

# Recent Progress in Direct DME Synthesis and Potential of Bifunctional Catalysts

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DOI: 10.1002/cite.202100167

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**Dedicated to Prof. Dr. Thomas Hirth on the occasion of his 60th birthday**

PtX technologies are one major building block of the future energy system based on renewables sources. Dimethyl ether (DME) is an important PtX product that can be used as intermediate the production of CO<sub>2</sub>-neutral base chemicals. New applications lead to an increase of the global production and the optimization of the process efficiency, especially when considering decentralized synthesis. This review article puts some spotlights on recent developments in methanol and the direct DME synthesis with a special focus on the modeling and bifunctional catalyst. This study is expected to provide a foundation for future works in the field of catalysis research based on catalysts design and kinetic modeling.

**Keywords:** Bifunctional catalysts, Catalyst design, Dimethyl ether, Kinetic modeling, Methanol

*Received:* August 31, 2021; *revised:* December 16, 2021; *accepted:* January 18, 2022

## 1 Introduction

It is well-known that the excessive use of fossil resources such as coal, oil, and natural gas results in adverse climate changes due to inadequately regulated large emission of the so-called greenhouse gases such as methane and carbon dioxide (CO<sub>2</sub>) [1]. It is generally accepted that CO<sub>2</sub> emissions need to be drastically reduced to net-zero, even to net-negative in the second half of the 21st century in order to limit human-induced global warming. Very recently, the Intergovernmental Panel on Climate Change, IPCC, concluded in their sixth assessment report, that global warming of 1.5 °C could already be exceeded in the early 2030s unless deep reductions in carbon dioxide occur in the coming decades [2]. This effort would also include major changes to power generation, mobility, and other industrial sectors such as chemical and construction industry as well as agriculture [3].

The use of synthetic carbon-neutral hydrocarbons and oxygenated hydrocarbons would significantly contribute to the future energy system [4]. In this context, it is of utmost importance to establish alternative production processes through innovative schemes such as the Power-to-X (PtX) approach, coupling the sector of renewable electrical energy with chemical transformations. However, by nature, corresponding renewable sources (e.g., from solar and wind power) are fluctuating in their availability and usually not accessible in large quantities (rather up to the MW than GW scale) at a certain location [5, 6]. Therefore, decentralized and load-flexible PtX technologies are promising options to efficiently convert renewable electricity into

chemical compounds, which can be easily stored, transported, and used in multiple applications. These PtX products can be either gaseous (potentially liquefied), e.g., H<sub>2</sub>, synthetic methane, dimethyl ether (DME), or liquid, e.g., Fischer-Tropsch hydrocarbons and methanol [4]. When both, the electricity used for generating hydrogen via electrolysis and the CO<sub>2</sub> used as carbon source in PtX process are not from fossil origin (consequently, renewable electricity and CO<sub>2</sub> from biomass or direct air capture), the resulting PtX products can be considered as CO<sub>2</sub>-neutral [7–9].

Taking into account the diverse conceptual considerations, methanol and DME are promising PtX products for chemical industry and heavy-duty transportation (direct methanol fuels cells, blended with gasoline for combustion engines, diesel replacement) [10]. Considering decentralized Power-to-Fuel (PtF) approaches, simplified and efficient processes are required. Not methanol synthesis itself, but

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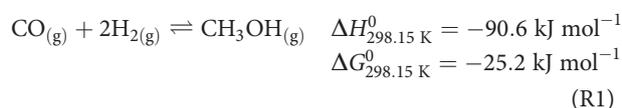
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the combination with the dehydration of methanol to DME [11] is a particular example of how the whole process can be made more compact by (i) increasing the CO resp. CO<sub>2</sub> conversion of the methanol synthesis through direct dehydration and (ii) reducing the number of reactors and the need for a large recycle stream [4, 9].

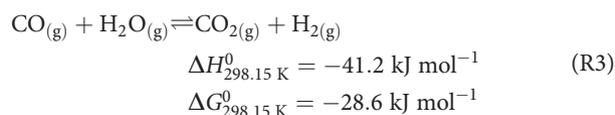
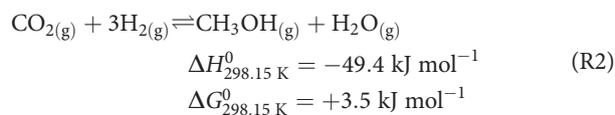
In this overview article, we summarize current developments in direct DME synthesis and provide an outline of the synthesis processes, new findings in the field of catalyst development and kinetic modeling approaches, some of which are closely linked to scientific progress in the field of methanol synthesis.

## 2 Methanol Synthesis and Recent Development

Conventionally, methanol (MeOH) is synthesized from synthesis gas (CO/H<sub>2</sub>) streams in the presence of a copper-zinc-based catalyst, according to the stoichiometric reaction (R1, STM: syngas to methanol). Traditionally, the complete process includes syngas production and purification, the methanol synthesis, and the rectification of crude methanol [4].



Currently around 110 Mt of methanol are produced per year, mainly from natural gas oxidation and/or reforming [8] and coal gasification using low and medium pressure processes [12, 13]. However, the syngas can be also derived from a variety of feedstocks such as crude oil, residual oil and bio-waste products being available all around the world, e.g., agriculture residues, forestry or landscaping and paper waste [14]. Recently, CO<sub>2</sub> from the air or from inevitable industrial emissions comes into focus as carbon source for the production of methanol, as it allows for considerable mitigation of the environmental impact caused by greenhouse gases and offers the opportunity to use a low-cost carbon source [15–17]. Using green hydrogen (i.e., produced from electrolytic processes using renewable energy) further adds value to the production of synthetic fuels from CO<sub>2</sub> [18, 19]. The hydrogenation of CO<sub>2</sub> to methanol (R2) is less exothermic than the methanol synthesis from pure syngas and it involves the water-gas-shift (RWGS, R3).



However, the use of CO<sub>2</sub> as (co-)feed in the production of methanol causes additional challenges, associated with loss of catalyst activity [17]. Various studies are being carried out in order to develop catalysts with higher service lifetime especially at high CO<sub>2</sub>-rich syngas conditions [17, 20, 21].

Both CO and CO<sub>2</sub> hydrogenation process are strong reversible exothermic reactions and therefore controlled by the kinetics and the thermodynamic equilibrium, which limits the syngas conversion. For this reason, the optimum process temperature of 200–300 °C has to be kept by efficient heat removal. Recently, once-through process with interstage [22] and in situ methanol removal [23] have been proposed to avoid the gas recycle, in order to improve the CO resp. CO<sub>2</sub> conversion and, thus, process yield. Details about the process will not be discussed within this review; however, an overview of reactor designs and technologies applied for methanol synthesis has been summarized and published recently in the literature [4, 23].

