energy barriers between them. Furthermore, the substitution of Zn into the Cu steps resulted in further strengthening of the binding of the intermediates and therefore in an increased activity of the catalyst. As key steps for the methanol synthesis, they identified a complex series of bond-cleavage and bond-formation processes on the catalyst surface involving the surface-bound species HCOO, HCO, HCOOH, H<sub>2</sub>COOH, H<sub>2</sub>CO, and H<sub>3</sub>CO. For a typical syngas mixture, a TOF of 75.6 h<sup>−1</sup> (mol of methanol/mol of Cu sites) was calculated at 60 bar and 210–250 °C.

Besides Cu/ZnO-based catalysts, a variety of other methanol catalysts containing copper have been developed. Copper supported on ZrO<sub>2</sub> or on a combination of ZrO<sub>2</sub> and ZnO was found to be an active and stable catalyst for the hydrogenation

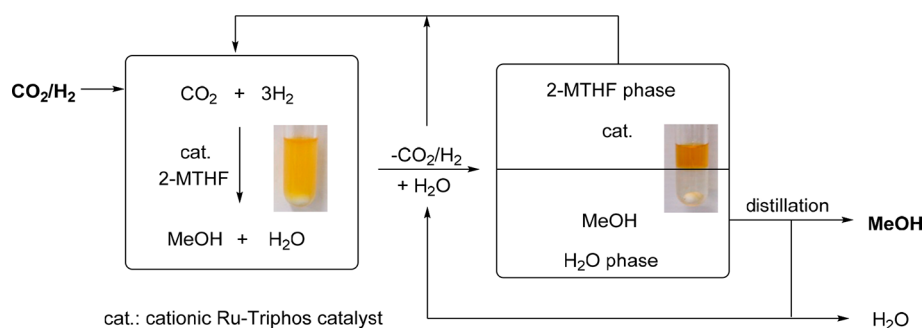


**Figure 16.** Aqueous biphasic system for recycling of the Ru–triphos catalyst in the organic 2-MTHF phase and removing the product MeOH in the aqueous phase for downstream processing.<sup>529</sup>

of CO<sub>2</sub>.<sup>270,406</sup> Słoczyński et al.<sup>508,509</sup> investigated the influence of different metal oxides (B, Ga, In, Gd, Y, Mn, Mg) on the activity and stability of Cu/ZnO/ZrO<sub>2</sub> catalysts. Again, especially the addition of gallium increases the activity, and the highest methanol yield could be obtained in this study. Toyir et al.<sup>510</sup> demonstrated the activity of the multicomponent catalyst Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> for the hydrogenation of CO<sub>2</sub> in a laboratory pilot scale unit and obtained methanol with a high purity.

Catalysts based on Cu and other supporting materials (e.g., SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) have also been studied.<sup>270,406</sup> In 2014, Graciani et al.<sup>511</sup> demonstrated the hydrogenation of CO<sub>2</sub> with a highly active Cu/CeO<sub>x</sub>/TiO<sub>2</sub> catalyst and calculated a TOF of around 29160 h<sup>-1</sup> at 300 °C. However, the comparison with the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> systems of Behrens et al.<sup>507</sup> is difficult since their calculation was based on a different model. Concerning the reaction pathway, the authors proposed an rWGS reaction and further hydrogenation of CO to methanol.

Systems based on other late transition metals such as Pd,<sup>512–514</sup> Pt,<sup>515–517</sup> and Ni<sup>518</sup> or transition-metal carbides<sup>519</sup> can also result in active heterogeneous catalysts. Especially a Ni–Ga-based catalyst developed by Studt et al.<sup>518</sup> was found to be a highly stable and active catalyst for the hydrogenation of CO<sub>2</sub>. In comparison to conventional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts, Ni<sub>3</sub>Ga<sub>3</sub> showed similar activity as well as lower generation of CO.

The first homogeneously catalyzed formation of methanol from a mixture of CO<sub>2</sub> and hydrogen was demonstrated by Tominga et al.<sup>298,299</sup> in 1993. Using [Ru<sub>3</sub>(CO)<sub>12</sub>] and KI as an additive, methanol was obtained from CO<sub>2</sub> with a TON of 32 (based on the number of ruthenium atoms) under harsh reaction conditions (240 °C, 90–140 bar). The presence of the salt was found to be necessary since the complex would otherwise decompose under these reaction conditions, resulting in the formation of methane over Ru nanoparticles. Meanwhile, various organometallic catalyst systems have been developed which use stoichiometric amounts of boranes or silanes instead of H<sub>2</sub> as reducing agents. An overview of these systems is provided in various reviews.<sup>270,520,521</sup> However, these systems are limited due to the use of stoichiometric amounts of reducing agents, the necessity to hydrolyze the formed intermediates with H<sub>2</sub>O and/or NaOH to release methanol, and the production of waste.

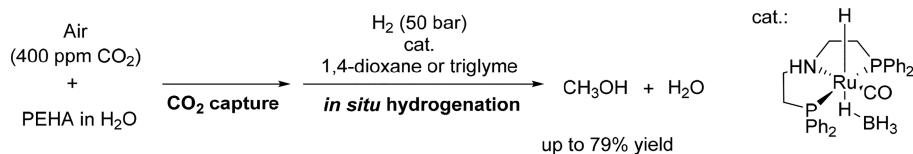
As the direct route from CO<sub>2</sub> to methanol remained challenging for molecular catalysts, several indirect routes for the hydrogenation of CO<sub>2</sub> with H<sub>2</sub> via methyl formate,<sup>522</sup> dimethyl carbonate,<sup>522</sup> methyl carbamates,<sup>522</sup> urea derivatives,<sup>523</sup> formamides,<sup>524</sup> or ethylene carbonate<sup>525</sup> as intermedi-

ates have been developed and described in detail in different reviews.<sup>1,521</sup> In a landmark study, Milstein and co-workers<sup>522</sup> obtained a TON of up to 4700 under optimized reaction conditions (110 °C, 50 bar of H<sub>2</sub>, THF, 14 h) using a Ru–PNN pincer complex as the catalyst for the hydrogenation of methyl formate to methanol. This study was particularly influential, pointing out the possibility of hydride transfer to formate intermediates as a pathway for organometallic hydrogenation of CO<sub>2</sub> beyond the formic acid level.

In 2011, Huff and Sanford<sup>526</sup> demonstrated a one-pot cascade reaction using the Milstein catalyst in combination with two other catalysts in one reaction mixture to catalyze three steps: the hydrogenation of CO<sub>2</sub> to formic acid, the esterification of formic acid to formate ester, and the hydrogenation of formate ester to methanol. However, only a low TON of 2.5 was achieved for methanol at 135 °C and 40 bar (CO<sub>2</sub>/H<sub>2</sub>, 10 bar/30 bar). In 2015, the same group described a similar cascade reaction with dimethylformamide as an intermediate product using the Ru–MACHO–BH<sub>4</sub> complex as the catalyst, K<sub>2</sub>PO<sub>4</sub> (50 equiv), dimethylamine, and 50 bar of H<sub>2</sub>.<sup>527</sup> First, CO<sub>2</sub> was hydrogenated to DMF at 95 °C. After 18 h, the temperature was raised to 155 °C and a TON of 550 for methanol was obtained, at a selectivity of 30%.

In 2012, Klankermayer and Leitner and their co-workers<sup>528</sup> reported the first hydrogenation of CO<sub>2</sub> to methanol with a single molecular ruthenium catalyst, initially also capitalizing on the formate ester route. The catalyst could be formed in situ from [Ru(acac)<sub>3</sub>] and triphos (1,1,1-tris[(diphenylphosphino)methyl]ethane), or the complex [Ru(triphos)(tmm)] (tmm = trimethylenemethane) could be used. Using 1 equiv of the acid HNTf<sub>2</sub> as a cocatalyst, a TON of 221 was achieved at 140 °C and a total pressure of 80 bar (CO<sub>2</sub>/H<sub>2</sub>, 20 bar/60 bar) in THF/EtOH as the solvent.<sup>528</sup> Further work of the same team finally revealed that the hydrogenation of CO<sub>2</sub> to methanol can be achieved with an organometallic catalyst without the need for a formate ester as an intermediate.<sup>529</sup> Under optimized conditions ([Ru(triphos)(tmm)]/HNTf<sub>2</sub>, 140 °C, CO<sub>2</sub>/H<sub>2</sub> ratio of 1:3, 120 bar of total pressure, kept constant by repressurizing), a TON of up to 895 was achieved after 64 h. A biphasic system (2-MTHF/H<sub>2</sub>O) for catalyst recycling, enabling in principle a continuous operation of the process, was presented (Figure 16), highlighting also the stability of the catalyst system toward water formed from the CO<sub>2</sub> hydrogenation.

In 2017, Beller and co-workers<sup>530</sup> extended the range of organometallic catalysts to non-noble-metal catalysts for the sequential hydrogenation of CO<sub>2</sub> to methanol. Using the in situ formed catalyst from [Co(acac)<sub>3</sub>], triphos, and HNTf<sub>2</sub>, TONs

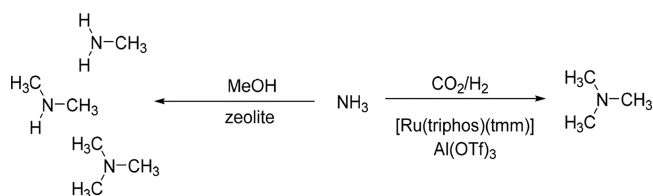
Scheme 23. CO<sub>2</sub> Capture from Air and Conversion to Methanol<sup>532</sup>

of up to 50 (100 °C, 90 bar of total pressure (CO<sub>2</sub>/H<sub>2</sub>, 20 bar/70 bar), 24 h, in THF/EtOH) were achieved. Another development is aimed at the combination of CO<sub>2</sub> capture and CO<sub>2</sub> hydrogenation to obtain methanol directly. The group of Milstein<sup>531</sup> reported CO<sub>2</sub> capture with amino alcohols at low pressure coupled with the hydrogenation of the captured product (oxazolidone) to form methanol with a Ru–PNN pincer complex as the catalyst in the presence of Cs<sub>2</sub>CO<sub>3</sub>. In 2016, Kothandaraman et al.<sup>532</sup> reported that hydrogenation of a solution of pentaethylenhexamine (PEHA) that was saturated with CO<sub>2</sub> from air resulted in a 79% yield of methanol using the Ru–MACHO catalyst at 155 °C and 50 bar of hydrogen pressure (Scheme 23). After the reaction, the CH<sub>3</sub>OH/H<sub>2</sub>O mixture obtained was separated by distillation, and the catalyst, solvent, and PEHA were reused.

Overall, the use of CO<sub>2</sub> for the synthesis of methanol is an attractive approach compared to fossil-based processes if renewable energy can be used. Several pilot plants exist for this transformation. The development of even more efficient and robust catalysts is still required, whereby an increasing understanding of the reaction mechanisms based on a combination of experimental and theoretical studies will be essential. Reaction engineering concepts to integrate the actual conversion step with CO<sub>2</sub> capture strategies and/or hydrogen supply from renewable energy sources are needed to exploit the full potential. Such extended concepts should also consider the product separation, which has been shown to influence also the overall process efficiency and thus the environmental impacts significantly. This is particularly relevant as the envisaged processing units are likely to be operated on a much smaller scale than today's mega methanol plants due to their integration in a more decentralized energy and raw-material landscape.

**2.4.2. Methylation Reactions.** **2.4.2.1. Background and Motivation.** The discussions of the various process options so far indicate that most direct integration of CO<sub>2</sub> in the synthetic pathway to the products is a very promising approach to reduce the carbon footprints significantly. From this point of view, synthetic processes seem highly attractive targets for CO<sub>2</sub> conversion in which methanol is used as a reactant. The envisaged “short cut” to harvest the maximum reduction in CO<sub>2</sub> footprint becomes even more pronounced if the reactions allow replacement derivatives of methanol such as methyl iodide, as they also eliminate the environmental impact associated with their production and/or use. The methylation of amines is the currently most advanced example for this general and certainly widely applicable concept.

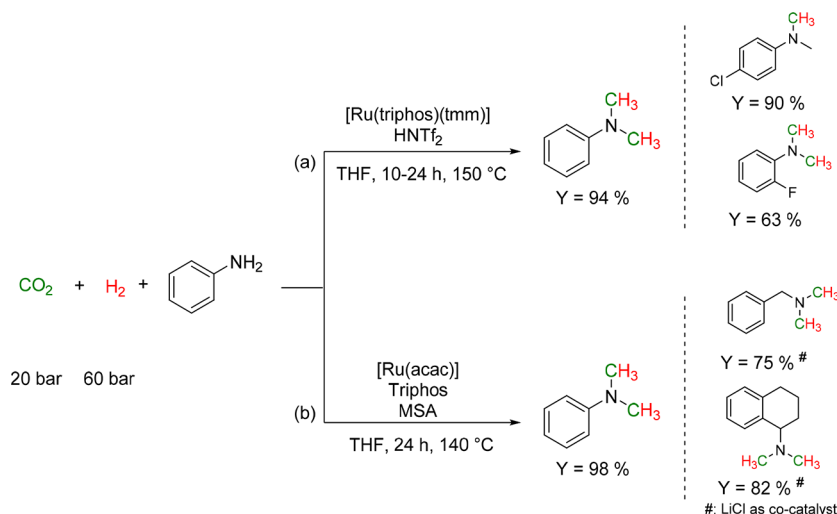
**2.4.2.2. Recent Trends in Catalytic Methylation of Amines Based on CO<sub>2</sub> Conversion.** One example where methanol as the methylating agent can be replaced directly with CO<sub>2</sub> and H<sub>2</sub> is the synthesis of methylamines (CH<sub>3</sub>NH<sub>2</sub>, MMA; (CH<sub>3</sub>)<sub>2</sub>NH, DMA; (CH<sub>3</sub>)<sub>3</sub>N, TMA). Commercially, methylamines are prepared by the exothermic reaction of ammonia (NH<sub>3</sub>) and methanol using an amorphous silica–alumina catalyst in a fixed bed reactor at 390–450 °C (Scheme 24, left).<sup>533–535</sup> The three

Scheme 24. Commercial Reaction Pathway for the Synthesis of Methylamines (Left) and Selective Ruthenium-Catalyzed Direct Methylation of Ammonia to Trimethylamine Using CO<sub>2</sub> and H<sub>2</sub> (Right)

possible methylated products MMA, DMA, and TMA are obtained in a complex product mixture with moderate selectivity for the individual product and largely controlled by the NH<sub>3</sub>/CH<sub>3</sub>OH feed ratio. Furthermore, MMA, DMA, TMA, and NH<sub>3</sub> form an azeotropic mixture, and the use of zeolite-based catalysts leads to the formation of dimethyl ether (DME) as an additional byproduct.<sup>536</sup> Consequently, the purification of the product mixture is an elaborate process including up to five distillation columns.<sup>537</sup>

An alternative pathway for the synthesis of methylamines could be the direct methylation using CO<sub>2</sub>. The formation of TMA was observed as a minor product in the Ru- or Os-catalyzed synthesis of dimethylformamide based on dimethylamine, CO<sub>2</sub>, and H<sub>2</sub>.<sup>538</sup> The methylation of NH<sub>3</sub> with CO<sub>2</sub> and H<sub>2</sub> was targeted directly using Cu- or Pd-based heterogeneous catalysts at elevated temperatures (200–300 °C).<sup>539–541</sup> However, only low yields and selectivity were achieved with this catalytic system. The triple methylation of NH<sub>3</sub> with CO<sub>2</sub> and H<sub>2</sub> can be achieved in very good yields at comparably mild conditions using the organometallic catalyst [Ru(triphos)(tmm)] and a Lewis or Brønsted acid as a cocatalyst (Scheme 24, right).<sup>542</sup> With this system, TMA was obtained with 77% yield using Al(OTf)<sub>3</sub> as a cocatalyst in 1,4-dioxane at 150 °C. In addition, the methylation of ammonium chloride was successful. In the absence of the cocatalysts, the methylated salt was obtained nearly quantitatively in a biphasic aqueous/organic system, which allows the separation and isolation of the product salt. These results demonstrate that the direct methylation not only may replace methanol, but also can offer novel selectivities in the transformation.

