


Challenges and Opportunities in the Production of Oxymethylene Dimethylether

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To reduce the NO_x and soot emissions of conventional diesel fuels, different renewable alternatives are investigated. One example are oxymethylene ethers (OME_x) of different chain lengths, which are intended to be used as diesel blends. Especially OME_{3-5} show properties comparable to diesel. The key to producing longer chain OMEs is OME_1 as feedstock, which can react with formaldehyde to afford larger molecules. This article reviews different synthesis routes for OME_1 , in order to elucidate energy-efficient methods.

Keywords: CO_2 , Diesel alternative, Oxymethylene dimethylether

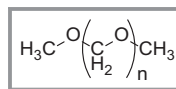
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1 Introduction

The increasing production of renewable energy is accompanied by the challenge of efficient storage and customized supply of the variable resources. An attractive option for storage of electrical energy on large scale and management of the fluctuations of solar and wind power generation is based on the production of liquid energy carriers. Tailored liquid energy carriers with adapted volumetric and gravimetric energy density represent a flexible element of future mobility, especially with regard to the transportation sectors. Currently, diesel fuel plays a major role in long distance transportation and 94 % of freight transportation relies on diesel engines. Moreover, modern diesel engines allow efficient propulsion with favorable CO and CO_2 emissions compared to gasoline engines. [1,2] However, the combustion in diesel engines comes with problematic NO_x and soot emissions, causing major challenges for after-gas treatment and motor management systems. [3] Accordingly, many existing diesel vehicles exceed the current limits for NO_x and soot emission and require adapted solutions for future utilization within the legal regulations. [4–6]

The Kopernikus P2X project has accepted this challenge and targets the effective transformation of CO_2 with renewable energy to fuels and chemical products. In the initial phase of Kopernikus P2X, a focus was the development of oxygenate fuels, enabling the development of diesel engines with strongly reduced NO_x and soot emissions. This approach was motivated by existing oxygen-containing liquids like ethanol, dimethyl ether, and dimethyl carbonate, already demonstrating a significant soot reduction in combustion processes. [7–9] The target structures of P2X were oxymethylene dimethyl ethers (OMEs), composed of oligomers with the repeating $-(\text{O}-\text{CH}_2)_n-$ unit and methyl/

methoxy end capping groups (Scheme 1). The absence of C–C bonds in OMEs is the decisive element, allowing a combustion with decreased soot formation. [10–15]



Scheme 1. Chemical structure of OMEs of different chain length n .

Excitingly, previous engine studies already emphasized the significant potential of OMEs as fuel additives for reducing soot and NO_x emissions. More specifically, an addition of 35 vol % of OMEs to standard diesel fuel reduces the soot formation by 90 %. [14] Interestingly, the soot reduction potential is not correlated to the chain length of the respective OMEs and physico-chemical properties like viscosity, cetane number, and flash point of OMEs with a chain length of 3–5 allow for the best fit to current diesel properties. [16]

The conventional production of OME_{3-5} proceeds by reacting methanol with a formaldehyde source (either trioxane or paraformaldehyde) for chain elongation. [17,18] According to the chemical equilibrium, a large excess of formaldehyde units is required for significant chain growth while any water present in the system compromises chain elongation. In this manner, the production of paraformaldehyde and trioxane as “dry” formaldehyde sources is well investigated. [19–22] Alternatively, dimethoxymethane

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(DMM or OME₁) can serve as feedstock to be combined with a formaldehyde source to produce higher OMEs (OME_{>1}) in an anhydrous approach. [23,24] However, the development of novel production pathways to OME₁ and OME_{>1} is still of major importance, aiming for energy-efficient processes with reduced number of process steps (Fig. 1).