### 2.1 Recent Developments in Catalyst Design

In line with the high importance, a large number of review articles exist on catalysts for methanol synthesis. In this context, reference should be made to some recent review articles on the relevant research topics “Conversion of Carbon Dioxide”, [24–29] “Bimetallic Catalysts” [25], “Methanol Production” [26]. The following sections summarize current developments on the most important catalyst groups for application in fundamental research and process development for methanol synthesis.

#### 2.1.1 Transition Metal-Based Catalysts

Commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts typically have a metal distribution in the range of 60 wt % Cu, 30 wt % Zn and 10 wt % Al. This type of catalyst was developed since the 1960s – initially by Imperial Chemical Industries (ICI) – to operate methanol synthesis under milder reaction conditions (5–10 MPa, 220–300 °C) [30–32]. The effect of ZnO in Cu-based multicomponent catalysts is generally based on two features resulting from the combination of favorable stoichiometry and optimized production method: On the one hand, ZnO assumes the function of a geometric spacer between the Cu centers in the nm-size range, thus improving Cu dispersion and the accessibility of the specific Cu surface [33, 34]. On the other hand, ZnO also has a modulating effect with regard to the electronic properties due to specific metal/support interaction (SMSI). In contrast, the function of Al<sub>2</sub>O<sub>3</sub> is exclusively that of a structural promoter, which favors a uniform distribution of Cu and, in particular, improves the mechanical stability of the catalyst.

#### *Active Sites and Structure – Activity Relationships*

Essentially, two possible active sites at the interface are discussed. One possibility (a) results from the synergy between

Cu and ZnO at their interface [35]. The second possibility (b) is the presence of Cu-Zn surface alloy sites, [36] which is related to the partial reduction of ZnO particles towards a  $Zn^{\delta+}$  state or favors the modification of the surface Cu by metallic Zn [29, 37–39]. Recent research results regarding possibility (a) have been published through experimental data and simulations, which give clear indications about the nature of the top layer of the catalyst surface in Cu/ZnO catalysts [40, 41]. Possibility (b) is supported by findings suggesting that Cu steps occupied by Zn atoms are the active sites where coexistence of defined bulk defects and surface species exists [20]. The SMSI-induced formation of a metastable  $ZnO_x$  phase on the Cu active sites has also been demonstrated on reduced industrial Cu-ZnO- $Al_2O_3$  catalysts [39]. The adsorption strength of relevant intermediates such as  $HCO^*$ ,  $H_2CO^*$  and  $H_3CO^*$  is also enhanced via Cu-Zn interaction according to DFT calculations [20]. Control of the nanoscale properties of catalysts for methanol synthesis is therefore generally an essential element in catalyst development.

Recently, inverse oxide/metal catalysts with metastable “graphite-like” ZnO layers in Cu/ZnO/ $Al_2O_3$  catalysts have also attracted considerable interest due to the metal-support interaction, [39, 40, 42, 43] with ZnO sites being considered as hydrogen reservoirs to favor methanol formation.

#### Preparation Methods

Amongst a variety of preparation methods to optimize the catalytic activity [44], the co-precipitation of metal salt precursors with a precipitating agent in aqueous medium, followed by aging, calcination, and reduction is the most widely used synthesis process [45, 46]. Accurate control of the synthesis conditions, in particular temperature, pH value, mixing and aging procedure is important [44]. Many improvements have been achieved to prevent metal agglomeration and sintering during the calcination, which is crucial for the metal dispersion and the catalytic performance, such as nitrate-free synthesis from a basic formate or acetate precursor, [47, 48] surfactant-assisted coprecipitation, [49] reverse co-precipitation, [50, 51] reverse co-precipitation with ultrasound irradiation [52, 53] and continuous co-precipitation [21].

In addition, there are various other synthesis methods, such as deposition-precipitation, [54] sol-gel synthesis, [55] citrate decomposition, [56] combustion synthesis, [57] solid state synthesis, [58] ammonia evaporation, [59] organometallic synthesis, [53, 60] and flame-spray pyrolysis [61–63].

#### 2.1.2 Precious Metal-Based Catalysts

Unfavorable factors in Cu-based catalysts are the increased mobility of ZnO when water is formed, the limited stability due to sintering and agglomeration, and partly pyrophoric properties [64, 65]. Amongst many others, [66] precious metal-based catalysts are a general alternative to this [67] as they have high stability and often better resistance to sintering and poisoning.

#### Monometallic Catalysts

Supported catalysts of Pd and Pt are known to be active for methanol formation by CO hydrogenation already at low temperatures [68]. Especially Pd catalysts on supports such as  $La_2O_3$ ,  $Nd_2O_5$ , [69] and  $CeO_2$  [70] catalyze the formation of methanol highly selectively. Existing oxygen vacancies also favor  $CO_2$  adsorption or activation, as shown for the use of  $CeO_2$  [71] and  $In_2O_3$  [72] as supports in Pd-based catalysts. Besides, Au-based catalysts on different supports [73–75] as well as Pt-based catalysts [67] demonstrated catalytic activity for methanol formation.

#### Alloy Catalysts

Pd and Pt form various alloys with metals that are active themselves in CO/ $CO_2$  hydrogenation. In such alloys, the surface properties are altered compared to the pure metals, so that new active sites can be created, [76] such as in Pd-Cu, Pd-Zn and Pt-Co alloys, among others.

In Pd-Zn alloys, the SMSI effect between metallic Pd and ZnO at high temperatures ensures the formation of a stable alloy, although the nature of the active sites is the subject of scientific debate [77]. On the one hand, the formation of PdZn alloys often correlates with catalytic activity and methanol selectivity, [78–81] however, Pd decorated with  $ZnO_x$  islands are partly discussed as active sites [82]. In this context, PdZn alloys could stabilize formate intermediates and inhibit the RWGS reaction at the same time [82, 83].

#### 2.1.3 Other Catalysts

##### *In<sub>2</sub>O<sub>3</sub>- and Ga-Based Catalysts*

In the past decade,  $In_2O_3$ -based catalysts have been introduced as a new class of highly selective methanol catalysts [84–87]. A key effect is that the competing reaction pathway via the reverse water-gas shift reaction (reverse reaction (R3)) is restrained [84, 88].

In combination with suitable support materials such as monoclinic zirconia ( $m-ZrO_2$ ), which increases the adsorption capacity towards  $CO_2$ , good long-term stabilities are achieved [89–91]. Recent developments include doping with hydrogenation-active metals, such as palladium, [92, 93] platinum, [94] rhodium [95] or nickel [92], among others, to increase the rate of  $H_2$  cleavage, which is low at bulk  $In_2O_3$ .