For amines other than ammonia, the methylation with CO<sub>2</sub> has been investigated intensively in recent years. Several catalyst systems based on different metals (Ru,<sup>543</sup> Ni,<sup>544</sup> Fe,<sup>545</sup> Zn,<sup>546,547</sup> Cu<sup>548</sup>) and even metal-free systems<sup>549–554</sup> have been developed for the methylation of amines using CO<sub>2</sub> and silanes or boranes as reducing agents.<sup>1,555</sup> Although these synthetic protocols can be very useful for specific synthetic challenges in complex molecules, a positive effect on the carbon footprint of the synthetic routes will require the use of hydrogen as a reductant. Several heterogeneous and homogeneous<sup>556,557</sup> catalysts have been described recently to achieve these conversions.

Scheme 25. *N*-Methylation of Amines Using CO<sub>2</sub> and H<sub>2</sub><sup>556,557</sup>

The reaction can be achieved with heterogeneous catalysts,<sup>558–562</sup> as exemplified for the Pd/ZrCuO<sub>x</sub> catalyst for the methylation of primary and secondary amines.<sup>562</sup> Good yields of up to 97% were achieved at relatively mild reaction conditions (150 °C, 10 bar of CO<sub>2</sub>, 25 bar of H<sub>2</sub>) and long reaction times (30–40 h). For most of the primary amines, a high selectivity for the monomethylated product was obtained. Homogeneous catalysts based on ruthenium represent so far the most widely applicable systems for methylation of aromatic amines with CO<sub>2</sub> and H<sub>2</sub>. Using the ruthenium catalyst [Ru(triphos)(tmm)] and HNTf<sub>2</sub> as a cocatalyst, a variety of primary and secondary aromatic amines were methylated with good to excellent yields of up to 94% at 150 °C (Scheme 25a).<sup>557</sup> Very similar results were obtained in an independent study using the in situ formed catalyst from [Ru(acac)]<sub>3</sub> and triphos in the presence of a Brønsted acid at 140 °C (Scheme 25b).<sup>556</sup> The methylation of more basic aliphatic amines was successful in moderate to good yields when LiCl was added as a cocatalyst.

The reductive *N*-methylation of imines was also demonstrated using the [Ru(triphos)(tmm)]/HNTf<sub>2</sub> system.<sup>563</sup> The methylation of isolated imines or in situ formed imines from an aldehyde and a primary amine provides an alternative pathway to asymmetric tertiary amines. The synthetic utility of the new method was demonstrated for the antimycotic agent butenafine that exhibits fungicidal activity particularly against dermatophytes, aspergilli, and dimorphic and dematiaceous fungi.<sup>563–565</sup> Using the new synthesis route starting from the commercially available substrates 1-naphthaldehyde and 4-*tert*-butylbenzylamine, butenafine was obtained by methylation of the corresponding imine with a yield of 80%. The direct three-component coupling gave butenafine in 60% yield in one step. In contrast to the established method, no toxic reagents are used, only water is formed as a byproduct, and the atom economy is increased from 35% to 85%.

The progress in this area clearly demonstrates the potential of CO<sub>2</sub> conversion for the direct methylation of amines. This ranges from commodity products such as trimethylamine to complex biologically active products involving the *N*-methyl unit. In the first case, direct use of all components, NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>, available at an ammonia plant may open new possibilities for process integration, whereas classical green chemistry metric such as reduced *E*-factors look promising for

the second case. Clearly, LCA studies are highly desirable to quantify the potential benefits of this new methodology in comparison to the current commercial processes.

### 3. CARBON DIOXIDE AS AN ENERGY VECTOR FOR TRANSPORTATION FUELS

#### 3.1. Addressing Global Warming Impacts and Local Emissions

Currently, approximately 23% of the global CO<sub>2</sub> emissions can be traced back to the combustion of fossil fuels in the transportation sector. Therefore, it is not surprising that the conversion of CO<sub>2</sub> into saturated hydrocarbons became the focus of potential future technologies to close the carbon cycle and reduce CO<sub>2</sub> emissions. Technologies that could be considered for CO<sub>2</sub>-based fuels comprise the Sabatier reaction for the production of methane and the Fischer–Tropsch synthesis of higher hydrocarbons. Both technologies provide access to existing infrastructures for utilization in transportation, but also for energy storage and later reconversion to grid electricity. This interconversion of electric and chemical energy enables balancing potential overcapacities resulting from fluctuations in the power generation via renewable sources, e.g., wind energy and photovoltaics.<sup>14,17,566</sup> Fuels thus produced from CO<sub>2</sub> and renewable energy, e.g., with hydrogen from water electrolysis, are discussed under various terminologies such as synthetic fuels, solar fuels, eFuel, electric fuels, or CO<sub>2</sub>-based fuels. Here, we prefer the term CO<sub>2</sub>-based fuels since it captures the defining feature making a fuel route relevant for the present review on CO<sub>2</sub> conversion. Several pilot projects already exist to evaluate the current technologies regarding the industrial feasibility of CO<sub>2</sub>-based fuels.<sup>567–570</sup>

Beyond the production of hydrocarbon substitutes for established fuels from CO<sub>2</sub>, novel alternative fuels and fuel components are emerging with potentially improved physical and chemical properties. Oxygenates, including lignocellulose-derived biofuels, as well as methanol and its derivatives such as dimethyl ether (DME) and oxymethylene ethers (OMEs) are of particular interest in this context.<sup>24,571,572</sup> Due to their oxygen content and resulting changes in the radical pathways of the combustion mechanisms, such structures have the potential to reduce soot formation during engine operation significantly.<sup>24</sup> Furthermore, miscibility with diesel as well as low

toxicity and corrosiveness can facilitate integration into today's transportation infrastructure.

Up to now, 13 integrated technoeconomic and life cycle assessment studies have been published regarding CO<sub>2</sub>-based fuels, along with one additional study focusing on an ecological evaluation only.<sup>494</sup> The cradle-to-gate boundary is sufficient for comparing different production pathways for the same fuel, since the combustion emissions are equal for all cases. Thus, we compare below the cradle-to-gate impacts for CO<sub>2</sub>-based methane of various studies to those of natural gas based on the lower heating value (LHV). More generally, however, the function of the CO<sub>2</sub>-based process is not to produce a specific molecular structure, but to provide an energy carrier to fuel a combustion process in a propulsion system. For the comparison of different CO<sub>2</sub>-based fuels, the system boundaries are therefore expanded to "cradle-to-grave", including the global warming impact of combustion to provide 1 MJ of energy (see section 1.2). Even though the transportation sector has been mentioned as a major driver for the development of CO<sub>2</sub>-based fuels, the combustion process is not further specified in the following and the impact of production and maintenance of the passenger vehicle is neglected, since these values are assumed to be the same for all regarded fuels. The benchmark in this section is the data for the EU 27 diesel mix at the refinery from the GaBi<sup>65</sup> database plus the impact of combustion as modeled by van der Giesen et al.,<sup>280</sup> resulting in an overall impact of 0.08 kg of CO<sub>2</sub> equiv/MJ for fossil diesel.

### 3.2. Methane

**3.2.1. Background and Motivation.** With the current debate on defossilization of the energy and transportation sector, methanation of CO<sub>2</sub> feedstocks has gained increasing attention during the past decade. If hydrogen is supplied via electrolysis, methanation of CO<sub>2</sub> becomes a viable option for energy storage in chemical bonds.<sup>66,573,574</sup> Besides the thermochemical route, methanation reactions can be carried out biologically at low temperatures (<70 °C) in trickle-bed or stirred tank reactors<sup>66,575,576</sup> or electrochemically at ambient pressures and temperatures of approximately 150 °C.<sup>577–579</sup> These technologies have a significant potential as cost-efficient and environmentally benign routes,<sup>580</sup> but are outside the scope of the present review that will focus on the Sabatier process as the main thermochemical route for the methanation of CO<sub>2</sub>.

**3.2.2. Current Status of CO<sub>2</sub> Conversion to Methane.** The methanations of both CO<sub>2</sub> and CO are strongly exothermic processes, releasing 164 and 206 kJ of heat/mol, respectively, and heat management during the reaction becomes a crucial aspect. The catalytic hydrogenation of CO<sub>2</sub> to methane is usually performed in the temperature range of 150–500 °C at pressures ranging from atmospheric to 100 bar. Therefore, various methanation reactor concepts ranging from adiabatic or cooled fixed-bed<sup>581,582</sup> over fluidized-bed reactors<sup>583</sup> to three-phase methanation concepts<sup>584,585</sup> are within the focus of research activities. A comprehensive overview on reactor concepts in terms of research activities and industrial practice was given recently by Rönsch et al. within their review on methanation.<sup>586</sup> The major differences between the given concepts lie within the temperature profiles inside the reactors. The fluidized-bed and three-phase methanation reactors, ideally being isothermal, are adversely affected by limited reaction rates and in the case of fluidized-bed reactors lower catalyst stability due to attrition. In contrast, cooled fixed-bed and structured reactors are polytropic; i.e., a hot spot exists close to the inlet,

and moderate temperatures are reached at the outlet of the reactor. In this case, reaction and conversion rates are higher, but the reactors are also more cost-intensive. Comparably high reaction rates are also achieved by adiabatic fixed-bed reactors with a distinct hot spot within the bed and thus high temperatures within the reactor. However, catalysts may suffer from thermal stress and thus deactivate more rapidly.

For most catalyst types presently in use, CO<sub>2</sub> methanation is considered to be a linear combination of the methanation of CO and the reverse water–gas shift (rWGS) reaction (see section 2.2), which is unavoidable in the presence of nickel catalysts. Both reaction equilibria are strongly influenced by pressure and temperature.<sup>587,588</sup> The direct CO<sub>2</sub> hydrogenation is considered to proceed via the following pathway: CO<sub>2</sub> preferably adsorbs on the interface of the active metal species and support followed by CO<sub>2</sub> dissociation on the active metal surface.<sup>589</sup> In a subsequent step, the adsorbed CO is hydrogenated.<sup>590–593</sup> In this regard for both CO and CO<sub>2</sub> as reactive species, the rate-determining steps would be the dissociation of CO to C and O surface sites as well as the hydrogenation of surface C,<sup>592–595</sup> while the hydrogenation of CH<sub>1–3</sub> species proceeds faster in comparison to the formation of the first C–H bond.<sup>594</sup> However, up to now, there has been no consensus on which elementary step is rate-determining under certain reaction conditions. While Weatherbee and Bartholomew<sup>592</sup> suggested CO dissociation being the rate-determining step at temperatures below 300 °C, Klose et al.<sup>596</sup> excluded CO dissociation at temperatures below 284 °C, and Sehested et al.<sup>595</sup> considered CO dissociation to be the rate-limiting step at temperatures between 270 and 400 °C.

To influence the activity and selectivity during the methanation reaction, the choice of catalyst is essential. The catalyst activity and selectivity can be influenced by the active metal species, the support, the promoters, and the synthesis strategies as will be highlighted in the following. The catalytic activity of several unsupported metal catalysts under methanation conditions follows the order Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag, as described by Fischer et al. already in 1925.<sup>597</sup> However, when considering the accessible metal surface area, a specific activity can be determined, following the trend of Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir.<sup>598</sup> According to Mills and Steffgen,<sup>599</sup> the trends of activity and selectivity can be summarized as follows for the metal catalysts that are most significant for methanation reactions: activity, Ru > Fe > Ni > Co > Mo; selectivity, Ni > Co > Fe > Ru.

In this regard, ruthenium is renowned to be the most active metal for the methanation of both CO and CO<sub>2</sub>.<sup>600</sup> However, Ru is less selective while being more cost-intensive in comparison to non-noble metals, which are therefore the focus of commercial application. Apart from noble metals, molybdenum catalysts exhibit the highest sulfur tolerance in comparison to all other metals mentioned above.<sup>599</sup> For instance, MoS<sub>2</sub> can be used either as an unsupported<sup>601</sup> or as a supported catalyst.<sup>602</sup> However, activity is lowest, and a higher selectivity toward C<sub>2+</sub> hydrocarbons renders Mo a less favorable choice for methanation reactions.<sup>603</sup> The latter also applies to iron catalysts, which is why they are used mostly for the Fischer–Tropsch process.<sup>604,605</sup> Even though cobalt and nickel exhibit similar activities and selectivities in methanation reactions,<sup>606</sup> the higher price of Co makes Ni the most commonly applied active metal for commercial methanation processes.

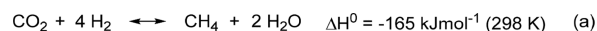
Supports used in methanation reactions are usually of large specific surface areas and high thermal stability, thus including

$\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub>.<sup>607</sup> CO<sub>2</sub> conversion was enhanced by supporting materials providing high affinity toward CO<sub>2</sub> adsorption, such as Al<sub>2</sub>O<sub>3</sub>.<sup>589</sup> Promoters such as Na, K, V, or La can enhance the activity of the catalyst further.<sup>589,608,609</sup> However, potassium is known to shift the selectivity of Ni catalysts toward undesirable higher hydrocarbons.<sup>610</sup> Similar to dry reforming of methane (section 2.2), MgO can improve the coke resistance and thermal stability, while enhancing the catalytic activity of nickel catalysts.<sup>611</sup> Furthermore, CeO<sub>2</sub>-doped Ni/Al<sub>2</sub>O<sub>3</sub> possesses a higher reducibility and stability compared to unmodified Ni/Al<sub>2</sub>O<sub>3</sub>.<sup>612</sup>

Metal catalysts in carbon monoxide hydrogenation processes are always prone to deactivation through carbon deposition, which can be retarded in methanation by addition of steam or adjustment of the H<sub>2</sub>/CO ratio.<sup>587</sup> Also, poisoning via sulfur compounds has to be considered as a major challenge in the methanation process, depending strongly on the reactant feed.<sup>613</sup> Furthermore, catalysts in fluidized beds might deactivate due to attrition, and thermal stress might be the cause of sintering or crushing of particles.<sup>614</sup> Therefore, future investigations will most likely focus on the improvement of catalyst stability as well as coke and sulfur resistance while aiming at high activity and selectivity for methanation reactions. Due to its price, Ni is still the most attractive active metal of choice.