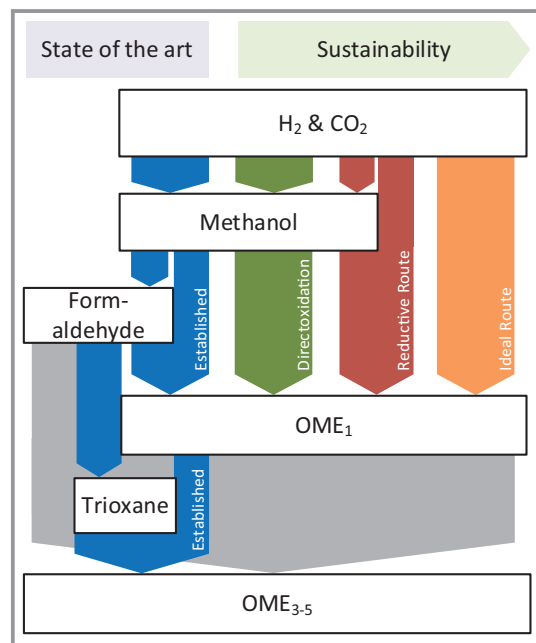


Figure 1. Pathways to OME₃₋₅ based on CO₂ and H₂.

Starting from CO₂, methanol can first be formed by either electrochemical reduction or chemo-catalytic hydrogenation with hydrogen provided by water electrolysis. In the conventional process concept, one third of methanol is subsequently re-oxidized over an iron-molybdenum catalyst or dehydrogenated via a silver catalyst in a high temperature gas-phase reaction providing formaldehyde (FA). In the presence of an acid catalyst in a low-temperature liquid phase reaction, methanol from the main stream and formaldehyde react to OME₁ (Fig. 1, established route). Despite the undesirable energy and redox profile, the multi-step nature accompanied by several purification steps enhances production costs. OME₁ can also be synthesized by direct oxidation of methanol on a bifunctional catalyst, reducing the number of process steps, but still following the undesirable redox profile (Fig. 1, direct oxidation). Recently, the group of Klankermayer was able to use CO₂ instead of formaldehyde in the reductive route in the presence of methanol to form OME₁ (cf. Sect. 4). Here, re-oxidation of methanol is avoided, overcoming the undesirable methanol oxidation and further reducing the number of required unit operations. Theoretically possible but not dem-

onstrated experimentally yet, the ideal route for OME₁ synthesis is via a one-step synthesis based solely on CO₂ and H₂ to yield formaldehyde and methanol within a single system which are combined to deliver OME₁ as the sole product.

The potential of these alternative process routes was also evaluated in a recent life-cycle assessment of OME₁, described by Deutz et al. [25] Here, the authors confirmed that a mixture of 35 vol % OME₁ and 65 vol % diesel could not only reduce the impact of global warming, but also significantly reduce soot and NO_x emissions (Fig. 2).

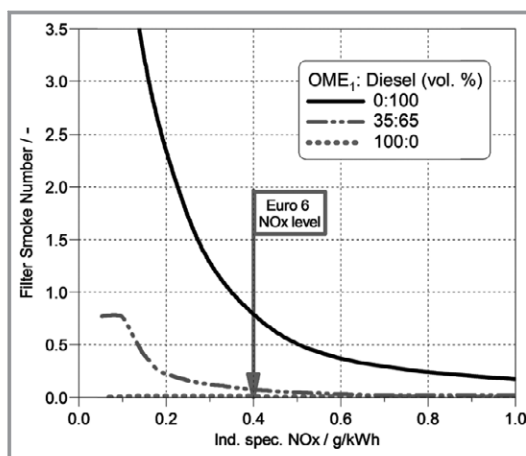
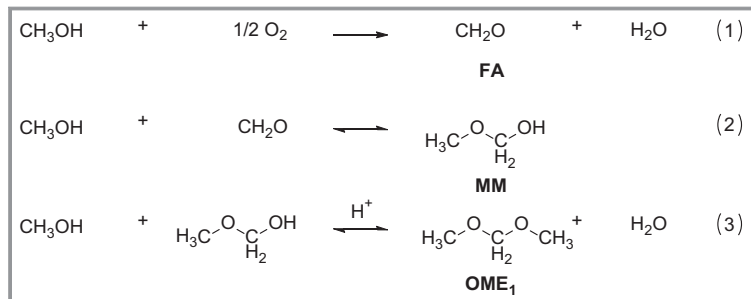


Figure 2. Filter smoke number (soot) of pure diesel and 35 % OME₁-diesel blend as well as pure OME₁ in comparison to NO_x-emissions measured in a single cylinder engine; adapted from [25].