Gallium has already been used in various types of catalysts for methanol synthesis [96]. For example, in  $Ga_2O_3$ -supported Pd catalysts it is proposed that gallium oxide promotes  $CO_2$  adsorption and Pd, similarly to the above mentioned effect in  $In_2O_3$ , catalyzes dissociation of  $H_2$ , mechanistically resulting in hydrogen spill over to the oxide surface followed by the formation of formate [97]. Among a number of alloys, the  $Ni_5Ga_3$  composition proved to be particularly active in terms of methanol selectivity [98].

##### *MOF/ZIF-Based Catalysts*

Due to the structure sensitivity of methanol catalysts, metal-organic frameworks (MOFs) and zeolitic imidazolate

frameworks (ZIFs) are highly interesting classes of materials that exhibit tailored surface accessibility, pore functionalities and reactive open metal sites [99]. The basic concept is that such frameworks enable the confinement of encapsulated, catalytically active metal NPs and minimize their aggregation and/or agglomeration [100].

Preparation methods are generally divided into bottom-up and top-down approaches. The bottom-up approach resembles impregnation, exemplified in the preparation of the composite ZIF-8-supported Pd catalyst, among others [79]. Similarly, a ZIF-8-supported Cu catalyst is synthesized, for which considerable methanol productivity has been demonstrated [101]. In contrast, the top-down approach requires encapsulation of the NPs in the framework, for which suitable precursors must be selected. High activity in methanol synthesis was shown for the MOF-supported Cu/ZnO<sub>x</sub> catalyst prepared by the top-down method, [102] as well as for the ZrO<sub>x</sub>-supported Cu/ZnO<sub>x</sub> catalyst [103]. A related approach utilizes the MOF directed synthesis of a Cu catalyst highly dispersed in graphene [104].

## 2.2 Process Modeling of Methanol Synthesis

The methanol synthesis has been studied for years, however, a comprehensive understanding of the reaction mechanism and recovery phenomena for typical Cu-based catalyst has still not been fully achieved. A full elucidation of the mechanism would allow for precise optimization of input parameters and reaction conditions, further improving the process efficiency and economic feasibility [105]. Several formal kinetic models have been proposed for the methanol synthesis [106–110]. Each model has its particular considerations and rate determining steps (RDS), as well as different parameters lumped and fitted to experimental data at different conditions. Due to these assumptions and fitting of unknown parameters, different effects may be merged with the kinetic model and may cause its divergence to the experimental data.

Detailed theoretical models have been also proposed for methanol synthesis derived from first principles density functional theory (DFT) calculations [111–117]. In these models, different surface reaction paths are considered, and all reactions are potentially rate limiting. It is considered that these theoretical-based models are more suitable to extrapolations than empirical models with several experimentally fitted parameters [115, 118]. Nevertheless, the implementation is more complex, and the simulations require higher computational effort, when compared to simplified kinetic models [119]. Previous theoretical [21, 38, 116] and experimental studies, [120–122] performed on methanol catalysts showed a synergistic effect of the metallic components in the methanol catalysts, thus causing reversible structural changes depending on the reaction conditions; this also has a strong effect on the active centers at the catalyst surface, hence affecting the catalytic activity (see also Sect. 2.2). Although these changes are known,

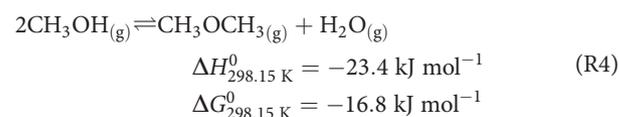
modeling of the dynamic behavior is challenging and has not been fully achieved yet [123]. This highlights the importance of transient mechanistic studies coupled with fundamental in situ catalysis studies for kinetic model development. Powerful analytical methods such as X-ray diffraction and absorption spectroscopy (XRD, XAS) [120] and diffuse reflectance IR spectroscopy (DRIFTS) [124, 125] have become increasingly available for in situ or operando analysis and allow for the development of more sophisticated models based on fundamental understanding of individual steps. For the latter however, as highlighted by Fehr and Krossing [125] for studies at technically relevant conditions, particular attention should be paid on the correct assignment of the IR-bands (CO<sub>2</sub> gas molecule vs. adsorbate) as the occurrence of several combination bands and overtones of CO<sub>2</sub> molecules entails the risk of misinterpretations.

Recently, detailed models based on multiscale modeling have been published in order to better describe the chemistry behind the methanol synthesis [109, 115, 126]. These models consider surface reaction kinetics, important intermediates, different active sites, and in some cases structural changes are also considered (see an example in Fig. 1). Nevertheless, additional improvements are still required to accurately describe the behavior of the methanol catalyst by kinetic and surface activity models.