**3.2.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Methane.** To date, all LCA studies conducted for CO<sub>2</sub>-based methanation are based on the Sabatier reaction (Scheme 26a).

**Scheme 26. Methanation Reaction of CO<sub>2</sub> (a) and CO (b) with Hydrogen**



Most LCA studies<sup>173,281,282,615,616</sup> have focused on the process simulation for Ni-catalyzed production of synthetic natural gas without recycle as proposed by Müller et al.<sup>617</sup> This process simulation is based on a pilot plant reported by Sterner<sup>618</sup> and achieves a conversion of 95% at a reaction temperature of 280 °C and 8 bar of operating pressure, which are common operating conditions for the Sabatier reaction (see section 2.2).

A comparative study by Sternberg et al.<sup>282</sup> indicates the importance of purification for the overall energy of the process. Whereas the process concept of Müller et al.<sup>617</sup> only includes water removal before the so-called substitute natural gas (SNG) is fed into the natural gas grid, an alternative concept by Saint Jean et al.<sup>619</sup> considered in addition a prior removal of hydrogen and CO<sub>2</sub>. This resulted in an increase of the energy demand by over 180%.<sup>282</sup>

Other process concepts include those assessed by Parra et al.<sup>620</sup> and Zhang et al.<sup>621</sup> operating the methanation reaction at temperatures in the range of 300–550 °C and at pressures of 4–80 bar and using a nickel-based catalyst due to the favorable costs relative to those of other more precious metals.<sup>622</sup> Reiter and Lindorfer<sup>623</sup> used reaction temperatures between 180 and 350 °C and pressures of 6–7 bar in their study. The composition of the reactor output was calculated from the stoichiometry of the reaction and information from Haldor Topsoe.<sup>624</sup> Table 7 provides an overview of the scenarios used in all LCA analyses.

The global warming impacts reported in the available LCA studies for CO<sub>2</sub>-based methane are shown in Figure 17, together with natural gas as a benchmark. Most presented studies for CO<sub>2</sub>-based methane assessed a cradle-to-gate boundary, neglecting the emissions caused by combustion. To make the results comparable, the emissions of combustion are eliminated from all studies, and the results are harmonized to 1 MJ of methane using the lower heating value. The studies presented by Hoppe et al. (2016)<sup>616</sup> and Parra et al.<sup>620</sup> are not included in Figure 17, since the results are identical to those of Hoppe et al. (2017)<sup>173</sup> and Zhang et al.,<sup>621</sup> respectively. The results from the LCA by Meylan et al.<sup>625</sup> are excluded from the comparison since it treated the indirect emissions caused by operating the process (e.g., purge, heat, electricity) only with an estimate of 10% of the incorporated CO<sub>2</sub> without further analysis.

The lowest global warming impact results in the scenario studied by Hoppe et al. (2017),<sup>173</sup> using CO<sub>2</sub> from cement production and wind power for the electrolysis. Heat recovery from the methanation and the cement plant to supply the heat demand for CO<sub>2</sub> capture was implemented. Varying the CO<sub>2</sub> source leads to a smaller credit for the CO<sub>2</sub> supply as shown by

**Table 7. LCA Studies on CO<sub>2</sub>-Based Methane<sup>a</sup>**

| reference                           | CO <sub>2</sub> source                                                                 | H <sub>2</sub> source                                                  | process description                                                                                             |
|-------------------------------------|----------------------------------------------------------------------------------------|------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| Hoppe et al. (2016) <sup>616</sup>  | biogas                                                                                 | electrolysis with wind power                                           | Müller et al. <sup>617</sup>                                                                                    |
| Hoppe et al. (2017) <sup>173</sup>  | fossil fuel power plants, air capture, biogas, incineration of wood, cement production | electrolysis with wind power                                           | Müller et al. <sup>617</sup>                                                                                    |
| Meylan et al. <sup>625</sup>        | fossil fuel power plants, air capture, biogas, cement production                       | electrolysis with wind power, photovoltaic, surplus energy, hydropower | assuming 10% emissions of the amount of CO <sub>2</sub> utilized                                                |
| Parra et al. <sup>620</sup>         | air capture, biogas                                                                    | electrolysis with Swiss grid mix                                       | Zhang et al. <sup>621</sup>                                                                                     |
| Reiter and Lindorfer <sup>623</sup> | fossil fuel power plants                                                               | electrolysis with wind power, photovoltaic, current EU grid mix        | Sterner, <sup>618</sup> Haldor Topsoe, <sup>624</sup> Breyer et al., <sup>626</sup> Cover et al. <sup>627</sup> |
| Sternberg and Bardow <sup>281</sup> | fossil fuel power plants                                                               | electrolysis with EU grid mix 2020                                     | Müller et al. <sup>617</sup>                                                                                    |
| Sternberg et al. <sup>282</sup>     | fossil fuel power plants, air capture                                                  | steam methane reforming                                                | Müller et al., <sup>617</sup> Saint Jean et al. <sup>619</sup>                                                  |
| Uusitalo et al. <sup>615</sup>      | fossil fuel power plants                                                               | electrolysis with wind power, surplus energy                           | Müller et al. <sup>617</sup>                                                                                    |
| Zhang et al. <sup>621</sup>         | fossil fuel power plants, air capture, incineration of waste, cement production        | electrolysis with wind power, photovoltaic                             | Grond et al. <sup>622</sup>                                                                                     |
|                                     |                                                                                        |                                                                        | energy requirements for compression and cooling are not considered                                              |

<sup>a</sup>All studies are based on the Sabatier reaction (Scheme 26a).

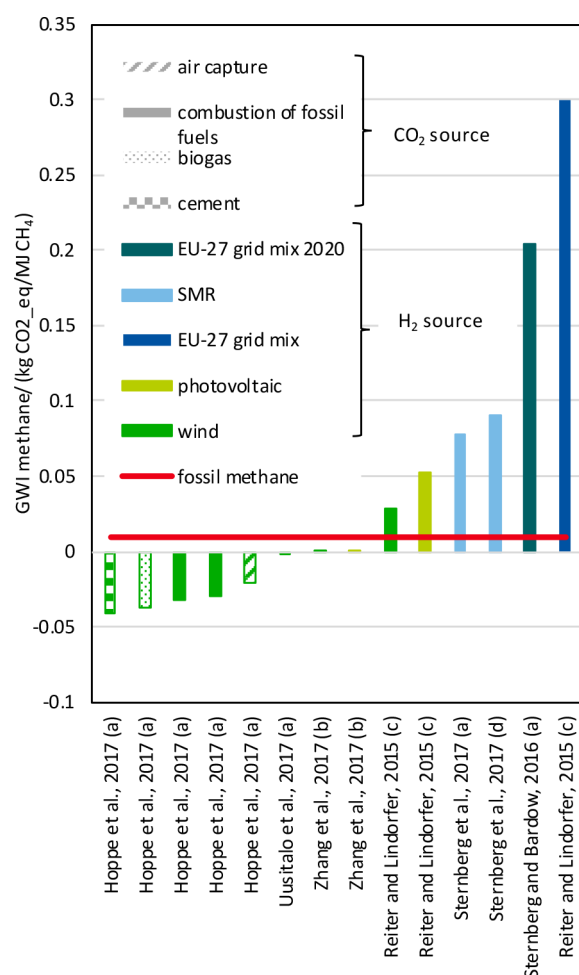


**Figure 17.** Comparison of global warming impacts for CO<sub>2</sub>-based methane production from cradle-to-gate, neglecting emissions of final combustion. The process concepts regarded in the LCA studies are proposed by Müller et al.<sup>617</sup> (a), Grond et al.<sup>622</sup> (b), Sterner<sup>618</sup> and Haldor Topsoe<sup>624</sup> (c), and Saint Jean et al.<sup>619</sup> (d). The functional unit is 1 MJ of methane. CO<sub>2</sub> sources are indicated by varying patterns, while H<sub>2</sub> sources are represented by different colors. CO<sub>2</sub>-based methane is benchmarked to fossil-based methane. The range of global warming impacts for CO<sub>2</sub>-based methane results from diverging assumptions of CO<sub>2</sub> and H<sub>2</sub> sources as well as from underlying process data for methanation (for details see Table 7).

the first four bars in Figure 17. For example, the global warming impact of methanation increases by a factor of 2 when cement

production is replaced with air capture as the carbon source.<sup>173</sup> Nevertheless, all envisaged processes have negative global warming impacts from cradle-to-gate and would thus clearly be more benign than the fossil-based benchmark.

Uusitalo et al.<sup>615</sup> also determined the global warming impact using CO<sub>2</sub> from a power plant and wind power for electrolysis (see entry 6 in Figure 17). They did not include heat integration of the methanation with the capture process, and therefore, their results differ from those of Hoppe et al. by the impact for heat supply by natural gas combustion required for CO<sub>2</sub> capture. The results presented by Zhang et al.<sup>621</sup> are based on a simplified process description, neglecting energy requirements for compression and cooling of the reactor. Additionally, no credit for utilized CO<sub>2</sub> is given, and a higher energy demand for capture is assumed, explaining why they obtain an overall higher value for the GWI.

The results from Reiter and Lindorfer<sup>623</sup> are not directly comparable to the results presented by Hoppe et al. (2017)<sup>173</sup> for a fossil carbon source and wind-power-driven electrolysis as the hydrogen supply, since they did not include a credit for converted CO<sub>2</sub>. However, within their study, the authors vary the scenario for the electricity supply to systematically study the resulting impact. When electricity from photovoltaics is used for electrolysis instead of wind power, the global warming impact increases by 80%. Using electricity from the current EU grid mix increases the global warming impact even by a factor of 10.

This high sensitivity to the assumed supply chains was also found in other studies. Sternberg et al.<sup>282</sup> compared the two process designs proposed by Müller et al.<sup>617</sup> and by Saint Jean et al.<sup>619</sup> Hydrogen supply from steam methane reforming was considered a base case corresponding to the current hydrogen supply. In this scenario, the process design by Saint Jean et al.<sup>619</sup> has a higher energy demand for separation, leading to higher impacts (Figure 17). For the process concept proposed by Müller et al.,<sup>617</sup> Sternberg and Bardow<sup>281</sup> also reported the global warming impact when using water electrolysis with electricity from the EU grid mix 2020 as the hydrogen supply. The impact of this hydrogen source is higher than for steam methane reforming, increasing the overall impact for methanation. These results further exemplify the very strong impact of the electricity source for hydrogen production on the global warming impact of CO<sub>2</sub>-based methane.

**3.2.4. Further Trends and Research Topics: Highly Dynamic Processes and Catalysts.** The production of CO<sub>2</sub>-based methane via the Sabatier reaction allows for very efficient utilization of large volumes of carbon dioxide as it achieves a

**Table 8.** Current Pilot and Commercial Scale CO<sub>2</sub> Methanation Projects

| project name                              | collaborators                            | location                    | capacity      | status                              |
|-------------------------------------------|------------------------------------------|-----------------------------|---------------|-------------------------------------|
| Hashimoto CO <sub>2</sub> recycling plant | IMR                                      | Sendai, Japan               | not specified | pilot plant 1996 (not in operation) |
| PtG ALPHA plant Stuttgart                 | ZSW, Etogas                              | Stuttgart, Germany          | 25 kW         | pilot plant 2009                    |
| PtG ALPHA plant Morbach                   | Juwi AG, ZSW, Etogas                     | Morbach, Germany            | 25 kW         | pilot plant 2011                    |
| PtG ALPHA plant Bad Hersfeld              | ZSW, IWES, Etogas                        | Bad Hersfeld, Germany       | 25 kW         | pilot plant 2012                    |
| PtG test plant Stuttgart                  | ZSW, IWES, Etogas                        | Stuttgart, Germany          | 250 kW        | pilot plant 2012                    |
| PtG project of University of Chicago      | University of Chicago, Electrochaea GmbH | Chicago, IL, USA            | 1 kW          | pilot plant 2013                    |
| PtG test plant Rapperswil                 | Erdgas Obersee AG, Etogas, HSR           | Rapperswil, Switzerland     | 25 kW         | pilot plant 2014                    |
| E-Gas/PtG BETA plant                      | ZSW, Audi, Etogas, EWE, IWES             | Werlte, Germany             | 6300 kW       | commercial operation 2013           |
| The Copenhagen project of PtG             | Electrochaea GmbH, BCH                   | Avedøre Copenhagen, Denmark | 1000 kW       | commercial operation 2016           |

high CO<sub>2</sub> conversion of 95%,<sup>617</sup> and the resulting gas can be fed into the existing gas grid after simple separation from water. It also has the potential to store significant amounts of renewable energy in chemical form and thus to transfer electricity into the mobility sector. The LCA results highlight that CO<sub>2</sub> and H<sub>2</sub> sources play a crucial role in the environmental benefits of CO<sub>2</sub> methanation processes: Global warming impact reduction requires the use of renewable electricity for the generation of hydrogen and is most pronounced if CO<sub>2</sub> emissions are avoided at the CO<sub>2</sub> source.

The required energy inputs and feedstocks lead to major challenges for the chemical conversion process since renewable energy often fluctuates and industrial CO<sub>2</sub> sources will most likely be accompanied by impurities (e.g., SO<sub>x</sub> or NO<sub>x</sub>) acting as poison to the methanation catalysts. In this regard, an important direction for future investigations is the development of flexible reactor concepts and corresponding robust catalysts adapting to the fluctuating supply of energy and hydrogen that can be operated at dynamically alternating load.