2 Indirect Synthesis of OME₁

Today, OME₁ synthesis proceeds via the indirect two-step production as described in the previous section. FA is either produced by methanol oxidation on an iron molybdate catalyst or dehydrogenation over a silver catalyst (Scheme 2, Eq. (1)). FA is stabilized in the presence of methanol via the formation of a methoxymethanol (MM) intermediate (Scheme 2, Eq. (2)). MM then condenses with methanol on an acid catalyst to OME₁ (Scheme 2, Eq. (3)). [26,27] The latter reaction is reversible and hence, the yield is limited by chemical equilibrium [18,28]. The equilibrium can be overcome by evaporating the low boiling OME₁ during the reac-



Scheme 2. Indirect synthesis of OME₁ starting from methanol.

tion [27,29,30]. Here, very good yields were achieved in a reactive distillation setup [31]. However, the separation is impeded by the formation of a low-boiling azeotrope of OME₁ and methanol with 92.2 wt % of OME₁. Pressure swing distillation allows increasing OME₁ purity up to 99.1 wt % [31–33].

OME₁ synthesis is well understood for soluble acid catalysts. H₂SO₄, HCl, *p*-TsOH as well as FeCl₃ were investigated and allowed an efficient production of OME₁ [34–37]. However, soluble acid catalysts bear a high corrosion potential, hamper product separation, and result in salt formation upon neutralization of the soluble acid. Consequently, solid acid catalysts, which overcome these challenges, have gained growing attention in recent years. [27, 30, 31, 38–41] The main groups considered in OME₁ synthesis are ion exchange resins, sulfonated tetrafluoroethylene resins, heteropoly acids, and zeolites. As the OME₁ synthesis is mainly limited by equilibrium, the catalysts are optimized based on engineering aspects like kinetic investigations, alternative formaldehyde sources, and demonstration in pilot plants. Kinetic investigations were demonstrated by the Hasse group for an Amberlyst 15 catalyst which fits well with experiments and clearly illustrates the limitation by chemical equilibrium. [30] Different sources of FA, comprising especially trioxane as FA trimer, were also investigated for the synthesis of OME₁. Zhang et al. demonstrated a reaction at 70 °C, applying methanol and trioxane in the presence of Amberlyst 15. [40] Reactive distillation enabled nearly complete conversion of FA independently of the catalyst. A corresponding demonstration plant was presented by Zhang et al. [31] They showed a conversion of FA of 99.6 % and a purity of OME₁ of 92.1 %. For further purification, pressure swing distillation was applied.

3 OME₁ Production via the Oxidation of Methanol

The direct oxidation of methanol to OME₁ enables reduction of the process steps (Scheme 3). A solid bifunctional catalyst is located in the reactor in a fixed bed where vaporized methanol and oxygen react to OME₁ (Fig. 3). Here, FA is initially formed in situ by partial oxidation of methanol. The subsequent acetalization of FA in the presence of methanol then leads to the corresponding OME₁ product. As oxygen is involved in this reaction, the explosion risk can be excluded by restricting the amount of methanol to a regime below 7 % or over 36 %.

The bifunctional catalyst has to facilitate two different reactions in a well-adapted fashion. First, the catalyst needs

a metal functionality allowing oxidization of methanol to formaldehyde. In a second step, acetalization proceeds on the acidic site of the catalyst in the presence of methanol and formaldehyde to form OME₁. Both functions must be aligned with regard to selectivity and reaction rate to suppress undesirable side reactions as well as enhance overall rate and selectivity of OME₁ production. [42] In the presence of rather strong oxidizing sites, side reactions can include the over-oxidation of methanol to CO₂, CO, or formic acid. The latter can react in the presence of methanol to methyl formate (MF). In addition, via the Tishchenko reaction, MF may arise from FA. [43] On the other side, if the strength of the acidic site is too high, the side product dimethyl ether (DME) can be produced by dehydration of methanol. Hence, an overall optimal strength of both active sites is indispensable to establish an efficient and highly selective reaction of methanol to OME₁. Noble and non-noble metal catalysts have shown their potential in OME₁ synthesis. The main category of noble catalysts comprises ruthenium-based and rhenium-based catalysts. On the other hand, molybdenum- and vanadium-based catalysts are potent non-noble alternatives.