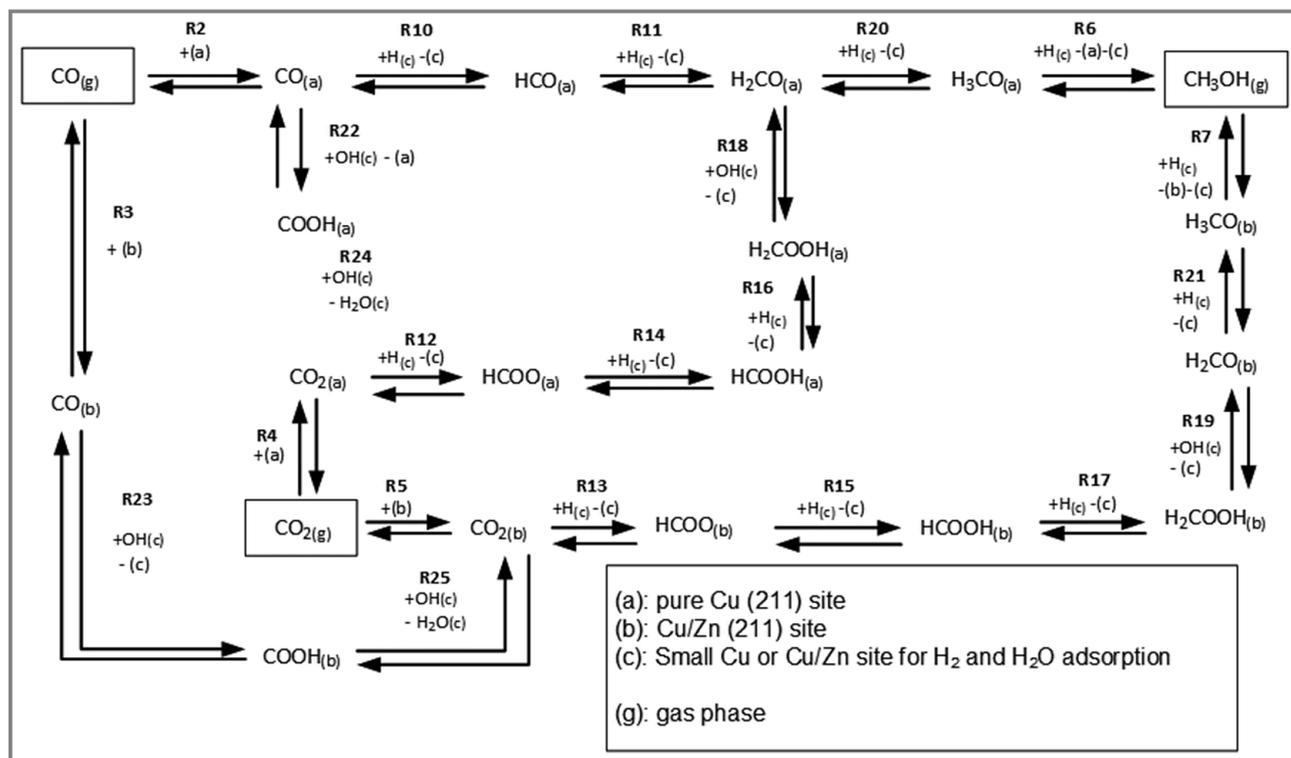
## 3 DME Synthesis

### 3.1 Two-Step Synthesis of DME

The large-scale production of DME is based on the dehydration of methanol (MTD: methanol to dimethyl ether). The first process step is the production of methanol from synthesis gas on Cu/ZnO-based catalysts at 240–280 °C and 3–7 MPa following reaction equation (R1). After a purification stage in a subsequent reactor, methanol is converted into DME via an acid catalyst (R4) [127].

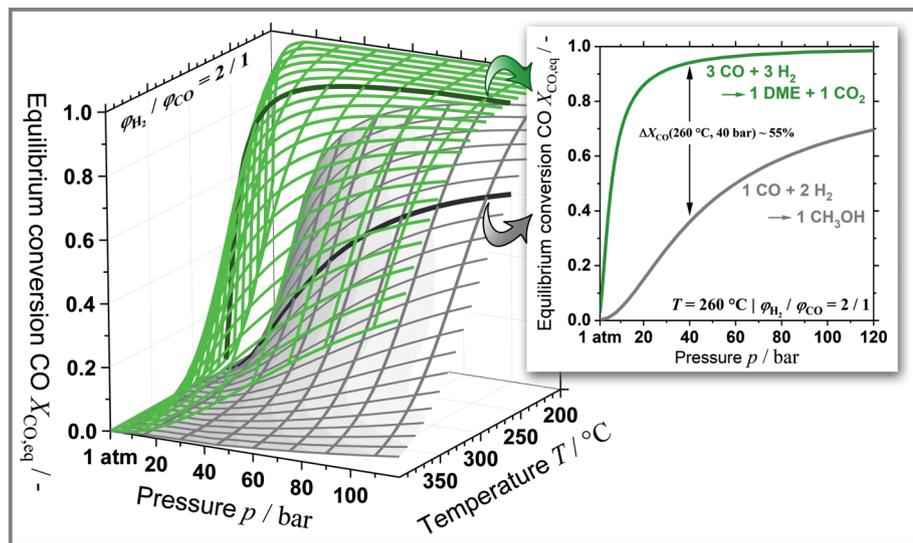


The overall process is referred to as the indirect process. Upstream, the generation of synthesis gas is the initial step for the subsequent conversion processes. The composition of the synthesis gas is primarily a function of the carbon content of the carbon source and ideally leads to a composition that corresponds to the stoichiometry of the methanol synthesis. Technical synthesis gas compositions usually contain proportions of CO<sub>2</sub> and CH<sub>4</sub> of <5% each. Exothermic methanol dehydration in the indirect process typically takes place at lower temperatures of around 200 °C, which at the same time also largely avoids the formation of by-products such as higher hydrocarbons and coke. The



**Figure 1.** Reaction network of the carbon-containing species in the methanol synthesis and the WGS. Adapted from Ref. [115] with permission from the Royal Society of Chemistry.

thermodynamic limitation of methanol formation in the indirect process allows only a low gas conversion per pass (15–25 %; see Fig. 2) and leads to comparatively high capital and operating costs at increased recirculation rates (see also Sect. 2.1).

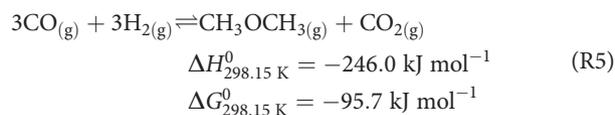


**Figure 2.** Thermodynamic equilibrium conversion of CO as a function of temperature and pressure for methanol and direct DME synthesis from CO/H<sub>2</sub> = 2/1 and stoichiometric feed according to net reactions (R1, R5) and (R2, R6), respectively.

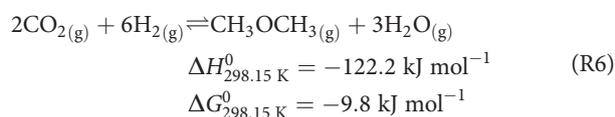
### 3.2 Direct Synthesis of DME

An alternative to the indirect process is the direct process (also known as the one-stage process, STD: syngas to dimethyl ether), in which both reactions, the methanol synthesis and the dehydration of methanol to DME, take place in the same reactor on a bifunctional catalyst system at conditions that favor primary methanol formation [128, 129]. The direct process is currently still undergoing non-commercial testing in experimental plants up to pilot demonstration scale. Economic advantages are often discussed for the direct process, as only one reactor is required and the conversion during methanol formation can basically be increased by the parallel methanol dehydration (see Fig. 2). Consequently, a lower pressure is required, and methanol synthesis can take place at a higher temperature and, thus, a higher reaction rate. On the other hand, however, higher reaction temperatures are considered unfavorable for the

formation of DME. With water being formed during dehydration, in the direct DME synthesis the RWGS reaction (reverse reaction (R3)) takes place. Thus, stoichiometrically the direct process requires a lower H<sub>2</sub>/CO ratio for DME formation than methanol synthesis alone and appears particularly interesting for the conversion of syngas produced from biomass [130].