The great interest in industrial CO<sub>2</sub> methanation processing can be illustrated by the number of pilot projects and commercial applications emerging since 2009<sup>586,628</sup> (see Table 8). Most of these methanation projects are located in Europe, with a focus in Germany due to increasing installation of renewable energy and the search for utilization and storage technologies. The Audi E-Gas project achieves a capacity of 6.3 MW.<sup>629</sup> Alkaline water electrolysis is used to produce renewable hydrogen for the methanation of ca. 2.800 t of CO<sub>2</sub> from a biomass plant to produce approximately 1.000 t of methane/year.<sup>630</sup> It is integrated with an innovative marketing concept, where the “e-gas fuel card” allows Audi to record the exact gas quantities customers withdraw at any filling station from the German natural gas network. This equivalent quantity of e-gas is fed into the natural gas grid by the methanation plant, allowing almost CO<sub>2</sub>-neutral transportation. Excess heat from the exothermic Sabatier reaction is provided to the amine scrubbing needed for the biogas conditioning step. Due to the high heat integration with the biogas treatment and gas purification, the overall energy efficiency of the plant is approximately 70%. However, a conventional tube-bundle fixed-bed reactor is used within the methanation project, limiting dynamic operation and adaption to load changes. Due to this limitation of stationary large-scale plants and their high specific costs,<sup>631</sup> new developments in reactor design are intensively investigated.<sup>586</sup> Among these, three-phase reactors<sup>584,585</sup> allow almost isothermal operation over a wide load range due to utilization of liquid heat transfer media with high heat capacity. The thermal inertia of the system allows compensation of fast load changes and downtimes of several hours, which is of significant importance when it comes to the fluctuating hydrogen supply.<sup>574</sup>

In addition to novel reactor concepts, catalysts need to be improved regarding thermal stability, coke and sulfur resistance, and adaptability to fluctuating energy and hydrogen supply. Supposedly, Ni will be among the most attractive active phases due to its good cost to efficiency ratio. Aiming at high porosity and specific surface area while improving the dispersion of the active metal species, enhancements in activity can be expectable due to the highly accessible active phase. In this regard and more recently, also novel catalyst supports, such as zeolites<sup>632,633</sup> and foams,<sup>634,635</sup> have been discussed. The major effect of these supports is to enlarge the accessible surface area of the active component, in this case via

stabilization of nanoparticles on supports, providing high specific surface areas. Furthermore, it has been suggested that CO dissociation into C and O surface species takes place on 5-fold-coordinated sites of the active metal, allowing carbon atoms to form multiple bonds.<sup>595</sup> To increase the ratio of 5-fold coordination sites to step edges, small crystallite sizes are favored. In this manner, the support of the active species may play a crucial role, as has been shown for mesoporous silica-coated Ni–alumina catalysts, which exhibit high CO conversions at temperatures below 220 °C.<sup>608</sup>

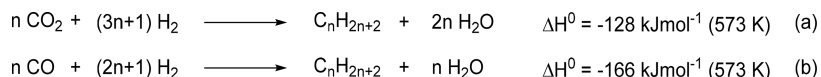
Mesoporous silica materials have gained increasing attention over recent years. Mesostructured silica nanoparticles (MSNs) containing Ni as the active phase were tested among other mesoporous silica materials. At temperatures ranging from 150 to 450 °C, these Ni/MSN systems afforded the highest activity, followed by Ni on mesoporous silica MCM-41, an HY-type zeolite, SiO<sub>2</sub>, or γ-Al<sub>2</sub>O<sub>3</sub> as a support.<sup>636</sup> The high activity was attributed to the high concentration of basic sites accessible due to the highly porous structure of the support. The presence of defect sites and vacancies within the MSN structure was considered to enable surface carbon species, which could then react with hydrogen dissociated by the Ni sites to form methane. Even after 200 h on stream, no deactivation was observed. Various metals were tested within this MSN support material at 350 °C at a H<sub>2</sub>/CO<sub>2</sub> ratio of 4:1, and in general, the reaction rate followed the expected order, with noble-metal systems such as Rh/MSN and Ru/MSN being the most active catalysts, shortly followed by Ni/MSN.<sup>636</sup> However, when the specific surface area of the supported catalyst was taken into account, the areal rate of Ni/MSN catalysts exceeded that of the noble-metal-based systems significantly.

Ordered mesoporous materials such as silica-based MCM-41- or SBA-15-type materials comprising a highly ordered structure and large pore sizes as well as specific surface areas have been investigated as potential support materials in the methanation of carbon monoxide.<sup>637,638</sup> Both catalysts containing 10 wt % Ni exhibit excellent activity and stability at 350 °C at a H<sub>2</sub>/CO ratio of 3:1 for at least 100 h on stream. The same approach can be transferred to the methanation of CO<sub>2</sub>.<sup>639,640</sup> Via conventional solvent impregnation, highly loaded and finely dispersed NiO particles supported on SBA-15 were accessible and investigated in comparison to NiO/SBA-15 obtained via hydrothermal synthesis. Unfortunately, the material prepared via solvent impregnation seems to suffer from the active species not being integrated into the SiO<sub>2</sub> scaffold during synthesis and was deactivated under the thermal stress. However, the hydrothermal synthesis provided thermally stable NiO/SBA-15 catalysts.

While methane is an attractive energy storage material due to its compatibility with the natural gas infrastructure, its use as fuel in the mobility sector is far less developed. The contribution of fossil-derived LNG-driven propulsion systems in today's passenger cars or vehicles for on-road transportation is only marginal, despite its great potential to reduce the carbon footprint in this sector. Therefore, liquid fuels based on CO<sub>2</sub> hydrogenation reactions are very actively investigated and highlighted in the following sections.

### 3.3. Fischer–Tropsch Products

**3.3.1. Background and Motivation.** The Fischer–Tropsch (FT) process enables the production of liquid hydrocarbons from CO<sub>2</sub> by direct reaction with hydrogen (Scheme 27a) or via an indirect route using synthesis gas as an

Scheme 27. Fischer–Tropsch Reaction of CO<sub>2</sub> (a) and CO (b) with Hydrogen to Hydrocarbons

intermediate (Scheme 27b). The processes can be carried out in a combination of individual steps or integrated over bifunctional catalysts.<sup>641,642</sup> In general, the direct CO<sub>2</sub> FT process is believed to proceed via reverse water–gas shift (rWGS) reaction and consecutive CO hydrogenation with unreacted hydrogen to form hydrocarbons via classical FT reaction mechanisms.<sup>643</sup> It is usually carried out at temperatures between 250 and 300 °C. Depending on the catalyst, reactor technology, and reaction parameters, the products formed consist of a distribution of molecules ranging from light hydrocarbons (C<sub>4</sub>) to medium chain fractions (C<sub>5</sub>–C<sub>10</sub>), to heavier hydrocarbons (C<sub>10</sub>–C<sub>20</sub>), and to waxes (C<sub>20+</sub>).<sup>406</sup> The carbon number in the molecules is determined from the chain growth mechanism, resulting in an Anderson–Schulz–Flory-type distribution. The distribution between saturated hydrocarbons and olefins is controlled mainly by the catalyst and the reaction temperature, as well as the formation of small amounts of oxygenates as side products. CO<sub>2</sub> hydrogenation via rWGS generates relatively low partial pressures of CO, which is the actual chain-growing agent during FT and therefore typically yields mainly shorter chain hydrocarbons which are less suitable as liquid transportation fuels.

Even though less exothermic than the methanation reaction, efficient heat removal from the reactor is one of the major technical challenges of FT processing. Various reactor concepts have been examined extensively for Fischer–Tropsch reactions, current industrialized technologies comprising fixed-bed, fluidized-bed, and slurry-phase reactors.<sup>644</sup> The development of alternative reactor concepts is closely related to the design of novel catalyst systems. Among these, especially microstructured reactors<sup>645</sup> are currently under investigation for scalable, decentralized, and self-sustained FT processing. For optimal process efficiency, the integration of the energy flow is mandatory. The high load flexibility of microstructured reactors within the chemical process would facilitate the attenuation of the fluctuating regenerative electrical energy.

**3.3.2. Current Status of CO<sub>2</sub> Conversion to Fischer–Tropsch Products.** Traditional catalysts used for FT synthesis are based on Fe, Co, Ni, and Ru. Co catalysts are mainly used in the recent industrial implementations, due to their high performance-to-cost ratio and good selectivity toward formation of heavy hydrocarbons. However, when applied in CO<sub>2</sub> hydrogenation, Co acts as a methanation catalyst, thus leading to low yields of the desired liquid hydrocarbons.<sup>646–649</sup> Product gases obtained with a Co/Al<sub>2</sub>O<sub>3</sub> catalyst contained almost only methane,<sup>648</sup> and even bifunctional Fe/Co catalysts exhibited low selectivities toward heavier hydrocarbons.<sup>650</sup>

Since iron-based catalysts are active catalysts for both the (reverse) water–gas shift reaction and the FT reaction, most research for direct CO<sub>2</sub> conversion has focused on Fe-based systems.<sup>651–657</sup> Most commonly, Fe-based systems are used as bulk<sup>658–661</sup> or supported iron oxides,<sup>662–666</sup> but form an FT-active iron carbide phase (Fe<sub>5</sub>C<sub>2</sub>) in situ during catalysis.<sup>667</sup> The rate of iron carbide formation strongly depends on the composition and structure of the precatalysts as well as the carbon chemical potential on the catalyst surface.<sup>668</sup> Still, no general consensus exists regarding the nature of the active sites responsible for either rWGS or FT reactions. It is

controversially discussed whether iron oxides (e.g., magnetite, Fe<sub>3</sub>O<sub>4</sub>)<sup>669,670</sup> or (partially) carbidic Fe sites<sup>671</sup> are responsible for rWGS activity or both reactions might occur competitively on the same active sites.<sup>672</sup> Furthermore, the carburization of the active sites is sensitive to the composition of the feed gas. Since the concentration of CO required as a carburization agent depends on the rWGS reaction if CO<sub>2</sub>/H<sub>2</sub> feed is applied, carburization occurs at a notably slower rate.<sup>673</sup>

Several promoters have been studied for improvement of stability and the selectivity to long-chained hydrocarbons.<sup>674,675</sup> Among these, transition metals (e.g., Cr, Mn, Cu, Zr, Mo, La, or Ta) as well as alkaline metals (e.g., Na, K, and Rb) and metal oxides (α-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) have been reported to affect the product distribution and catalytic activity.<sup>642,665,676–678</sup> Mn can act as both a structural promoter, improving the dispersion of the active metal and stability of the catalyst, and an electronic promoter, affecting the conversion and selectivity,<sup>674,679,680</sup> while enhancing the catalysts surface basicity.<sup>681</sup> However, too high doping results in blocking of the active sites and thus in a reduction of the activity and selectivity.<sup>681,682</sup> Cu can enhance the rWGS activity,<sup>683</sup> the dispersion of metal catalyst particles,<sup>684</sup> and the dissociation of hydrogen. Potassium is considered to be the most effective promoter. It can accelerate the carburization of iron<sup>685</sup> while suppressing undesired methanation reactions.<sup>682</sup> The Anderson–Schulz–Flory model, expressing the hydrocarbon product distribution, exhibits a high chain growth probability for K/Mn/Fe-based catalysts in the CO<sub>2</sub> hydrogenation, only slightly lower in comparison to that for iron catalysts in conventional FT systems.<sup>646,682,686</sup>

Supports for Fe-based catalysts are used to stabilize the active species and prevent sintering or agglomeration of the active sites. Typical supports include γ-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub>.<sup>646,653,687,688</sup> Among these, γ-Al<sub>2</sub>O<sub>3</sub>-supported catalysts have been considered as the best performing catalysts, as strong metal–support interactions and inherent distribution of the active sites prevent sintering and thus loss in activity.<sup>689</sup> Furthermore, if Al<sub>2</sub>O<sub>3</sub>-supported catalysts are promoted with potassium, improved catalytic activity can be achieved. This effect might be ascribed to a possible potassium alanate (KAlH<sub>4</sub>) phase, which is known for reversible hydrogen sorption at moderate temperatures (250–300 °C).<sup>690</sup> This would result in slower hydrogenation of surface carbon species, thus inhibiting methane production while higher hydrocarbons are preferred. On the other hand, chemisorption experiments on Fe–Al<sub>2</sub>O<sub>3</sub>-based catalysts have shown a contrary trend, indicating that CO<sub>2</sub> adsorption is preferred over H<sub>2</sub> adsorption upon addition of potassium.<sup>646,688</sup> So far, there is no consensus on the promoting effect of potassium; however, both arguments verify the beneficial effect of K-doping for catalytic activity and selectivity.

**3.3.3. Life Cycle Assessment of CO<sub>2</sub> Conversion to Fischer–Tropsch Products.** At present, two LCA studies for Fischer–Tropsch products from CO<sub>2</sub> can be found in the literature. Van der Giesen et al.<sup>280</sup> analyzed a process based on the reverse water–gas shift reaction to produce CO, followed by Fischer–Tropsch synthesis in a second reactor (Scheme 27b). Since the second step starts from syngas, the final product

is assumed to be largely identical to so-called gas to liquid (GTL) fuels that have combustion properties comparable to those of fossil diesel and are already produced commercially. The authors considered CO<sub>2</sub> capture from a biomass-fired and natural-gas-fired power plant as well as air capture as the CO<sub>2</sub> source. For the cases wherein CO<sub>2</sub> is obtained from a power plant, the power plant also provides the required electricity for electrolysis and the CO<sub>2</sub> conversion process. For air capture, the required electricity is produced via photovoltaic cells. The life cycle inventory data of the FT process are taken from a GTL plant of Shell in Qatar,<sup>280</sup> wherein a tubular fixed-bed reactor and a cobalt-based catalyst are used. In addition to cobalt, the catalyst consists of zirconium, titanium, and chromium as the promoters, which are common FT catalyst components, and a support of silica, alumina, or silica–alumina.<sup>691</sup> The process is operated at 25 bar and a temperature of 230 °C. The results are presented per 1 MJ of liquid fuel and are compared to fossil diesel, pure bioethanol from sugar cane, and GTL and biomass to liquid (BTL) diesel. The authors concluded that the energy demand and climate impacts of the CO<sub>2</sub>-based synthetic hydrocarbon fuel are higher than the impacts of existing fossil fuels if nonrenewable technologies are used. Using renewable energy, CO<sub>2</sub>-based fuels might show a slight improvement compared to the existing fossil fuels.<sup>280</sup>

The LCA by Falter et al.<sup>279</sup> studied the economic and ecological impact of the production of jet fuels from a CO<sub>2</sub>-based Fischer–Tropsch process. The required CO is produced through a solar thermal dissociation reaction, whereby CO<sub>2</sub> and H<sub>2</sub>O are converted to syngas (Scheme 6) using a ceria-based catalyst. Subsequently, the produced syngas is fed into the Fischer–Tropsch reactor at a pressure of 30 bar. The authors assumed a plant location in a sunny region with 3000 (kW h)/(m<sup>2</sup> a) of direct normal irradiation. Air capture is assumed as the CO<sub>2</sub> source and compared to the capture from natural gas in a scenario analysis. The functional unit used is 1 L of jet fuel and 0.87 L of naphtha. The analysis included the emissions caused by combustion. Overall, the authors reported a global warming impact of 0.49 kg of CO<sub>2</sub> equiv/L of jet fuel and 0.55 kg of CO<sub>2</sub> equiv/L of naphtha. To obtain product-specific global warming impacts, the process emissions have been allocated to the products according to their energy densities. The results are compared to a base case wherein the solar energy is replaced by electricity from the current grid mix. In this case, the global warming impact of the jet fuel increases to 4.92 kg of CO<sub>2</sub> equiv/L of jet fuel. The authors conclude that further impact reductions are possible if the solar thermochemical process is located in regions which surpass the 3000 (kW h)/(m<sup>2</sup> a) of direct normal irradiation and the thermodynamic efficiency is increased.