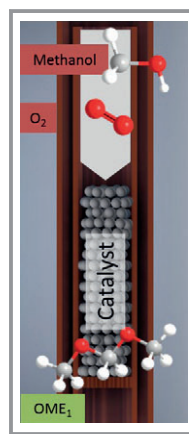
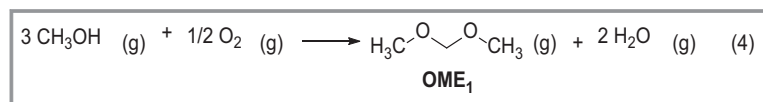


Figure 3. Gasphase reactor for the direct oxidation of methanol to OME₁.

Rhenium-based catalysts (ReO_x) were the first reported systems to catalyze the oxidation of methanol to OME₁. At a temperature of at least 240 to 300 °C, Re-based catalysts showed a good performance in the OME₁ synthesis. Catalysts affording a selectivity of 90 % or higher towards OME₁ are stated in Tab. 1. The conversion employing these catalysts ranges from 5 % up to 50 %. It was found that rhenium can provide both functionalities of a bifunctional catalytic system. [44,45] The bifunctional character is achieved by the presence of two oxidation states. Therein, Re⁴⁺ species were proposed to facilitate the methanol oxidation step whereas its oxidized species Re⁷⁺ (Re⁴⁺ oxidizes in presence of oxygen) act as acidic sites catalyzing the acetalization step.

Non-noble catalysts play an important role in the sustainability of processes and, hence, products in chemical industries. Tab. 2 provides an overview of non-noble metal catalysts for the



Scheme 3. Direct synthesis of OME₁ starting from methanol.

Table 1. Re-based catalyst for the OME₁ synthesis via methanol oxidation.

Entry	Catalyst	GHSV [L h ⁻¹ g ⁻¹]	Conversion [%]	Selectivity [%]					Ref.
				OME ₁	FA	DME	MF	CO+CO ₂	
1	SbRe ₂ O ₆	10	6.5	92.5	–	6.3	1.2	–	[45]
2	10%Re/V ₂ O ₅	40	21.5	93.7	–	4.3	–	2	[46]
3	10%Re/α-Fe ₂ O ₃	40	15.5	90.5	2	1	6	0.5	[46]
4	10%Re/γ-Fe ₂ O ₃	40	48.4	91	2.4	1	4.6	1	[46]

n.a. = not available

direct OME₁ synthesis based on methanol oxidation. Vanadium and molybdenum oxides are promising candidates for non-noble metal catalysts in OME₁ production, facilitating superior performance to Re-based catalysts. At an optimum process temperature of about 140 °C, above 90 % selectivity can be achieved (Tab. 2). In general, vanadium-based catalysts perform very well in methanol oxidation to OME₁. They are mainly composed of vanadium pentoxide (V₂O₅) and well established in industrial oxidation processes. [43] The excellent oxidation properties of vanadium-based catalysts have to be combined with an acidic function, either by using an acidic support material or via the addition of acidic additives. The group of Shen inserted either Ti(SO₄)₂ or H₂SO₄ on V₂O₅/TiO₂ by impregnation (entry 5 & 6). Both acids showed similar OME₁ selectivity of around 90 % and conversions between 41 % and 49 %. In another approach, V₂O₅/TiO₂ catalysts were modified with sulfur (VTiS), with rapid compression (RC) [47, 48], sol-gel (SG) [49, 50], and mechanical grinding (MG) [49] presenting the most efficient methodologies. More specifically, these catalysts afforded similar OME₁ selectivities; however, the conversion