The direct hydrogenation of CO<sub>2</sub> or the conversion of CO<sub>2</sub>-rich synthesis gas in the direct process is thermodynamically less favorable, hence the DME yield is lower [131]. On the other hand, one key driver of current process technology development is to significantly reduce the carbon footprint of peak power generation from CCU fuels through the use and recycling of CO<sub>2</sub>. The synthesis of methanol resp. DME from CO<sub>2</sub>-rich synthesis gas involves the reverse water gas shift reaction (reverse reaction (R3)), CO<sub>2</sub> resp. CO hydrogenation (R1, 2) and methanol dehydration (R4) yielding a net reaction (R6) for the direct synthesis of DME from CO<sub>2</sub>/H<sub>2</sub> synthesis gas:



Preferably, CO<sub>2</sub> hydrogenation should be carried out near equilibrium to maximize the yield of DME produced, i.e., at high pressure or at lower temperatures [132]. High temperatures enhance the RWGS reaction, consuming more CO<sub>2</sub> and H<sub>2</sub>. This also increases the H<sub>2</sub>O content, which in turn hinders the formation of DME, on the one hand for thermodynamic reasons and on the other hand due to the competing adsorption on the active centers of the methanol catalyst [133] and on the acidic centers of the dehydration catalyst [134]. The direct process is currently still undergoing non-commercial testing in experimental plants up to pilot demonstration scale [4].

### 3.2.1 Process Development

In the context of decentralized, yet highly efficient direct synthesis of DME from H<sub>2</sub>/CO/CO<sub>2</sub>, several reactor concepts have been proposed and investigated for process intensification. In the following, focus is laid on microstructured and membrane reactors being two approaches for process intensification [135], also promising for the direct synthesis of DME.

#### Microstructured Reactors

The term “microstructured reactor” describes reactor concepts whose key features are the tailored structuring of the reaction and/or cooling section of the reactor. Due to the

microstructuring, both, heat and mass transport characteristics can be improved. It is worth mentioning that the term “microstructured” (a) does not refer to the size of the reactor itself, and (b) is also commonly used for structures in the dimension of 10<sup>-3</sup> m [136]. While most microstructured devices are based on stacking prefabricated foils, recent developments in additive manufacturing allow for additional degree of freedom in terms of the design of the internal structure inaccessible with conventional microfabrication techniques such as milling, slotting or etching.

In general, for the implementation of the catalyst in such microstructures, two main concepts are applied. Besides a packing of the catalyst, coatings on the inner wall of the microchannels is reported. For the latter, tailored (multi-functional) coatings not only allow for a low pressure drop and improved heat transfer from the reaction volume to the reactor wall [137] but can add additional features to the reactor system (see Sect. 4). As a third (and rare) case, the manufacturing of the complete reactor out of the catalytically active material, e.g., Rh [138], Cu or Ag [139] is reported.

In the context of H<sub>2</sub>/CO/CO<sub>2</sub> conversion, microstructured reactors with tailored cooling concepts have been demonstrated for the synthesis of hydrocarbons (methanation [140], Fischer-Tropsch synthesis [141]) and oxygenates, such as methanol synthesis [95] and DME [142]. Allahyari et al. [143] have described the performance of microreactors with different coatings (washcoating) of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-HZSM-5 catalyst. It is noted that increasing catalyst loading leads to a less-uniform morphology. However, catalyst layer thicknesses from 20 μm to 60 μm are reported and the authors observed that an increase of the catalyst thickness (increases of the number of active sites) up to 60 μm even reduces the microreactor performance, which was assigned to mass transport limitations and the reduced residence time at a given flow rate.

#### Membrane Reactor

The key feature of a membrane reactor is directed to the coupling of a chemical reaction and product separation within one single unit. The “in situ” removal of the product or by-product from the reaction zone via the membrane allows to increase the conversion affecting the thermodynamic equilibrium by withdrawal of the (by)product, and also in the case of selective product separation, to receive the product with increased purity [144, 145].

A general challenge, however, is to integrate the membrane (porous, organic, or inorganic) into the reactor, maintaining a high selectivity (defect free membrane) also under reaction conditions. Here, systems with the catalyst inside a tubular membrane or planar systems are usually applied [146, 147].

For methanol and direct DME synthesis, the removal of the by-product water using a membrane is discussed to increase product yield by increasing and decreasing the partial pressure of the reactants and the inhibiting by-product

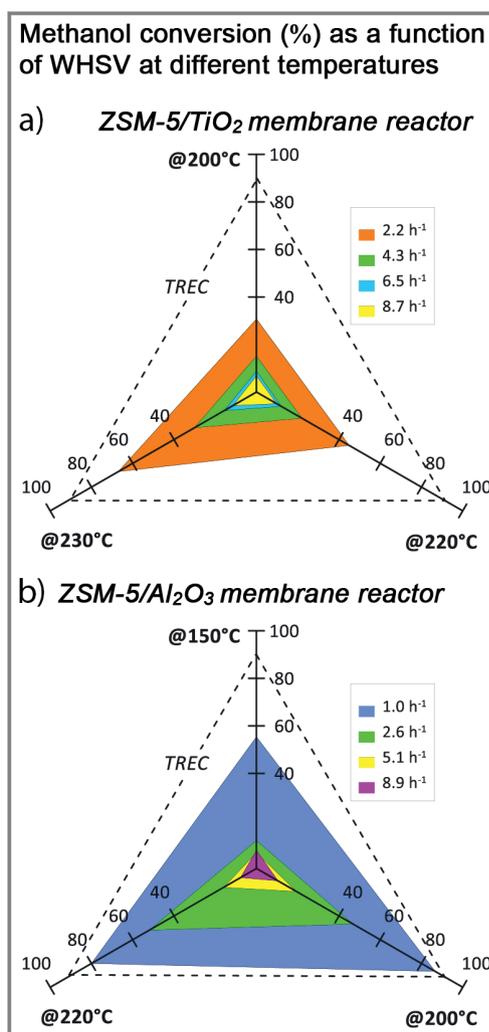
water, respectively, which also helps to protect the catalyst from deactivation [148,149]. Improved CO<sub>2</sub> conversion and high methanol yield were reported employing a zeolite-based membrane reactor at different H<sub>2</sub>/CO<sub>2</sub> feed ratios and temperatures compared to a conventional reactor [150,151].

By measuring the permeation of a H<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O mixture, within the range of interest for methanol synthesis (160–240 °C, 10–27 bar), Gorbe et al. [152] have quantified the capability of a zeolite A membrane to selectively separate water and methanol. The authors have compared the water partial pressure in permeate and retentate sides. The temperature has been selected as 160–260 °C in retentate side and the pressure of H<sub>2</sub>O in feed has been 10–18 kPa. They have reported a “surprisingly high” water partial pressure in the permeate, which was attributed to the radial temperature in the experimental system.