To compare the two studies by van der Giesen et al.<sup>280</sup> and Falter et al.,<sup>279</sup> the results are harmonized to 1 MJ of fuel and the emissions from combustion are included for both studies. The impacts are calculated for a scenario using electricity from the EU grid mix for 2020 and for a best-case scenario using renewable energies as proposed in Table 1. The harmonized global warming impacts are presented in Figure 18. Fossil diesel is presented as a benchmark. Both CO<sub>2</sub>-based fuels show higher global warming impact than fossil diesel if the 2020 grid mix is employed. For the GTL-type process, the global warming impact of 0.33 kg of CO<sub>2</sub> equiv/MJ in the scenario 2020 is mainly caused by the hydrogen supply and the electricity demand. In the best-case scenario, the impact can be reduced to 0.01 kg of CO<sub>2</sub> equiv/MJ of Fischer–Tropsch fuel. This

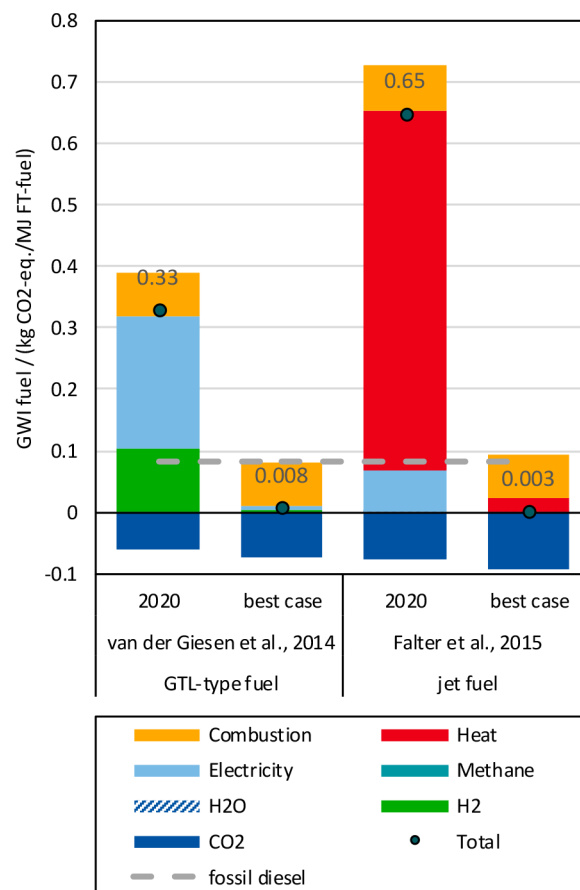


**Figure 18.** Global warming impacts (GWIs) for CO<sub>2</sub>-based Fischer–Tropsch fuels and fossil diesel as the benchmark (cradle-to-grave). The functional unit is 1 MJ of net energy based on the lower heating value of the fuel. The LCA data have been taken from van der Giesen et al.<sup>280</sup> and Falter et al.<sup>279</sup> The global warming impacts were harmonized for a scenario for 2020 and a best-case scenario according to Table 1.

reduction originates from the decreased global warming impact of the electricity supply. Similarly, the impact of jet fuel is reduced from 0.65 kg of CO<sub>2</sub> equiv/MJ in the scenario 2020 to 0.003 kg of CO<sub>2</sub> equiv/MJ in the best-case scenario. Herein, the main reduction results from the replacement of the natural-gas-fired boiler for the heat supply by power-to-heat using wind electricity.

**3.3.4. Further Trends and Research Topics: Processes and Catalysts for Dynamic Operation and Decentralized Production.** The available LCA studies show that CO<sub>2</sub>-based Fischer–Tropsch synthesis opens pathways to liquid fuels with a very low carbon footprint: While CO<sub>2</sub>-based Fischer–Tropsch products lead to higher impacts than current fuels if fossil-based energy is used as the input, the total global warming impact can be significantly lower than that of fossil diesel if renewable energy is available. In the best case, both the GTL diesel and the jet fuel studied would be practically carbon-neutral fuels. This best-case scenario, however, assumes that (a) renewable electricity is available for the production of hydrogen and a heat supply with impacts as low as those of current wind electricity and that (b) an ideal CO<sub>2</sub> source is available where CO<sub>2</sub> emissions can be avoided without any further impacts.

As both criteria require the utilization of renewable and thus fluctuating energy and resources, both the reactor and catalyst designs become crucial for high long-term stability at varying

load or even to comprise (short-term) downtimes. Furthermore, the inputs are likely to be available in a more distributed infrastructure, and the envisaged process concepts can thus not capitalize on the economy of scale in the same way as Fischer–Tropsch units based on gas or coal. In regard to the renewable energy system, small-scale and modular reactor setups will become important to enable decentralized and self-sustained production of fuels, while catalysts have to be optimized in regard to activity and selectivity toward optimum product distribution for the desired application.

In this regard, several reactor concepts are under investigation for CO<sub>2</sub>-based Fischer–Tropsch reactions. As both a slightly endothermic reaction and a highly exothermic reaction occur within a single reactor, slurry-phase or fluidized-bed reactors have been investigated in terms of efficient heat removal in comparison to fixed-bed reactors.<sup>644</sup> However, removal of water during the course of the reaction becomes a crucial factor for all three of these reactor types, as the shift of the rWGS reaction toward CO<sub>2</sub> and hydrogen inhibits the chain growth probability, thus limiting selectivity to higher hydrocarbons. Membrane reactors have been under investigation to enable water removal and push the rWGS equilibrium toward favorable partial CO pressures.<sup>692</sup> Another attractive option comprises the development of microchannel reactors for the Fischer–Tropsch synthesis, that allow scalability by numbering-up.<sup>645</sup> The modular design and significantly higher output per volume of the reactor of this technology allow for economic operation even at smaller plant sizes and variable workloads, thus reducing financial risks. In comparison to conventional fixed-bed reactors, improved thermal management enables long-term stability in combination with constant selectivity to C<sub>5+</sub> hydrocarbons, as was shown for a micro-packed-bed reactor–heat exchanger loaded with a Co–Re/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (20–40 wt % Co, 0.5–1 wt % Re).<sup>693</sup> Furthermore, the catalysts within microstructured reactors can be applied without dilution with inert materials (e.g., SiC) as would be needed for efficient heat transfer in conventional slurry or fixed-bed reactors. However, deactivation and regeneration of catalysts within the microchannels are still a challenge for industrial application, and catalyst development therefore still plays a crucial role in the FT process design.

As for the methanation technology, the preparation method of the catalyst can have a positive effect on the catalytic activity, selectivity, and stability. Tuning the morphology, including the porosity and specific surface areas, can enhance the catalytic performance drastically. For example, nitrogen-doped carbon nanotube (CNT) supported iron catalysts were highly suitable in the CO<sub>2</sub> hydrogenation.<sup>675</sup> The nitrogen-doping of the support is believed to promote the reduction of the supported Fe<sub>2</sub>O<sub>3</sub> particles to the active species. The Fe/CNT catalysts achieved significantly higher activities and selectivities to short-chain olefins compared to Fe/SiO<sub>2</sub> catalysts. On the other hand, the reducibility of the Fe<sub>2</sub>O<sub>3</sub> species into the active phase can be enhanced by improving the accessibility. In this regard, Albrecht et al. could show that cellulose-templating enhanced the reducibility of Fe<sub>2</sub>O<sub>3</sub> into carbides, thus resulting in a selectivity higher than or close to that of the state-of-the-art Fe-based catalysts in the presence of promoters, such as K, Cu, Mn, or Ru.<sup>655</sup> Also for microstructured reactors for Fischer–Tropsch synthesis, the catalyst morphology plays a crucial role, as mass transfer limitations can be overcome by structured catalysts. Catalyst geometries comprise honeycomb-like structures, monoliths, structured packings, and foams.<sup>694</sup> Heat

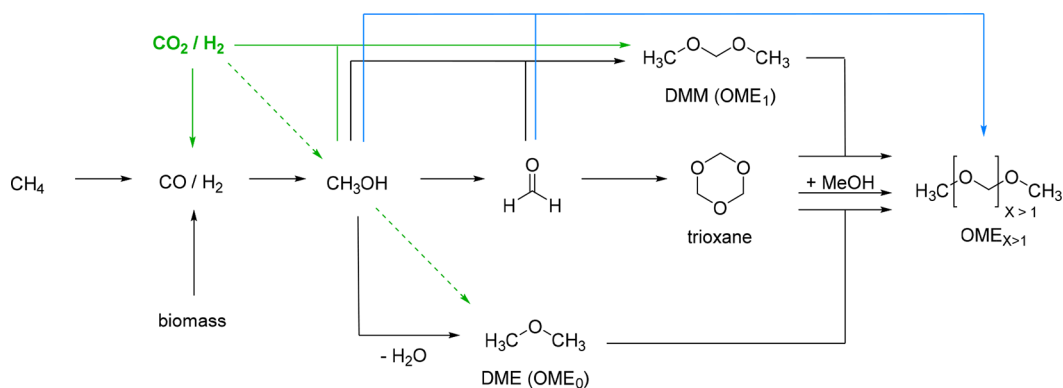
transfer and diffusion limitations can be avoided in this manner, even in the absence of dilutants, such as inert SiC.<sup>695</sup>

The catalyst support could also be used for direct selectivity toward branched FT products. To enhance branching of the Fischer–Tropsch products, which is considered to be crucial for increasing the octane number of liquid FT products, conventional catalytic reforming is carried out to upgrade the primary product. As high H<sub>2</sub> partial pressures are applied during CO<sub>2</sub> hydrogenation, hydroisomerization of long-chain alkanes can be carried out simultaneously over one catalyst system combining the necessary active phases for each reaction step.<sup>696</sup> In this manner, the reverse water–gas shift reaction would be catalyzed by oxidic Fe phases, while iron carbides catalyze the production of FT alkanes, and a zeolitic support acts as an acidic catalyst for the olefin oligomerization, isomerization, and cracking reaction. A selectivity of 55% to isoalkanes was reported for the integration of FeZn/ZrO<sub>2</sub> catalysts into HY-type zeolite supports.<sup>697</sup> When blending K-doped iron carbide catalysts with ZSM-5-type zeolites, a selectivity of 70% toward branched C<sub>4</sub>–C<sub>6</sub> hydrocarbons can be realized at a CH<sub>4</sub> selectivity below 10% during processing at 300 °C and 25 bar at typical H<sub>2</sub>/CO<sub>2</sub> ratios of 3:1.<sup>696</sup> However, a major drawback of these systems is the possible and irreversible migration of potassium into the zeolite, decreasing the isomerization activity and thus deactivating the catalyst permanently. Further deactivation of CO<sub>2</sub> hydrogenation catalysts can occur due to an increase in the crystallinity of the active species, leading to phase separation of the active metal and its promoters, as well as poisoning of the catalyst due to carbon deposition.<sup>406,660,688</sup> For iron-based catalysts, this deactivation occurs mainly due to the formation of the stable but inactive Fe<sub>3</sub>C–carbide phase, formed by Fe<sub>5</sub>C<sub>2</sub> carburization.<sup>698</sup>

Pilot plants and demonstration activities at various scales and comprising different technologies are currently operated to investigate the feasibility of the Fischer–Tropsch synthesis from CO<sub>2</sub> and H<sub>2</sub> as renewable resources, and have to be covered comprehensively here. Connected to the above discussion about decentralized infrastructures, the microstructured reactor design was demonstrated by Velocy's Fischer–Tropsch technology.<sup>699</sup> While economical production in conventional FT plants requires production capacities above 30000 barrels/day, the microchannel technology becomes viable at capacities of 1500 barrels/day according to their analysis. To overcome heat and mass transfer limitations, several thousand process channels with diameters in the millimeter range are surrounded by water-filled coolant channels, enabling easy heat removal even at high catalyst loadings. The technology has been currently demonstrated for small-scale gas-to-liquid applications starting from synthesis gas, but should be equally transferrable to direct CO<sub>2</sub> conversion.

An ultracompact microstructured reactor with integrated evaporative cooling has been developed at the Karlsruhe Institute of Technology (KIT)<sup>700</sup> and was validated on the pilot scale. The demonstration of CO<sub>2</sub> conversion into kerosene in a modular container-based plant was carried out within the Helmholtz Energy Lab 2.0.<sup>701</sup> In the first reactor, CO<sub>2</sub> is converted into synthesis gas via rWGS reaction prior to conversion into liquid fuels. For further development of the technology to market maturity, the spin-off INERATEC was founded.<sup>702</sup> Within a plant setup consisting of three major units, namely, the direct capture of carbon dioxide from air, an electrolysis unit producing hydrogen from solar power, and the

**Scheme 28.** Synthesis Pathways to Oxymethylene Ethers (OMEs) of Variable Chain Lengths, Comprising Dimethyl Ether (DME or OME<sub>0</sub>), Dimethoxymethane (DMM or OME<sub>1</sub>), and Oligomeric Oxymethylene Dimethyl Ethers (OME<sub>x>1</sub>)



microstructured chemical reactor developed, it is envisaged to convert  $\text{CO}_2$  and hydrogen into liquid fuels (including gasoline, diesel, and kerosene). A demonstration-scale process was most recently started by the company Soletair in Finland.<sup>703</sup>

The company Sunfire reported the demonstration of an integrated production of the synthetic crude oil substitute “Blue Crude” from  $\text{CO}_2$  and water, using renewable energy on a ton scale.<sup>704,705</sup> High-temperature electrolysis at solid oxide electrolyzer cells supplied the hydrogen necessary for the rWGS reaction followed by FT synthesis of the liquid fuel. Efficient reintegration of the waste heat to the steam production for high-temperature electrolysis reduces the required electricity by 16% and allows for an energy efficiency of 70%. The plant has been continuously operated for more than 1500 h as an industrial-scale endurance test. The liquid fuel derived was tested by the Audi AG and featured high cetane numbers and favorable combustion properties, as it contains no sulfur or aromatic compounds and produced almost no soot. Most recently, plans for the construction of a larger scale plant have been announced for production of up to 8000 t of  $\text{CO}_2$ -based diesel fuel by 2020 based on this technology by the company Nordic Blue Crude and its partners in Herøya, Norway.<sup>706</sup>

### 3.4. Oxygenates

**3.4.1. Background and Motivation.** Oxygenates gained considerable attention within the past decade to introduce renewable fuels and fuel components into the transportation sector.<sup>24</sup> Biomass has been a focus of research as a carbon source for tailor-made fuels to substitute hydrocarbons. As oxygen-containing fuel components in general have the potential to significantly reduce soot formation,<sup>707</sup> molecules assembled from  $\text{CO}_2$  are also highly attractive. As shown in Scheme 28, a set of currently investigated  $\text{CO}_2$ -based oxygenate fuels can be classified as so-called oxymethylene ethers (OMEs), comprising dimethyl ether (DME; corresponding formally to “OME<sub>0</sub>”), dimethoxymethane (DMM or OME<sub>1</sub>), and oligomeric oxymethylene dimethyl ethers (OME<sub>x>1</sub>). With increasing chain length, cetane numbers higher than those of conventional diesel can be obtained, which can lead to increased operation efficiencies of diesel engines.<sup>708</sup> Today, OMEs are produced via fossil-based synthesis gas, mainly from coal or natural gas. Using the syngas platform, OMEs would also be accessible from biomass or carbon dioxide applying the same basic technologies.<sup>709–711</sup> A direct route starting from  $\text{CO}_2$  and renewable hydrogen seems highly attractive to enhance productiveness and decrease the number of production and purification steps significantly.