reached with these systems differed significantly ranging from 15 up to 49 %, respectively. Sima et al. protected VTiS by cetyltrimethylammonium bromide (CTAB) during the synthesis. Hence, nanoparticle of vanadium species and acidic sites were obtained by suppressing particle agglomeration. An increase in the activity was mainly observed at higher conversion (~54%, entry 10). Inspired by the small particle size and its good activity, TiO₂ nanotubes (TiNT) where dispersed as monolayer on V₂O₅. [51, 52] Pure V₂O₅ only showed a selectivity of 51 % towards OME₁. Modifying the monolayer with H₂SO₄ significantly improved the selectivity even at high conversion (58 %, entry 11). Another surface modification relies on the incorporation of metal oxides into the support material. The highest potential was shown for SiO₂ which was introduced in the TiO₂ structure to create more acidic sites (VTiSi, entry 13). Here, a selectivity of 99 % was achieved at 51 % conversion. [50] Another issue in the oxidation of methanol towards OME₁ is the reduction of the operating temperature of this reaction. Here, Meng et al. could show that V-based MO₃/Al₂O₃ decreases the reaction temperature to 120 °C while keeping

Table 2. Non-noble catalysts for the OME₁ synthesis via methanol oxidation.

Entry	Catalyst	GHSV [L h ⁻¹ g ⁻¹]	Conversion [%]	Selectivity [%]					Ref.
				OME ₁	FA	DME	MF	CO+CO ₂	
5	5%V ₂ O ₅ /TiO ₂ -H ₂ SO ₄	11.4	48.2	91.6	0.1	2.4	6	n.a.	[55]
6	30%V ₂ O ₅ /TiO ₂ -Ti(SO ₄) ₂	11.4	41	90	0	1	9	–	[56]
7	11.7%VTiS-RC	5	48.6	91.8	2	0.6	5.6	0.1	[48]
8	22.8%VTiS-SG	11.4	33	93	–	1	6	–	[49]
9	24.8%VTiS-MG	11.4	15	90	2	7	1	–	[49]
10	VTiS-CTAB	0.924	53.4	92.8	n.a.	n.a.	n.a.	n.a.	[57]
11	SVTiNT-673	11.4	58	92	2	–	6	–	[52]
12	VTiS-673	11.4	43	92	1	2	5	–	[58]
13	VTiSi	12	51	99	–	1	–	–	[50]
14	V ₂ O ₅ -MoO ₃ /Al ₂ O ₃	4	54.2	92.1	–	5.6	2.3	–	[53]
15	SbVO _x	80	12	100	–	–	–	–	[54]
16	NbO _x	n.a.	58	~100	–	–	–	–	[59]

n.a. = not available; CTAB used as protective agent.

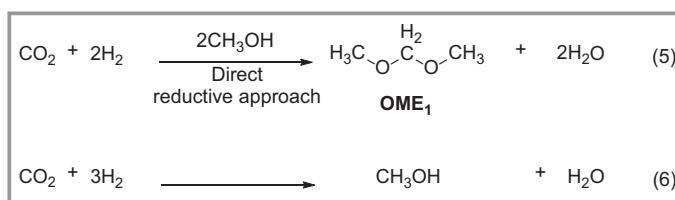
a conversion of 54 % and 92 % selectivity. [53] A further increase in selectivity was possible by reducing the conversion to 12 % on antimony V-based catalysts. Here, a selectivity of 100 % was observed by Golinska-Mazwa et al. (entry 15). [54]

4 One Step Synthesis of OME₁ From the Direct Hydrogenation of CO₂ with H₂

In comparison to the oxidative approach to produce OME₁ starting from methanol, the reductive approach comprises the direct hydrogenation of CO₂ with H₂ in presence of methanol in a multicomponent combination fashion to form OME₁ in only one step (Scheme 4, Eq. (5)). Although a detailed process design is not yet available, a simplified assessment analysis by Deutz et al. expected that the general demands of resources and energy for the direct route of OME₁ synthesis from CO₂ are relatively lower (economically beneficial) compared to the oxidative (formaldehyde) route, especially if H₂ is obtained from renewable resources. [25] In this manner, the need for an oxidative step to produce FA from methanol is eliminated and the use of CO₂-based methanol is also feasible (Scheme 4, Eq. (6)), leading to a more sustainable synthetic pathway of OME₁ and addressing an overall reduction of hydrogen consumption as well as CO₂ emissions (Tab. 3). [25]