In the work by Li et al. [149], a Na<sup>+</sup>-gated water-conducting membrane was incorporated into the direct DME synthesis reactor to generate a dry reaction environment. According to the authors, due to the absence of water, the activities of the CO<sub>2</sub> hydrogenation catalyst (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) and the methanol dehydration catalyst (HZSM-5) are boosted 4- and 10-fold, respectively. Moreover, single-pass CO<sub>2</sub> conversion of up to 73.4%, which is by far beyond the thermodynamic equilibrium of the bare methanol synthesis, and DME yields of up to 54.5% have been reported. In addition, a reduced catalyst deactivation was demonstrated. In the work by Brunetti et al. [153], ZSM-5 type zeolite supported membranes are used as catalytic membrane reactors for DME synthesis via MeOH dehydration. The effect of two different support structures (TiO<sub>2</sub> vs. γ-Al<sub>2</sub>O<sub>3</sub>) for the zeolite membrane is assessed as a function of the temperature and feed pressure, spanning a wide range of accessible feed compositions. ZSM-5 supported on γ-Al<sub>2</sub>O<sub>3</sub> always exhibited a higher methanol conversion as the TiO<sub>2</sub> supported membrane (see Fig. 3) revealing an influence of the membrane support, correspondent to a contributing effect induced of γ-Al<sub>2</sub>O<sub>3</sub>, which further enhanced the methanol dehydration. In addition, both membrane reactors showed exclusive formation of DME.

Rodriguez-Vega et al. [154] studied a packed bed membrane reactor (PBMR) for direct DME synthesis by the hydrogenation of CO<sub>2</sub> and CO<sub>2</sub>/CO mixtures equipped with a hydrophilic LTA zeolite membrane to remove H<sub>2</sub>O. It is noted that LTA zeolite has superior permeation properties among the studied zeolites (LTX and SOD). With a mechanically mixed Cu/ZnO/ZrO<sub>2</sub>/SAPO-11 catalyst system, feed and sweep gas (permeate side) are identical in terms of composition and flow rate. It was shown that within the temperature range studied, the CO<sub>2</sub> conversion achieved with the PBMR exceeds the conversion in the conventional PBR (without membrane) by up to 37% at 325 °C.

For a further discussion on the state of the separation and on the reaction mechanism in the catalytic membrane reac-



**Figure 3.** Methanol conversion as a function of temperature and WHSV in a catalytic membrane reactor with the zeolite ZSM-5 membrane supported on TiO<sub>2</sub> (a) and Al<sub>2</sub>O<sub>3</sub> (b). Dashed lines connect the equilibrium MeOH conversion at the temperatures indicated. Feed pressure = 120 kPa. MeOH concentration = 100% molar. Reproduced with permission [153] Further permissions related to the material excerpted should be directed to the ACS.

tors, the interested reader is referred to the recent review article by Li et al. [155] discussing various high temperature water/gases separating membranes and their applications in MR for CO<sub>2</sub> utilization.

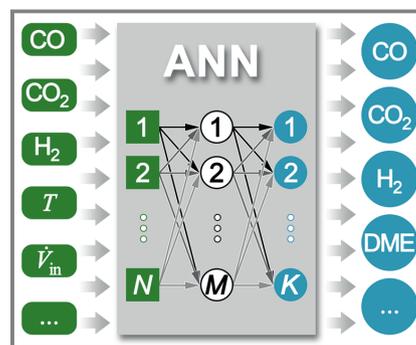
### 3.2.2 Process Modeling DME

Identification and quantification of dependencies between process parameters and process performance of DME synthesis is fundamental to the entire process efficiency, using a suitable mathematical description and accurate derived predictions of all relevant chemical and physical processes [156].

Numerous investigations have been carried out to describe and simulate the influence of feeds with variable

CO/CO<sub>2</sub> content and different catalyst bed compositions, based on the thermodynamics and kinetic data. Accordingly, models have been proposed to quantitatively describe the process of direct DME synthesis and to derive predictions [131, 157, 158]. Model-based optimization studies on the composition of the dual catalyst bed revealed that an optimized distribution with an increased amount of methanol catalyst enhances the catalytic performance, allowing a significant shift towards the equilibrium CO resp. CO<sub>2</sub> conversion [156, 158, 159].

Different modeling approaches have been used to model the direct DME synthesis, the coupling of methanol formation models [106, 107, 110] and its dehydration [160, 161] is one of the first approaches used, however, in the last years, lumped kinetic models based on prior knowledge on the direct CO/CO<sub>2</sub> conversion to DME are being developed [157, 158, 162]. These simplified models suffer from difficulties associated to possible model shortcomings caused by assumptions and uncertainties of the mathematical description, especially outside the fitted operation conditions. Although formal kinetic models have been widely used, their limitations in describing important changes on the catalyst during the time on stream have motivated a microkinetic modeling approach [119, 163]. Some theoretical microkinetic studies have been published for the methanol dehydration to DME [163–166] but to the best of our knowledge none for the direct DME synthesis, yet. Recent approaches such as the use of artificial neural networks (ANNs) have been applied, due to their flexibility and robustness [167–171]. Studies regarding the application of ANNs to optimize process conditions and predict performance for the direct DME synthesis have also been reported [167, 172–174]. Fig. 4 illustrates how the elementary units (neurons) can be organized into layers in a multilayer feedforward ANN for the DME synthesis. Here, “N” refers the input layer, “M” the hidden layers and “K” the



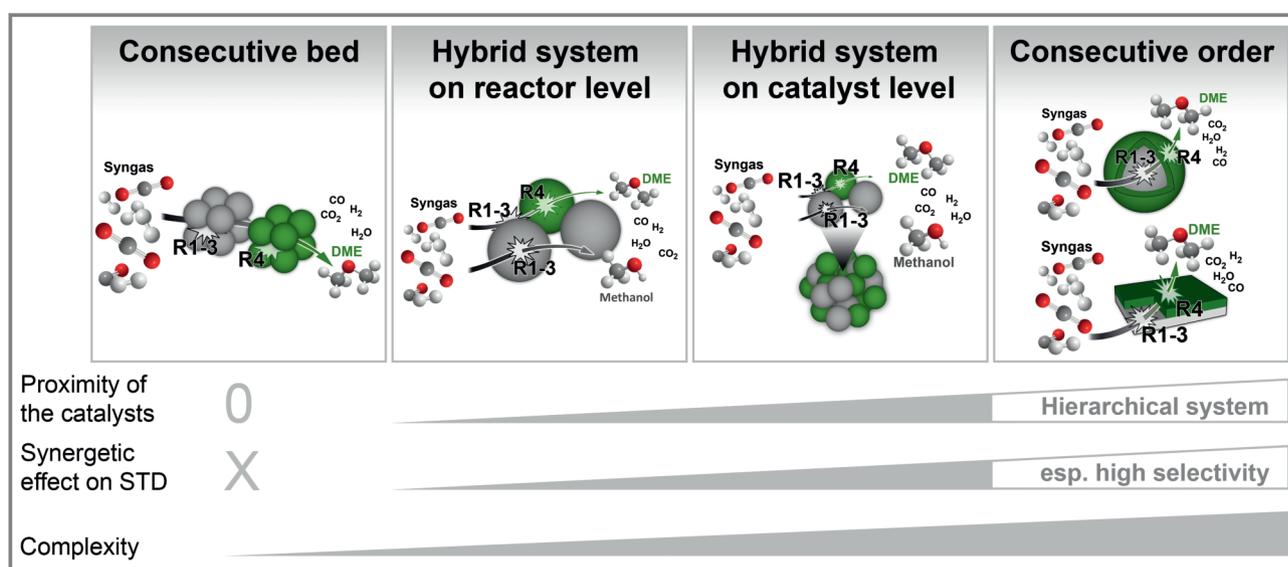
**Figure 4.** Structure of a multilayer feedforward artificial neural network for the DME synthesis. Adapted from Ref. [157] with permission from Wiley-VCH GmbH.