**3.4.2. Current Status of  $\text{CO}_2$  Conversion to Oxygenates.** DME (OME<sub>0</sub>) is conventionally synthesized via condensation reaction of 2 equiv of methanol. DME is therefore a common (unwanted) byproduct of methanol production (see section 2.4). DME constitutes an intermediate within the methanol-to-gasoline (MTG) and methanol-to-olefine (MTO) processes, where DME is further converted into  $\text{C}_{2-5}$  alkenes via dehydration. Both MTG and MTO processes are catalyzed via acidic zeolite catalysts, and the DME yield is highly dependent on the contact time during these processes. Similarly, DME is commercially produced via acid-catalyzed condensation of 2 equiv of methanol.<sup>712</sup> For example, in their commercial demonstration plant, Oberon Fuels (Brawley, CA) converts methane from biogas or natural gas resources via this route to approximately 10000 gal of fuel-grade DME/day for the local market in North America.<sup>713</sup> The produced fuel is currently used by the Volvo Group for the commercial demonstration of DME-powered heavy-duty vehicles. The global market size in terms of volume has been estimated to be approximately 3.7 million t within 2014, and the world production of DME has risen to approximately 5 million t/year today.<sup>714</sup> By 2020, China’s National Development and Reform Commission expects the production capacity to rise even further to 20 million t of DME/year. The global production of DME is mainly carried out in China, but also Korea, Japan, and Brazil built new production facilities, while Egypt, India, Indonesia, Iran, and Uzbekistan started or planned further capacity additions. Major applications of DME cover propane substitution in home heating and cooking gas (mostly in China), aerosol spray-can propellants, solvents, and chemical feedstock, while exploration of DME as a transportation fuel is still under investigation.

Alumina ( $\text{Al}_2\text{O}_3$ )-based materials are the most common catalysts for the dehydration reaction of methanol to DME, e.g., applied in a fixed-bed reactor.<sup>715,716</sup> Typical reaction temperatures are in the range of 250–400 °C at pressures between 10 and 25 bar. Methanol conversion under these conditions ranges from 70% to 85%, respectively, at high selectivity.<sup>717–719</sup> Only trace amounts of formaldehyde are observed as a byproduct. Research interest is also directed to bifunctional catalysts containing both the metallic methanol catalyst and acidic sites as direct single-step synthesis of DME becomes feasible.<sup>720–722</sup> To shift the thermodynamic equilibrium, membrane reactors might be used for the selective removal of water during the course of reaction.<sup>723</sup> Otherwise, product purification, including removal of residual methanol and water, is an energy

consuming but necessary final step within the process scheme. Even though DME can be considered a promising diesel substitute,<sup>724</sup> it is a liquid gas with a boiling point of  $-24.8\text{ }^{\circ}\text{C}$ . Thus, modifications of both engines and infrastructure become inevitable.

DMM ( $\text{OME}_1$ ) production is commercially carried out via an acid-catalyzed condensation of methanol and formaldehyde. The overall sequence starting from MeOH thus involves two reaction steps: methanol oxidation to formaldehyde in the gas phase, followed by acetalization of the latter with methanol in the liquid phase.<sup>725,726</sup> Methanol oxidation is catalyzed via metallic silver catalysts at atmospheric pressures and temperatures ranging from  $560$  to  $600\text{ }^{\circ}\text{C}$ . The conversion reaches up to  $75\%$ , and by recycling of the unreacted methanol, an  $89\%$  formaldehyde yield is achieved. The oxidation can also be carried out over iron molybdate mixed oxide catalysts at temperatures below  $400\text{ }^{\circ}\text{C}$ , yielding  $95\%$  formaldehyde at  $98\text{--}99\%$  conversion.<sup>727</sup> The FeMo catalysts are less sensitive to impurities, and their long-term stability exceeds that of silver catalysts. For the further condensation to DMM, strong mineral acids such as  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  can be applied as homogeneous catalysts. Due to the challenging removal of these and the inherent production of hazardous waste, heterogeneous acid catalysts would be preferable in terms of easier separation. The most common heterogeneous acids applied include ion exchange resins, sulfonated fluoroalkylene resins, and aluminosilicates.<sup>572</sup> Since the condensation reaction is limited by the reaction equilibrium, catalytic distillation is applied to continuously extract DMM from the reactor. At a reaction temperature of  $90\text{ }^{\circ}\text{C}$ ,  $99.8\%$  conversion and  $99.1\%$  DMM selectivity can be achieved, while methanol is the major impurity.<sup>728</sup>

Currently, most DMM producers and suppliers are located in Asia, mainly in China. The supply ability ranges from small quantities to  $5000\text{ t/month}$ .<sup>729</sup> The Turkish company FKLC Laboratory and Waste Oil Recycling Technologies (Adana, Turkey) offers a supply ability of up to  $10000\text{ t/month}$ . The main suppliers in Europe are INEOS Paraform (Mainz, Germany)<sup>730</sup> and Lambiotte & Cie (Brussels, Belgium).<sup>731</sup> In 2012, INEOS Paraform invested  $\text{€}2$  million into the construction of their new process line to synthesize DMM.<sup>732</sup> However, no production capacities are given for their process.<sup>733</sup> Global market reports for DMM production for the top manufacturers in each country can be accessed via the FIOR Markets platform.<sup>734</sup> So far, DMM is mainly used as a precursor to several polymers and ion exchange resins as well as a solvent for various applications.

Recently, Thavornprasert et al.<sup>572</sup> published a comprehensive review on the state-of-the-art for various catalyst systems for the direct synthesis of DMM from methanol without addition of formaldehyde. Various catalytic systems have been reported, and the most studied catalysts can be summarized as  $\text{RuO}_2$ ,  $\text{Re}$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Fe}_2(\text{MoO}_4)_3$  unsupported or on various supports, such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{SnO}_2$ , among many others.<sup>735–739</sup> Recently, the successful synthesis of DMM in the liquid phase was also achieved, applying molecular  $\text{RuCl}_3$  as a catalyst for the oxidation/condensation reaction in one step.<sup>740</sup> Among all of these, the FeMo-based catalysts showed the most promising performance, yielding up to  $90\%$  DMM at  $60\%$  conversion of methanol, when high feed methanol ratios ( $40\%$ ) were applied at temperatures of  $280\text{ }^{\circ}\text{C}$ , resulting in a productivity of  $4.6\text{ kg}_{\text{DMM}}\text{ h}^{-1}\text{ kg}_{\text{cat}}^{-1}$ .<sup>739</sup> Since FeMo-based catalysts are highly stable and cost-efficient and are

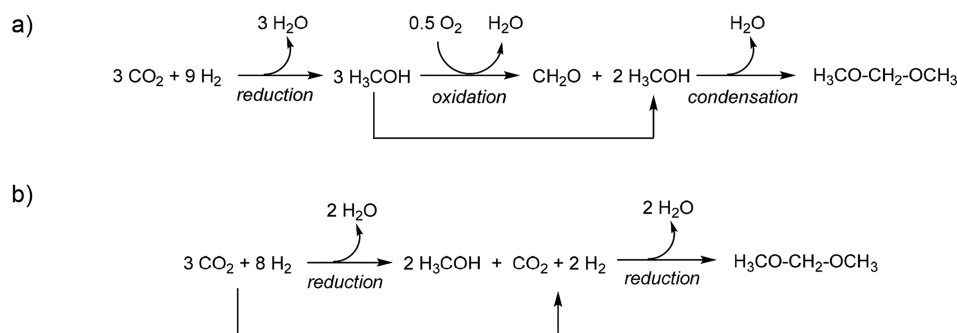
already provided at industrial scale for the methanol oxidation to formaldehyde, these systems offer a good opportunity for an integrated direct DMM synthesis starting from methanol. However, methanol production from  $\text{CO}_2$  would thus still be a separate step necessary prior to DMM production, and the integrated process would still require an oxidative step to achieve the formaldehyde level of the central  $\text{CH}_2$  unit.

To circumvent this redox-inefficient pathway, a reductive approach to obtain DMM directly from methanol and  $\text{CO}_2/\text{H}_2$  has been suggested as an attractive alternative.<sup>741</sup> Using a molecular triphos-based ruthenium catalyst,  $[\text{Ru}(\text{triphos})-(\text{tmm})]$  [triphos =  $1,1,1\text{-tris}[(\text{diphenylphosphino})\text{methyl}]\text{-ethane}$ ; tmm = trimethylenemethane], in combination with selected Lewis and/or Brønsted acidic cocatalysts, methanol could be converted to DMM in the presence of  $\text{CO}_2$  and  $\text{H}_2$  (in a  $1:3$  ratio) under mild conditions ( $p_{\text{total}} = 80\text{ bar}$ ,  $T = 80\text{--}120\text{ }^{\circ}\text{C}$ ) in a direct reductive reaction pathway. The highest TON of 214 toward DMM was achieved in the presence of  $\text{Al}(\text{OTf})_3$  as an acidic cocatalyst at  $80\text{ }^{\circ}\text{C}$ . In a very recent study, the group of Klankermayer substituted ruthenium by cobalt as a nonprecious transition-metal catalyst for the production of DMM from methanol,  $\text{CO}_2$ , and  $\text{H}_2$ .<sup>742</sup> Via modification of the triphos ligand with selected substituents on the phenyl group, the TON could be increased from 92 to 157 for the corresponding  $\text{Co}(\text{BF}_4)_2/\text{triphos}^{\text{tol}}/\text{HNTf}_2$  catalytic system, exhibiting an activity comparable to that of the precious metal catalyst  $\text{Ru}/\text{triphos}$ . Furthermore, the reaction allows the synthesis of a broad range of other dialkoxymethane ethers from the respective alcohols,  $\text{CO}_2$ , and  $\text{H}_2$ .

**3.4.3. Life Cycle Assessment of  $\text{CO}_2$  Conversion to Oxygenates.** There are three LCA studies for oxygenate-based fuels presented in the literature.<sup>277,494,743</sup> Schakel et al.<sup>277</sup> based their studies on a process simulation of the DME synthesis. The  $\text{CO}_2$  is converted to syngas via dry reforming of methane (Scheme 6), using a  $\text{Ni}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst, and then injected into the reactor at a temperature of  $250\text{ }^{\circ}\text{C}$  and a pressure of  $79\text{ bar}$ . As the catalyst for the DME synthesis, the most common catalyst for DME production,  $\gamma\text{-Al}_2\text{O}_3$ , is used. Both process steps are modeled as Gibbs free energy reactors in Aspen+. The study considered the  $\text{CO}_2$  supply from hydrogen production via steam methane reforming and water–gas shift reaction.  $\text{CO}_2$  is captured between the water–gas shift reaction and the hydrogen purification by pressure swing adsorption. The upstream processes, including hydrogen production and  $\text{CO}_2$  capture, are excluded from the system boundaries of life cycle assessment. The authors reported a global warming impact of  $35.8\text{ g of CO}_2\text{ equiv/MJ of DME}$ .

In a study reported by Matzen et al.,<sup>494</sup>  $\text{CO}_2$ -based methanol is converted to DME in a condensation reaction. The hydrogen for methanol production is supplied by electrolysis driven by wind power, and the  $\text{CO}_2$  is captured from biomass fermentation. As a result, a global warming impact of  $0.5\text{ t of CO}_2\text{ equiv/MJ of DME}$  is reported and compared to the global warming impact of methanol. Matzen et al.<sup>494</sup> also report on four other impact categories, namely, acidification potential, photochemical oxidation formation, particulate matter formation, and human toxicity. All results are compared per megajoule of product to those of methanol. In conclusion, methanol shows lower impact values in all categories. This study is not regarded further, since the results are not comparable to those of other studies due to a lack of information on energy demands and material flows.

**Scheme 29.** Stoichiometry of the Production Routes to Dimethoxymethane (DMM) from CO<sub>2</sub> and H<sub>2</sub> via (a) Methanol Oxidation and (b) Reductive Formation of the CH<sub>2</sub> Unit



Deutz et al.<sup>743</sup> carried out an LCA on CO<sub>2</sub>-based DMM, which is combusted in a 35 vol % blend with diesel. In this study, two pathways are compared: the oxidative and reductive production routes (parts a and b, respectively, of Scheme 29). In both routes, the required methanol is produced from CO<sub>2</sub> and H<sub>2</sub>. The stoichiometric material balance for the oxidative route is shown in Scheme 29a. For the LCA, the process data are taken from process simulations in the literature.<sup>744–750</sup> For the reductive production route (Scheme 29b), the overall stoichiometry shows that the direct conversion of methanol with CO<sub>2</sub> and H<sub>2</sub> requires less hydrogen to generate the central CH<sub>2</sub> unit of DMM. For the reductive process, no detailed process simulations exist yet.<sup>743</sup> Thus, the direct route has been assessed assuming stoichiometric inputs and 100% conversion. The final separation step has been assumed to be identical in both routes.

As the CO<sub>2</sub> source, the LCA study considered air capture and CO<sub>2</sub> from a biogas plant. In the biogas plant, the energy demand for capture was neglected since the CO<sub>2</sub> has to be separated anyway for biogas upgrading to the gas grid. Thus, no additional energy demand occurs if this CO<sub>2</sub> is now used instead of being emitted. Therefore, the impact of the capture process was attributed to the biogas plant and not to the CO<sub>2</sub> capture. This CO<sub>2</sub> source then corresponds to the best-case scenario used in this review (Table 1). The hydrogen was supplied by electrolysis, using the European mix of wind energy and the European electricity grid mix 2020 in the best-case and the worst-case scenarios, respectively.

The two production routes were compared within “cradle-to-gate” system boundaries for a functional unit of 1 kg of DMM. Using wind power for the hydrogen supply and biogas as the CO<sub>2</sub> source, a global warming impact of −1.59 kg of CO<sub>2</sub> equiv/kg of DMM was estimated for the route via methanol oxidation to formaldehyde. The reductive route showed a similar global warming impact of −1.6 kg of CO<sub>2</sub> equiv/kg of DMM. The reductive route requires less hydrogen and CO<sub>2</sub> than the oxidative route, and the direct CO<sub>2</sub> emissions are reduced due to the one-stage process design. However, the direct route requires a higher amount of energy since less waste heat is available from methanol production if the two processes are colocated. Overall, this leads to a trade-off between direct and indirect emissions, resulting in global warming impacts similar to those for the oxidative route. From a fundamental thermodynamic viewpoint, the direct reductive route seems beneficial with an exergetic efficiency of 86% in contrast to 74% for the oxidative routes. The exergy efficiency properly accounts for different forms of energies and quantifies the fraction of input exergy, which ends up in the final product.