The key step for this direct approach is the catalytic reduction of CO₂ to “FA reduction level”, which is thermodynamically not favored compared to the reduction of CO₂ to formic acid. Consequently, the reduction of CO₂ to formic acid and its subsequent esterification with methanol to a methyl formate (MF) intermediate would represent an alternative route to a favorable synthesis of OME₁ directly from CO₂ (Eq. (7)). In this manner, the subsequent hydrogenation of the MF intermediate to the corresponding methoxymethanol (MM) hemiacetal (possessing the FA-reduction level), followed by fast acetalization (trapping) with methanol, would overcome the addressed thermodynamic limitations and yield OME₁ as a more stable product (Scheme 5). In accordance, the development and use of a multifunctional catalytic system catalyzing the different sequences (hydrogenation/esterification/acetalization) in a one-pot manner is an important, challenging, and highly recommended task. [60] This can be clearly reflected by the very few research reports published in the last few years and mainly describing the use of homogeneous catalytic systems employing defined molecular catalysts for the direct hydrogenation of CO₂ to OME₁.

In 2016, the group of Klanker-mayer reported the first catalytic hydrogenative approach to synthesizing OME₁ directly from CO₂/H₂ as C₁ building block in



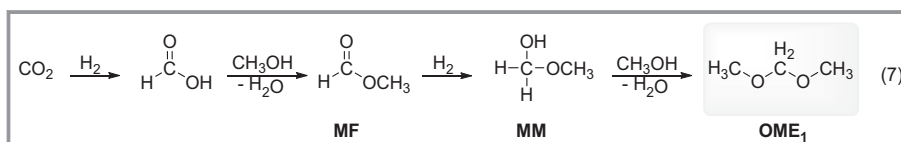
Scheme 4. Direct synthesis of OME₁ starting from CO₂/H₂ and methanol.

Table 3. Life cycle inventory data for the indirect formaldehyde (FA) route and the direct route for the production of OME₁ from H₂ and CO₂ via methanol as described by Deutz et al. [25].

Flow	CO ₂ (Direct route)	FA (Indirect route)
<i>Masses [kg kg_{OME1}⁻¹]</i>		
Feedstock H ₂	+0.22	+0.26
Feedstock CO ₂	+1.77	+1.89
Product OME ₁	-1.00	-1.00
Direct CO ₂ emissions	-0.034	-0.15
<i>Energies [MJ kg_{OME1}⁻¹]</i>		
Electricity	+0.23	+0.42
Heat at 385 K	+7.64	+4.56

Negative values denote outputs, while positive values are inputs.

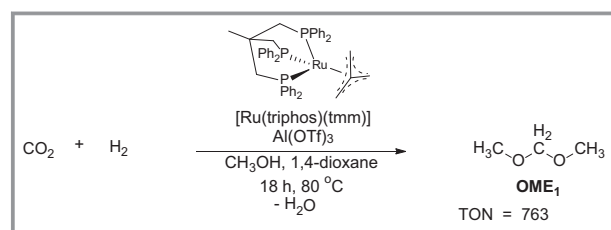
the presence of methanol [61]. The developed multifunctional catalytic system described in this work comprises a ruthenium catalyst for the hydrogenation steps and an acidic co-catalyst for both activating the ruthenium catalyst as well as catalyzing the esterification/acetalization steps of the reaction sequence. More specifically, the catalytic system employed for this reaction was based on the [Ru(tri-phos)(tmm)] catalyst (triphos = (1,1,1-tri(diphenylphosphinomethyl) ethane, tmm = trimethylene methane) in combination with aluminum triflate (Al(OTf)₃) Lewis acid as co-catalyst (Scheme 6). The direct reaction of CO₂ to OME₁ was carried out with 20/60 bar of CO₂/H₂ at a mild temperature of 80 °C to afford OME₁ in a TON (turnover number) of 214 whereas the expected MF intermediate was obtained with a TON of 104 at the end of the reaction. Further optimization of the reaction conditions resulted in the formation of OME₁ with up to 763 TON when 1,4-dioxane was used as a co-solvent of the reaction. [62] The multifunctionality of this catalyst system was proven to be crucial for the complex reaction sequence described in Scheme 5. This