output layer, a detailed description can be found in the literature [157]. The ANN-based models are flexible in adapting new data, their accuracy is higher, and they proved to be applicable to extrapolations outside known experimental conditions.

#### 4 Concepts on Catalyst Application for Direct DME Synthesis

As mentioned in Sect. 3.2, the combination of methanol synthesis and its dehydration allows to exceed the CO resp. CO<sub>2</sub> equilibrium conversion of the bare methanol synthesis. However, in order to achieve such a synergetic effect, the two catalysts involved (i.e., methanol synthesis catalyst, see Sect. 2.2, and the solid acid catalyst for methanol dehydration) have to be implemented accordingly. Here, different concepts depicted in Fig. 5 are discussed.

With increasing proximity of the two catalysts involved not only potential synergy is affected, but also the design



**Figure 5.** Schematic depiction of different catalyst integration strategies for the direct synthesis of DME.

and the preparation of the catalyst system. The simplest system would be mixing the particles or pellets physically on the reactor level (hybrid catalyst bed) [63, 133, 175]. A physical mixture on the particle level increases the proximity of the active sites for the two reactions and, thus, decreases the probability for the intermediate (MeOH) to leave the reactor without getting dehydrated to DME [176–182]. For the aforementioned scheme, one could utilize mixing the dried STM- and MTD catalysts [177, 180, 182]. Furthermore, this can be facilitated by preparing a suspension of the two catalysts followed by filtering, washing, drying and calcination before pelletizing [178, 183]. Besides, co-precipitation of the STM catalyst in an MTD-catalyst-containing suspension [63] resp. self-assembly of the metallic and acidic functionalities has been reported [184]. Both methods allow to further enhance – and to some extent also tailor – the proximity of the two constituents. Even though these preparation approaches allow for an adjustment of, e.g., a desired STM-/MTD-catalyst weight ratio, often the arrangement of the two catalysts within the pellet cannot be controlled precisely. To compensate for this possible disadvantage synthesis of hierarchically structured bifunctional catalysts is a promising alternative. The aim is to achieve a desired predefined arrangement of the two catalysts by synthesizing at least one catalyst in the presence of the other as for example in a STM-@MTD-catalyst core@shell system. Such an arrangement has been reported to be very promising in terms of increasing the DME selectivity, as the methanol formed at the core of the core@shell catalyst by nature has to diffuse through the shell with dehydration functionality [185–188]. It is worth mentioning that the concepts described above for particulate systems (hybrid bed, hybrid particle, core@shell particle) are also applied to planar counterparts resulting in, e.g., bifunctional wall coatings [143, 189].

#### 4.1 Synthesis Methods and Performance of Advanced Bifunctional Catalyst Systems

While a physical mixture of the two catalysts on the reactor level or on the particle level by physical mixing and pelletizing is rather simple to implement, for the synthesis of hybrid catalysts a large matrix of different parameters is to be considered with each parameter potentially having an influence on the individual catalyst as well as on the interplay between the two catalyst constituents. Investigated methods are co-precipitation, impregnation, coprecipitation-sedimentation, sol-gel, sol-gel impregnation and liquid-phase syntheses [190, 191]. More recently, for STD synthesis, there have been reports on advanced methods like colloidal approach [178, 192] and ultrasound-assisted co-precipitation [193].

The hybrid configuration on the catalyst level is of paramount importance due to the fact that the intimate contact between the methanol synthesis and methanol dehydration

active sites can be tailored. However, a possible disadvantage is that hybrid catalysts can suffer from deactivation under reaction conditions due to the proximity of the methanol forming catalyst to the acidic sites of the dehydration catalyst [192, 194, 195] like the migration of Si to a CZA catalyst [194], the pore blockage caused by carbonaceous species deposition [196–198] or the sintering of Cu nanoclusters due to contact with aluminosilicates [196, 199]. Migliori et al., [200] investigated the role of metal-acid interaction in methanol dehydration over hybrid Cu/ZnO/ZrO<sub>2</sub>-zeolite (FER and MFI) catalysts. The authors conclude that there is a paramount effect as the dehydration catalyst showed a higher degree of deactivation over time on stream, accompanied with a decrease in DME selectivity in favor of by-product formation (methyl formate and dimethoxymethane). These effects are attributed to the migration of active metal to the acid sites as well as to sintering supported by the water being formed at the dehydration catalyst.

The simplest way to avoid issues as previously discussed is the minimization of the contact between the active metallic and acidic phases, e.g., by applying a physical mixture on the reactor level. This, however, also reduces the potential synergetic effect to be expected from a bifunctional system (see Sect. 4.1), however, has been reported to improve CO<sub>2</sub> conversion in direct DME synthesis [201].

The use of hierarchically structured catalysts has been considered as a promising approach for optimization of the catalyst performance in the direct STD reaction by achieving both, bringing together the two catalysts involved, while the aforementioned deactivation phenomena are reduced. Synthesis and testing of both possible configurations, namely DME synthesis function in the core and methanol synthesis function in the shell or vice versa have been synthesized, characterized, and tested in detail [185, 202–205]. Additionally, in the core@shell configuration an intermediate inactive layer can be applied to avoid direct contact between the two active phases [206].