To assess the potential for the mobility sector, the cradle-to-grave impacts of a 35 vol % DMM blend with diesel were compared to those of fossil diesel. Due to the smaller lower heating value of DMM in comparison to that of fossil diesel, only a 23.5 mass % concentration of the diesel is substituted in a 35 vol % DMM blend. In addition to fuel production, this analysis also included combustion in a single-cylinder test engine to parametrize full driving cycle simulations. The functional unit was in this case 1 km of driving in a passenger vehicle. Construction and maintenance of the vehicle were neglected since these impacts are assumed to be similar for the fossil diesel and the blend. The underlying scenario again assumed wind electricity and CO<sub>2</sub> capture at a biogas plant. The global warming impact was found to be reduced by about 22% for both production routes of the CO<sub>2</sub>-based DMM blend compared to fossil diesel due to less production emissions. Since replacing a 23.5 mass % concentration of diesel by DMM reduced the global warming impact by 22%, DMM could be seen as an almost carbon-neutral blending component. During combustion to generate propulsion, the global warming impacts of the DMM blend are similar to those of fossil diesel, showing that the blend retains the efficiency of the current diesel. At the same time, the local emissions of NO<sub>x</sub> and soot are largely reduced by 43% and 75%, respectively.

The authors also showed that the global warming impact strongly depends on the supply chains. For the worst-case scenario using air capture as the CO<sub>2</sub> source and the European grid mix 2020 for electrolysis, the global warming impact doubled compared to the numbers cited above. In this worst-case scenario, the blend produced by the reductive and the oxidative routes increases the global warming impact by 31% and 33%, respectively, compared to that of fossil diesel.

The results for DMM are compared to the study on DME of Schakel et al.<sup>277</sup> in Figure 19. The LCA results for oxygenate-based fuels presented above have been harmonized according to Table 1. For the comparison, the global warming impacts only of the pure components are considered. For this purpose, the cradle-to-gate emissions from production are added to the combustion emissions, which were computed assuming stoichiometry.

In the scenario 2020, the global warming impacts from DME are already about equal to those of fossil diesel, where DMM would increase emissions by 64% and 77% for the reductive and the oxidative routes, respectively. In the best-case scenario, the comparison in Figure 19 shows that the global warming impact can be largely reduced to 0.05 and 0.005 kg of CO<sub>2</sub> equiv/MJ of fuel for DME and DMM, respectively. The reduction in comparison to the scenario 2020 mainly originates

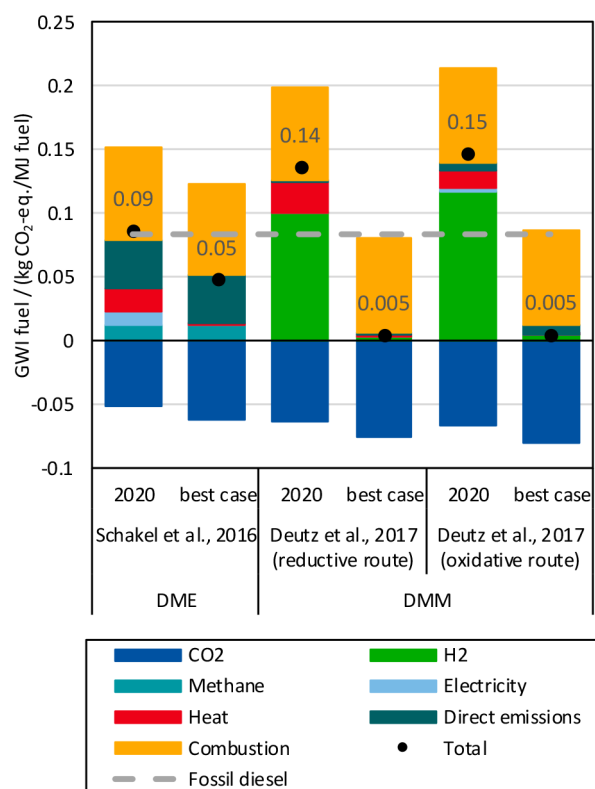


**Figure 19.** Global warming impacts (GWIs) of three CO<sub>2</sub>-based pathways for oxygenate-based fuel production to fossil diesel as the benchmark (cradle-to-grave). The following pathways are considered: production of DME (Scheme 28; green dashed line) reported by Schakel et al.,<sup>277</sup> DMM production by the reductive route (Scheme 29b), and DMM production by the oxidative route (Scheme 29a) reported by Deutz et al.<sup>743</sup> The functional unit is 1 MJ of net energy based on the lower heating value of the fuel. The global warming impacts were harmonized for a scenario for 2020 and a best-case scenario according to Table 1.

from the replacement of fossil-based power plants by wind power, which leads to a lower global warming impact for electricity in comparison to the grid mix. If the global warming impact for electricity is sufficiently low, the hydrogen supply by electrolysis is preferable to steam methane reforming, and even heat is provided by power-to-heat instead of natural gas combustion.

Besides the unavoidable combustion, the global warming impact of DME is mainly caused by direct emissions and the fossil supply of methane, which is still used for dry reforming to produce syngas, in the best-case scenario. For the best-case scenario, it would be possible to use CO<sub>2</sub>-based methane to avoid this carbon emission (Figure 17).

Both oxygenate-based fuels DME and DMM are typically used as a blend with fossil diesel in varying proportions. Thus, the global warming impact of the resulting blend is higher than the values shown for the pure components, since the impacts of diesel production have to be added according to the diesel mass fraction in the blend.

**3.4.4. Further Trends and Research Topics: Adopting the Fuel Design Process to CO<sub>2</sub>-Based Oxygenates.** The production of the CO<sub>2</sub>-based oxygenates DME and DMM (or OME<sub>0,1</sub>) as fuels has been shown to allow reduction of the global warming impact of the transportation sector. The prospect that (almost) carbon-neutral fuel production from

CO<sub>2</sub> and hydrogen is viable if electricity generated from renewable energy is applied for heat and hydrogen production opens numerous pathways for alternative and renewable fuels. Importantly, oxygenates not only close the carbon cycle in transportation, but also provide the potential to strongly reduce both soot and NO<sub>x</sub> emissions, even if used only as a blend component. To exploit the molecular diversity resulting from these options, a systematic fuel design<sup>24</sup> process should include the following steps: (i) selection of promising targets on the basis of combustion properties, including the emission profile; (ii) identifying and evaluating synthetic pathways and process options; (iii) analyzing the potential from a systems perspective. While this design process typically aims at a broad range of molecular targets in step i, we will exemplify here only steps ii and iii for OME-type fuels as a prototypical case study.

**3.4.4.1. Synthetic Pathways and Process Options for OME<sub>x</sub>.** While the previously discussed oxygenates DME and DMM are characterized by low boiling points and high vapor pressures, OME<sub>x</sub> oligomers with a chain length of  $3 < x < 5$  have vapor pressures and boiling points comparable to those of common diesel fuel and are liquid under a wide range of operating conditions. Therefore, they are more readily compatible with the current infrastructure of distribution and handling of liquid fuels. The synthesis of oligomeric OME<sub>x</sub> can be achieved via several distinct routes all commencing from methanol. The routes involve formaldehyde, trioxane, DME, or DMM both as key intermediate steps and as substrates. To economically produce OME<sub>x</sub>, low-cost substrates such as methanol and formaldehyde would seem most attractive. However, the control of the oligomer distribution for at least partially reversible condensation processes and challenges in separation of aqueous product streams make the evaluation of the preferred pathway more complex.

The synthesis of OME from methanol and formaldehyde using catalytic amounts of sulfuric acid was already described by Staudinger et al. in 1920.<sup>751</sup> Various formaldehyde sources, including formalin, paraformaldehyde, or trioxane, can be used in the presence of acidic catalysts.<sup>752–758</sup> The major obstacle of the direct synthesis of OME<sub>x</sub> lies in the formation of byproducts and intermediates, including water, hemiformals, and glycols.<sup>758</sup> In this regard, purification via rectification to obtain the desired chain-length fractions at low impurity levels (e.g., water, hemiformals, glycols, and residual formaldehyde) can be challenging and cost-intensive.<sup>759</sup>

In 1948, the Imperial Chemical Industries (ICI) and DuPont patented the synthesis of short-chained oligomeric OMEs starting from DMM and formaldehyde catalyzed via mineral acids.<sup>760,761</sup> The best results were obtained in the absence of water. In 1987, this concept was further improved via the addition of lithium halides as promoters, resulting in higher OME yields.<sup>762</sup> With the recognition of OMEs as potential fuels or fuel components in 1998,<sup>763,764</sup> interest in further optimization of the current state-of-the-art process was drastically increased.

Various homogeneous and heterogeneous acid catalysts have been reported, including sulfuric acids, zeolites, ion exchange resins, metal oxides, and heteropolyacids.<sup>756,757,765</sup> Numerous investigations and optimizations regarding the anhydrous synthesis route starting from DMM and trioxane have been carried out within the past several years.<sup>571,759,765,766</sup> BASF described the formation of OME to occur with a product composition of 24.5% OME<sub>2</sub>, 11.7% OME<sub>3</sub>, 5.2% OME<sub>4</sub>, and

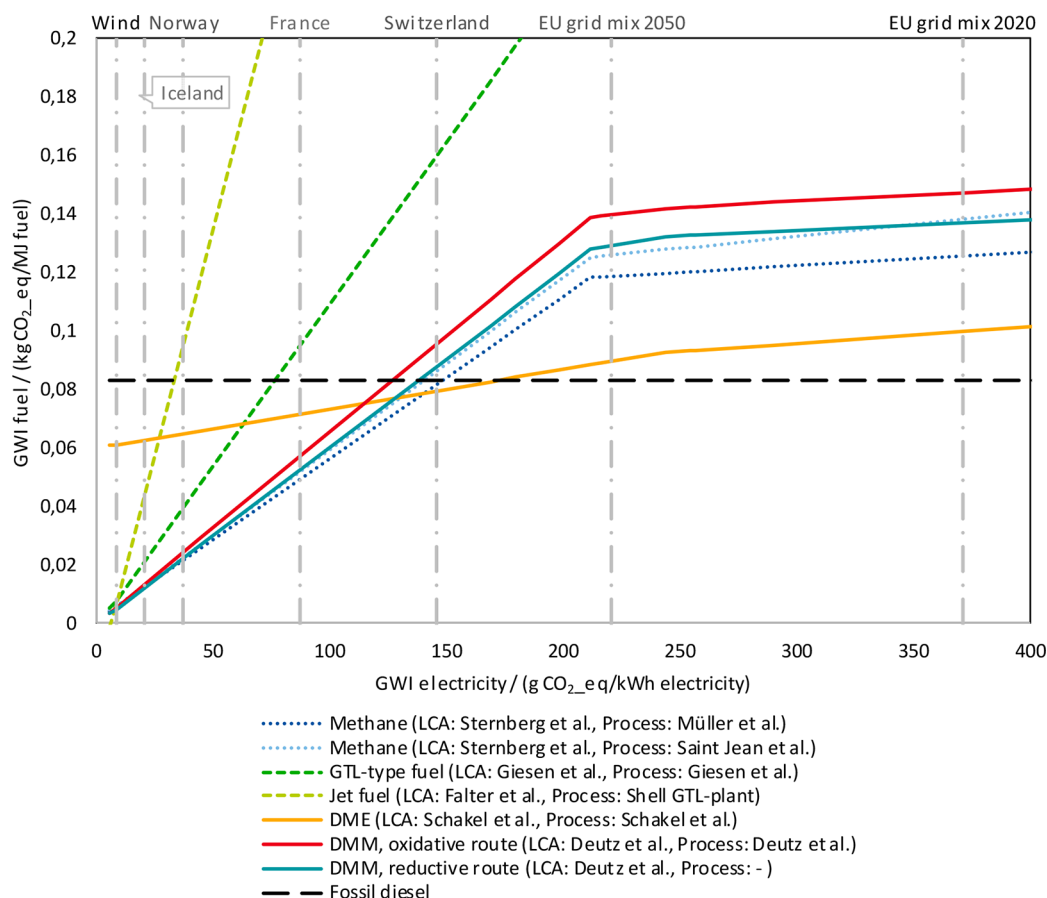


**Figure 20.** Global warming impacts (GWIs) for all discussed  $\text{CO}_2$ -based fuels and fossil diesel as the benchmark (cradle-to-grave). The fuels are grouped by fuel category: methane (dotted line), Fischer–Tropsch fuels (dashed line), and oxygenate-based fuels (solid line). The global warming impacts for methane<sup>282</sup> are calculated according to the process simulations of Müller et al.<sup>617</sup> and Saint Jean et al.<sup>619</sup> The Fischer–Tropsch fuels are calculated according to Falter et al.<sup>279</sup> and van der Giesen et al.<sup>280</sup> for the jet fuel and the GTL-type fuel, respectively. DME is estimated according to Schakel et al.<sup>277</sup> The global warming impacts of DMM are calculated according to Deutz et al.<sup>743</sup> Different national grid mixes are given as gray dashed–dotted lines. The functional unit is 1 MJ of net energy based on the lower heating value of the fuel. The global warming impacts were harmonized according to Table 1.

9.1%  $\text{OME}_{x>4}$  after 16 h at 100 °C using catalytic amounts of sulfuric acid. The continuous process is divided into the OME reactor containing the acidic catalyst and a basic fixed bed for the neutralization of the product mixture followed by three distillation columns for the product fraction separation.<sup>767</sup> The advantage of this synthesis route compared to the other methodologies is the higher OME selectivity, as formation of byproducts, such as hemiacetals, can be avoided due to the absence of methanol and water. The synthesis of OMEs can also be carried out starting from DME and trioxane.<sup>768</sup> In comparison to other synthesis approaches, the DME-based methodology is significantly less developed, however.

Within the past decade, more than 100 patents concerning the  $\text{OME}_x$  synthesis via various substrates, process technologies, and catalysts have been released, with very dynamic activities in China. Here, coal can be used to provide the feedstock to generate methanol as the starting point for the production chain, thus allowing the production of liquid fuels with low emission profiles from this resource.<sup>769–773,773–775</sup> For example, the Lanzhou Institute of Chemical Physics patented the batchwise production of  $\text{OME}_x$  from methanol and formic acid via various acidic ionic liquids at 80–140 °C, yielding up to 43%  $\text{OME}_{3–8}$ .<sup>773</sup> Recently, Zhang et al. illustrated the current developments in the synthesis of poly(oxyethylene) dimethyl

ethers, including running plants and projects in the planning or construction stage as well as their total OME production capacities.<sup>776</sup> Accordingly, five operating plants in China enable a total production capacity of approximately 52000 t/a of  $\text{OME}_x$ . A new large-scale plant with a 400000 t/a production capacity is under construction and planned to be finished in September 2017. Five more plants are currently in the planning stage and will cover a further total production capacity of 760000 t/a, illustrating the strong industrial interest in the OME production even further.