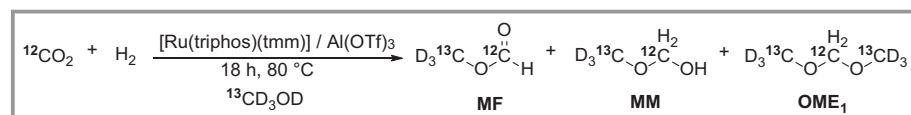
Scheme 5. Reaction pathway for the direct synthesis of OME₁ using CO₂/H₂ and methanol.

suggested sequence was further supported by performing a set of experiments employing non-labeled CO_2/H_2 in the presence of labeled methanol ($^{13}\text{CD}_3\text{OD}$), resulting in the formation of MF and MM intermediates as well as the OME_1 product in which the labeled atoms were tracked in the ($^{13}\text{CD}_3\text{O}-$) groups only (Scheme 7). These observations reveal that the final product OME_1 incorporated only the methyl groups (CH_3-) generated from the methanol substrate whereas the ($-\text{CH}_2-$) units were generated solely from the CO_2 and H_2 .

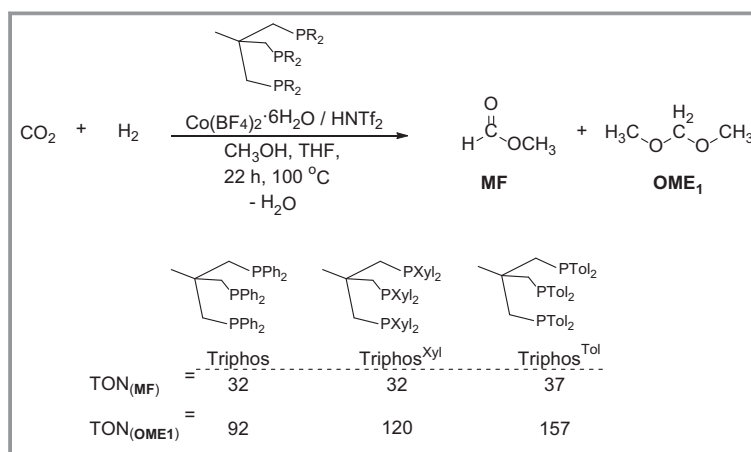
In 2017, a catalytic system for the direct hydrogenation of CO_2 to OME_1 based on a non-precious transition metal catalyst could be established. [63] In detail, various cobalt salts in combination with selected triphos ligands and acidic co-catalysts enabled a straightforward direct synthesis of OME_1 via the formation of MF and MM intermediates. More specifically, $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was employed as the most active cobalt precursor together with triphos ligand and Brønsted acid co-catalyst HNTf_2 (bis(trifluoromethanesulfonyl)imide), leading to an active system for the formation of OME_1 with a TON of 373 starting from MF as substrate, and with a TON of 92 starting from CO_2 (Scheme 8). When compared to the ruthenium/triphs system, a higher temperature of 100°C was required for the cobalt/triphs system as well as the use of tetrahydrofuran (THF) as a co-solvent. Moreover, the investigation of the influence of a set of other triphos ligands (with variable ligand sphere induced by different sterically hindering functionalities) was reported and showed that the reactivity of the cobalt system could be enhanced. In particular, the use of $\text{Triphos}^{\text{Tol}}$ ligand (1,1,1-tris(bis(4-methylphenylphosphino)methyl)ethane) for the synthesis of OME_1 from CO_2 enhanced the TON up to 157 (Scheme 8), yielding a comparable activity to the ruthenium/triphs precious-metal catalyst. [61]



Scheme 6. $[\text{Ru}(\text{triphs})(\text{tmm})]/\text{Al}(\text{OTf})_3$ -catalyzed direct synthesis of OME_1 from CO_2/H_2 as C_1 synthon in presence of methanol.



Scheme 7. Isotopic labeling observed by NMR spectroscopy for the $[\text{Ru}(\text{triphs})(\text{tmm})]/\text{Al}(\text{OTf})_3$ -catalyzed synthesis OME_1 from CO_2/H_2 in presence of labeled methanol $^{13}\text{CD}_3\text{OD}$.