In order to avoid harsh synthesis conditions usually applied for enwrapping a STM-catalyst core with a zeolite shell physical coating was also investigated for generating the shell. Sánchez-Contador et al. [185] prepared a bifunctional Cu/ZnO/ZrO<sub>2</sub>-core@SAPO11-shell type catalyst, which showed both higher CO resp. CO<sub>2</sub> conversion and DME selectivity as compared to the hybrid reference catalyst, prepared by physical mixture of the individual components. Phienluphon et al. [188] enwrapped a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> STM-catalyst core likewise with a SAPO11 dehydration catalyst using the physical coating method and observed enhanced performance in terms of CO conversion and DME selectivity. For the implementation of *planar bifunctional systems* in microstructured reactors, methods such as washcoating [143] or screen printing [189] have been described. To the best of our knowledge, with hierarchically structured catalyst layers (e.g., double layer) experimental results for the direct synthesis of DME have not been published in open literature.

## 4.2 Modeling Design of Different Catalyst Configurations

Several studies have been directed to analyze the effects of the design approach resp. the configuration in bifunctional catalyst systems, such as hybrid beds, pellets, and hierarchical structures, both in particulate and planar application on a theoretical basis [11, 189, 207–209].

Through using mathematical modeling, Gufftani et al. [207] concluded from investigations on the active phase distribution at the pellet scale in catalytic reactors that a significant impact of the different spatial distribution of the active phases on the reactor performance exists. According to the authors, intraparticle diffusion limitations within the catalyst bed result in lower DME yield compared to hybrid systems on the pellet level. However, for the latter system the authors found a more pronounced hotspot formation. This effect in turn was less pronounced in STM-catalyst core@MTD-catalyst shell systems, which showed comparable yields of DME as the hybrid catalyst system.

To describe the DME synthesis over a Cu/ZnO/ZrO<sub>2</sub> based core@SAPO11-shell catalyst Ateka et al. [209] have proposed a micro kinetic model. This model enables quantifying the influence of particle size on the reaction performance metrics and predicts that increasing catalyst particle size up to 4 mm (interesting for its use in fixed bed reactors on a larger scale) has little impact on DME yield and CO<sub>2</sub> conversion. Ding et al. [208] used a 1D heterogeneous model to simulate diffusion and reactions within a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-based core@zeolite-shell catalysts and showed that thickness and activity of shell have significant influence on the catalytic performance. Baracchini et al. [11, 189] compared hybrid catalysts with the two catalysts in either close or medium proximity vs. double layer configuration. The simulation results for the catalyst configurations of the given material properties investigated reveal that, at a given STM catalyst to MTD catalyst weight ratio, the hybrid system with the catalysts being in close proximity allows for remarkably higher CO conversions compared to the double layer system, while DME selectivity is comparable. The low conversion rate of the core@shell system was attributed to the fact that the highly intergrown zeolite shell opposes mass transport limitations while resulting in high selectivity to DME.

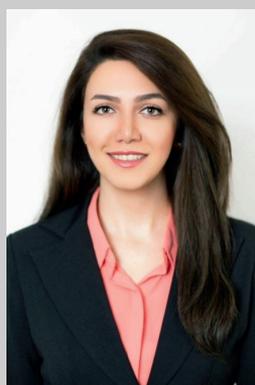
## 5 Conclusion and Future Perspective

Decentralized and load-flexible “Power-to-X” (PtX) technologies are promising options to efficiently convert renewable electricity into PtX-CO<sub>2</sub>-neutral products. Increasing CO<sub>2</sub> emissions has encouraged the use of CO<sub>2</sub> as carbon source for the production these carbon containing chemicals. Especially when converting CO<sub>2</sub>-rich synthesis gas, tailored catalysts and advanced reactor concepts are required to overcome the thermodynamic limitations allow-

ing to implement efficient processes. Decentralized CO<sub>2</sub> sources and the fluctuating availability of H<sub>2</sub> from electrolytic process leads to new challenges, hence, the dynamic operation of PtX technologies is increasingly the subject of current research. Particularly, methanol and DME will increase in importance for the future chemical industry.

Under fluctuating conditions, the direct synthesis of DME is considered to be more practical than the more conventional but established indirect synthesis via methanol as an intermediate product. It has been shown that not only the two catalysts involved but also the reactors and process parameters need to be adjusted when converting CO<sub>2</sub>-rich synthesis gas facing increased thermodynamic limitations. This summary contribution highlights advances in both catalyst synthesis and kinetic modeling for further increasing the technology readiness level of the direct DME synthesis. However, technical improvements (e.g., reactor concepts and customized product separation) are still necessary to achieve a significant increase in the overall process performance. Future studies should also be directed towards long-term stability of promising bifunctional catalyst systems, as well as on progress in model-based optimization of catalysts, process conditions and reactor designs, based on theoretical and experimental mechanistic studies.

The authors from IMVT would like to acknowledge funding by the German Research Foundation (DFG priority program 1570 “Porous Media with Defined Pore Structure in Process Engineering - Modelling, Application, Synthesis”; Grant No. DI 696/9-3 and SCHW 478/23-3) and the Vector Foundation (“CO<sub>2</sub>mpactDME”). The authors acknowledge the financial support from the Helmholtz Research Program “Materials and Technologies for the Energy Transition (MTET), Topic 3: Chemical Energy Carriers”. Open access funding enabled and organized by Projekt DEAL.



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## Symbols used

|            |                         |                              |
|------------|-------------------------|------------------------------|
| $\Delta G$ | [kJ mol <sup>-1</sup> ] | Change in Gibbs free energy  |
| $\Delta H$ | [kJ mol <sup>-1</sup> ] | Enthalpy of reaction         |
| $p$        | [bar]                   | Pressure                     |
| $T$        | [°C]                    | Temperature                  |
| $WHSV$     | [h <sup>-1</sup> ]      | Weight hourly space velocity |
| $X$        | [%]                     | Conversion                   |

## Abbreviations

|      |                                    |
|------|------------------------------------|
| ANN  | Artificial neural network          |
| DFT  | Density functional theory          |
| DME  | Dimethyl Ether                     |
| MeOH | Methanol                           |
| MOF  | Metak-organic framework            |
| MR   | Membrane reactor                   |
| PBMR | Packed bed membrane reactor        |
| PBR  | Packed bed reactor                 |
| PtX  | Power-to-X                         |
| RWGS | Reverse water-gas-shift            |
| SMSI | Specific metal/support interaction |
| STD  | Syngas to dimethyl ether           |
| STM  | Syngas to methanol                 |
| ZIF  | Zeolitic imidazolate framework     |

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DOI: 10.1002/cite.202100167

## Recent Progress in Direct DME Synthesis and Potential of Bifunctional Catalysts

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**Review Article:** DME is a promising CO<sub>2</sub>-neutral energy carrier that can be efficiently produced via methanol from syngas streams derived from a variety of feedstocks such as non-fossil CO<sub>2</sub> resources, bio-waste and green H<sub>2</sub> provided through electrolysis using renewable electricity. This review considers recent developments with focus on modeling and bifunctional catalyst. ....