Although most catalyst studies focus on strongly acidic ion exchange resins as heterogeneous catalysts, acidic zeolite catalysts might be a viable alternative. Acidic zeolites of the ZSM-5 type were investigated by Wu et al.<sup>777</sup> but were shown to have comparably low catalytic activity. After 45 min at 120 °C, a ZSM-5 catalyst with a Si/Al molar ratio of 580 yielded 88.5%  $\text{OME}_{2–8}$  at 47.5% DMM and 85.3% trioxane conversion. At these high temperatures, methanol and formaldehyde were the major byproducts and traces of methyl formate were formed. More recently, Lautenschütz et al.<sup>778</sup> tested various zeolites (BEA25, Y30, MFI27, and MOR30) in comparison to the acidic ion exchange resin Amberlyst36. The most efficient BEA25 catalyst converted 49.1% of DMM and 94.5% of trioxane in 60 min at atmospheric pressure and room

temperature, yielding a 21.3% OME<sub>3–5</sub> fraction (30.7 wt %), followed shortly by the Amberlyst36 and Y30 zeolite. Since the reaction is carried out at room temperature, formation of byproducts could be efficiently suppressed. This enables facile recycling and refeeding of the substrates into the process stream. The authors ascribe the higher activity of BEA25 and Y30 to high accessibility of the active centers due to mesoporosity rather than to the acidic strength of the zeolite. Even though the product spectra corresponded to the Anderson–Schulz–Flory distribution, OME<sub>3–5</sub> can be separated via distillation, and DMM, OME<sub>2</sub>, OME<sub>6–10</sub>, and trioxane can be recycled and fed back into the process, allowing for 100% atom efficiency. One drawback of the synthesis approach from DMM and trioxane comprises residual trioxane carried into the OME<sub>2</sub> fraction during rectification as impurities. In their recent publication, Deutsch et al.<sup>766</sup> were able to overcome this obstacle by addition of only substoichiometric amounts of trioxane (DMM/trioxane ratio of 15:1), which was fully consumed during OME synthesis. OME<sub>2</sub> samples of high purities were obtained using a zeolite H-BEA25 and have been investigated regarding their physicochemical and fuel properties.

All currently established synthesis approaches have in common that rectification or even several distillation steps are necessary to obtain isolated OME fractions of high purity. Tailor-made selective homogeneous or heterogeneous catalysts providing access to specific oligomeric OMEs could enable selective OME synthesis starting from CO<sub>2</sub> and renewable H<sub>2</sub>, thus providing a chemically and environmentally benign pathway. Therefore, in comparison to methanation and Fischer–Tropsch technologies which are already at high technology readiness levels, fundamental catalyst and process designs are still absolutely essential for the selective, cost-efficient, and sustainable production of oxygenates as fuel substitutes or components. Nevertheless, a comparison of the different fuel types from a systems perspective can be attempted by analyzing the basic data for material and energy flows.

**3.4.4.2. Comparison of CO<sub>2</sub>-Based Fuels from a Systems Perspective.** To compare the CO<sub>2</sub>-based fuels discussed in the previous sections, the LCA results of all studies are normalized to 1 MJ of fuel using the scenario 2020 and the best-case scenario presented in Table 1. This allows not only a comparison of the global warming impacts under the given boundary conditions, but also allows for a sensitivity analysis to evaluate the influence of a dynamically changing energy landscape. The impact of electricity is varied between 6 and 662 g of CO<sub>2</sub> equiv/(kW h), which are the global warming impacts of hydropower and electricity from waste incineration, respectively. The global warming impact of electricity changes the impacts resulting from power-to-heat and water electrolysis. To minimize the global warming impacts, power-to-heat and water electrolysis are replaced by a fossil-based heat and hydrogen supply, when the global warming becomes higher than the impacts of the fossil processes. Water electrolysis is replaced by a fossil-based hydrogen supply at 212 kg of CO<sub>2</sub> equiv/(kW h). Power-to-heat is replaced by natural gas at 257 g of CO<sub>2</sub> equiv/(kW h).

The results are presented in Figure 20. It should be emphasized that the input data on the CO<sub>2</sub>-based fuels still contain large uncertainties and depend strongly on the underlying assumptions regarding the processes. Thus, the comparison should only be used to analyze general trends, and

no final “ranking” of fuels in absolute terms should be derived. Still, we regard it as important to benchmark different pathways potentially serving the same purpose and hope that a more mature process and LCA data will become available in the future to present a more reliable analysis.

The CO<sub>2</sub>-based fuels are compared to fossil diesel as a benchmark (black dashed line in Figure 20). Break-even points can be identified to quantify the global warming impact for electricity required for each fuel to equal the global warming impact of fossil diesel. The global warming impacts of several electricity mixes are plotted as gray horizontal lines. Remarkably, for the national electricity grid mix of Iceland, all CO<sub>2</sub>-based fuels would already reduce global warming impacts compared to their fossil counterparts. However, the different routes show quite distinct points at which they become favorable options. For example, DME already has lower global warming impacts (GWI) than fossil diesel if electricity is available with a GWI lower than 180 g of CO<sub>2</sub> equiv/(kW h) for electricity. In contrast, the jet fuel presented by Falter et al.<sup>279</sup> requires electricity with a GWI of less than 34 g of CO<sub>2</sub> equiv/(kW h) to become beneficial with respect to fossil kerosene. The global warming impact of kerosene is similar to that of fossil diesel; thus, only one benchmark is presented in Figure 20.

The intersections of the fuel curves and the line for wind electricity correspond to the best-case scenario (Table 1), allowing comparison of the different routes under these almost ideal conditions. In this case, DMM produced by the reductive route (Scheme 29b) shows the lowest global warming impact with an impact lower than 0.005 kg of CO<sub>2</sub> equiv/MJ of fuel. DME has the highest global warming impact of 0.06 kg of CO<sub>2</sub> equiv/MJ of fuel due to the assumed methane input and the high direct emissions of the considered process (see section 3.4). However, all global warming impacts are very low in the best-case scenario such that the uncertainty of the underlying data is probably still much higher than the differences. Consequently, local infrastructures or regional supply chains may become critical factors for the choice of approach, in addition to absolute values of the global warming impact.

It is also important to note that CO<sub>2</sub>-based fuels will lead to significantly higher cumulative energy demands in the overall system. For example, adding 35 vol % DMM to diesel almost doubles the cumulative energy demand compared to that of pure diesel.<sup>743,743</sup> Thus, using renewable energy in the transportation sector for CO<sub>2</sub>-based fuels would require a significant expansion of the electricity system. The electricity system would have to supply not only the current demand of electric power, but also the additional demand due to fuel production. In this context, using renewable electricity for CO<sub>2</sub>-based fuels would compete with alternative use in battery-driven vehicles or other sectors (e.g., heating) which may offer greater reductions of global warming impacts per energy unit.<sup>779</sup> For an energy system based on fluctuating renewable electricity, however, the CO<sub>2</sub>-based fuels also offer potential for long-term energy storage in transportable form. Furthermore, the potential to decrease local emission impacts for future propulsion systems as well as for existing vehicle fleets is also to be considered. It seems therefore highly important to dedicate future research to the development of such advanced low-carbon and low-emission fuels.

This discussion shows that an analysis solely based on global warming impacts is insufficient to grasp the full opportunities and challenges of CO<sub>2</sub>-based fuels. Thus, full LCA studies along

with technoeconomic analysis and energy systems study are required to quantify the potential of CO<sub>2</sub>-based fuels, for which new targets and production routes can be created through catalytic CO<sub>2</sub> conversion.

#### 4. CONCLUSIONS AND FUTURE PERSPECTIVES

In the present review, we discuss selected examples for CO<sub>2</sub> conversion covering 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. A combined analysis of the state-of-the-art of synthetic methodologies and of processes with their life cycle assessment was used 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<sub>2</sub> utilization as a measure for global CO<sub>2</sub> mitigation. Whereas the latter focuses on reducing the end-of-pipe problem “CO<sub>2</sub> emissions” from today’s energy system, the approach taken here tries to identify opportunities by exploiting a novel feedstock that avoids the utilization of fossil resources in transition toward more sustainable future production. Thus, the motivation to develop CO<sub>2</sub>-based chemistry does not depend primarily on the *absolute* amount of CO<sub>2</sub> emissions that can be avoided by a single technology. Rather, CO<sub>2</sub>-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.<sup>780,781</sup>

Currently, there are only a limited number of life cycle assessment (LCA) studies available that allow an analysis of the environmental benefits and challenges of CO<sub>2</sub> conversion. In line with the focus on the carbon footprint, most of them concentrate on energy balances and global warming impact (GWI) reduction. While global warming impact is certainly a very important metric and was therefore also used as a key criterion in this review, it is by no means the only performance measure that should be considered. The integrated review of available LCA studies for CO<sub>2</sub>-based chemistry shows that current state-of-the-art CO<sub>2</sub> conversion processes can provide benefits beyond global warming impacts and simultaneously reduce a broad spectrum of environmental impacts such as for CO<sub>2</sub>-based polyols discussed in section 2.1.2. There can, however, also be trade-offs between environmental impacts, as in syngas production with higher impacts for some impact categories due to current electrolyzer production (section 2.2). CO<sub>2</sub>-based production can even increase all environmental impacts as would be the case for CO<sub>2</sub>-based fuels in today’s supply chains. However, this situation is reversed if CO<sub>2</sub>-based fuels are coupled with renewable energy to reduce environmental impacts as described in section 3. Thus, future LCA studies on CO<sub>2</sub> conversions should go beyond global warming impacts and try to provide a comprehensive assessment of environmental impacts. These studies further need to resolve the methodological issues in LCA for CO<sub>2</sub> conversion discussed in section 1.2. More LCA studies on CO<sub>2</sub> conversion are desirable since they can provide important targets for technology development.

Remarkably, the available results show that there are cases where CO<sub>2</sub>-based processes have been proven or can be expected to reduce global warming impacts over fossil-based production routes even today. This may seem counterintuitive given the thermodynamic stability of the CO<sub>2</sub> molecule. The

two examples exemplifying this opportunity in this review may help to clarify this apparent paradox: (i) The CO<sub>2</sub>-based production of polyols via copolymerization of propylene oxide and CO<sub>2</sub> is designed in such a way that the products replace polyols obtained from the homopolymerization of the epoxide. In other words, the epoxide does not capture the CO<sub>2</sub>, but the CO<sub>2</sub> partly substitutes the high-energy fossil feedstock epoxide, with its high environmental impacts leading to more efficient polyol production; (ii) in the formic acid production, both routes via CO or CO<sub>2</sub> face an energy-intensive separation of the product solutions. However, starting from the carbon source CO<sub>2</sub> has the potential to reduce the number of conversion steps compared to conventional processes starting from the fossil carbon source methane, which is first converted to CO. As a result, the overall balance of the environmental impacts can be advantageous for the CO<sub>2</sub>-based process. In other words, while chemical CO<sub>2</sub> conversion does not constitute a carbon sink over the life cycle of the products since CO<sub>2</sub> is released at the end of life, it can lead to more environmentally friendly production processes.

The use of CO<sub>2</sub> as a C1 building block for the catalytic construction of carboxylic acid functions and methyl groups demonstrates the potential to create entirely new synthetic pathways. In both cases, CO<sub>2</sub> is not “funneled” into existing transformations, but allows redesign of the entire synthetic methodology. Therefore, the assessment of the potential impact of these transformations is not as straightforward as in the other cases. Classical green chemistry principles such as replacement of hazardous reagents or atom economy point to a very significant potential of the carbon dioxide routes. Comparing the new catalytic routes to traditional synthesis of carboxylic acids starting from chlorinated substrates via a Grignard reaction or to the use of methyl iodide as a methylation reagent may just serve as obvious examples. It would be highly desirable if such generally assumed positive effects would be validated for specific examples of real products or even classes of products and quantified by life cycle assessment.

The largest reduction in the absolute amount of greenhouse gas emissions could be achieved by coupling of highly concentrated CO<sub>2</sub> sources from CO<sub>2</sub>-emitting sectors with carbon-free hydrogen or electrons from renewable power in so-called “Power-to-X” scenarios. The diversification of the energy systems requires a regional differentiation and a temporary outlook for scenarios that set the boundary conditions of the assessment. For example, methanol from CO<sub>2</sub> has a low carbon footprint in settings with low-carbon electricity such as Iceland already today. Power-to-methanol thus looks very attractive in areas with increasing deployment of renewable electricity, but it would be counterproductive in a purely fossil infrastructure.

This effect becomes even more pronounced if methanol is considered not as a chemical but as a fuel. Again, the production of fuels from CO<sub>2</sub> does not provide a carbon “sink” over their full life cycle, but a very substantial benefit can result from reducing the global warming impacts compared to those of current technologies in a well-to-wheel analysis. In this way, CO<sub>2</sub>-based fuels should be seen as a technology to harvest renewable electricity into the mobility sector, rather than a CO<sub>2</sub> mitigation strategy. It must be noted that CO<sub>2</sub>-based fuels then compete with other technologies using renewable electricity such as battery-driven vehicles, fuel cells, or power-to-heat concepts, which may well offer higher reductions of CO<sub>2</sub> emissions per kilowatt hour of renewable energy used.<sup>779</sup> However, only analyzing CO<sub>2</sub> reduction efficiency again falls

short for a sustainability assessment as the comparison of Fischer–Tropsch (FT) fuels and oxymethylene ethers (OMEs) illustrates: Both CO<sub>2</sub>-based fuels have potential to reduce CO<sub>2</sub> emissions by using renewable energy as the input. In addition, FT fuels have the advantage of established production technologies and immediate retrofitting with existing infrastructure and engine technology. As pure hydrocarbons, they also provide very high energy density. OMEs, however, have also been demonstrated to have a significant potential to improve local emissions and thus show additional benefits beyond traditional propulsion systems. Such additional benefits and other issues such as energy security might eventually be the critical factors for societies to decide about the implementation of CO<sub>2</sub>-based fuels.

Although it is probably one of the core messages of this review not to overgeneralize statements and criteria for the potential of CO<sub>2</sub> conversion in chemical production, we believe that certain patterns and take-home messages can be derived from our analysis: Replacing energy-intensive feedstock by CO<sub>2</sub> seems highly promising. Furthermore, it becomes evident from the available examples that the largest positive impact on the carbon balance typically results from the most direct incorporation of CO<sub>2</sub> into the product. While the production of synthesis gas from CO<sub>2</sub> is attractive to provide a platform for established downstream conversions, dedicated processes should strive for maximum integration. This clearly sets a challenge for catalysis research to provide multifunctional and robust systems or to establish novel reaction pathways and molecular mechanisms.

The quest to tackle the kinetic barriers and thermodynamic boundaries of using CO<sub>2</sub> as a feedstock will surely continue to stimulate the creativity of chemists and chemical engineers. In this context, the authors are convinced that the collaboration and exchange with LCA experts does not impose any restrictions, but will help to identify very fundamental research questions to address the most relevant technological targets. At the same time, the progress in synthetic methodologies using carbon dioxide as a building block challenges the LCA methodology, which should be further advanced to provide a sound and holistic assessment of environmental impacts. We therefore hope that this review “catalyzes” a fruitful interdisciplinary dialogue and motivates basic science in both disciplines to cope with the challenges and to capitalize on the opportunities of CO<sub>2</sub> conversion.

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### Notes

The authors declare no competing financial interest.

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