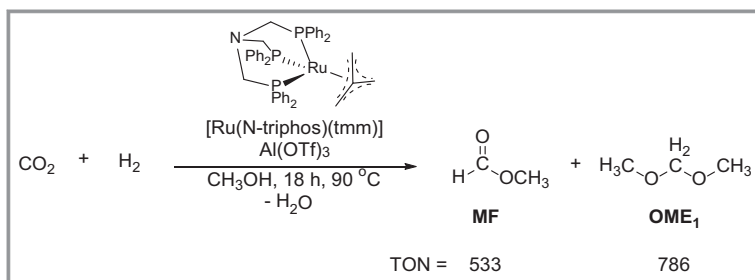
Scheme 8. $\text{Co}(\text{BF}_4)_2/\text{Triphos}^{\text{R}}$ -catalyzed synthesis of OME_1 from CO_2/H_2 as C_1 synthon in the presence of methanol.

In addition, the versatility of the novel ruthenium- and cobalt-catalyzed direct synthesis of OME_1 from CO_2/H_2 and methanol was extended to the synthesis of dialkoxy-methanes by replacing methanol with a variety of other alcohols. [61, 63] Interestingly, reacting CO_2/H_2 and ethanol resulted in diethoxymethane which is identified as a promising fuel candidate “bio-hybrid fuel” from a production perspective. [64, 65]

More recently, the group of Trapp used the developed catalyst lead structure and prepared catalyst derivatives (ruthenium/N-triphs/ $\text{Al}(\text{OTf})_3$) in combination with consequent optimization of the reaction conditions for OME_1 and MF synthesis from CO_2/H_2 and methanol. [66] The authors extensively investigated the effects of variations in the reaction conditions with respect to temperature, partial pressure of H_2 and CO_2 , reaction time, and additive as well as catalyst and Lewis acid concentration. Consequently, the optimized conditions resulted in the formation of OME_1 and MF in TONs of 786 and 533 (Scheme 9). Later, a multi-variate optimization method was applied, finally leading to TONs of OME_1 and MF up to 3874 and 1445. [67]

5 Conclusion

The established synthesis of OME_1 is centered on the condensation of methanol and formaldehyde, including challenging separation steps on the pathway to the target product. However, the recent investigations on OME_1 as effective fuel additive for diesel engines demand the development of sustainable and more energy-efficient production routes. Recent investigations in direct methanol oxidation towards OME_1 enabled to decrease the number of process steps and increase efficiency and productivity. Consequently, high OME_1 selectivity can be achieved at



Scheme 9. [Ru(N-triphos)(tmm)]/Al(OTf)₃-catalyzed direct synthesis of OME₁ from CO₂/H₂ as C₁ synthon in the presence of methanol.

medium to high methanol conversions with non-noble metal catalyst systems. The high conversion obtained in this reaction reduces recycling and purification procedures, makes vanadium-based catalysts attractive for industrial processes. Enforcing even higher sustainability, it was shown that CO₂ can be directly incorporated as a building block of OME₁ in a reductive approach using H₂ in the presence of methanol. When compared to the oxidative approach, the reductive method starting from CO₂/H₂ and methanol reduces the number of steps in the process, as re-oxidation of methanol to formaldehyde is eliminated. This direct hydrogenation of CO₂ to OME₁ is enabled with molecular catalyst systems and recent optimizations of the established lead structure allowed reaction with largely increased TONs. Consequently, tailoring of the catalyst system in combination with the development of adapted process concepts may in an interdisciplinary approach pave the way to a continuous OME₁ production based on renewable hydrogen and CO₂.

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Abbreviations

CTAB	cetyltrimethylammonium bromid
DME	dimethyl ether
FA	formaldehyde
MF	methyl formate
MG	mechanical grinding
MM	methoxymethanol
OME ₁	dimethoxymethanol
RC	rapid compression
SG	sol-gel
THF	tetrahydrofuran
TiNT	TiO ₂ nanotubes
VTiS	sulfate-modified V ₂ O ₅ /TiO ₂
VTiSi	silica-modified V ₂ O ₅ /TiO ₂

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