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Future perspectives for formaldehyde: pathways for reductive synthesis and energy storage

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Future perspectives for formaldehyde: pathways for reductive synthesis and energy storage

Leo E. Heim,† Hannelore Konnerth† and Martin H. G. Prechtl*

Formaldehyde has been a key platform reagent in the chemical industry for many decades in a large number of bulk scale industrial processes. Thus, the annual global demand reached 30 megatons per year, and currently it is solely produced under oxidative, energy intensive conditions, using high-temperature approaches for the methanol oxidation. In recent years, new fields of application beyond the use of formaldehyde and its derivatives as i.e. a synthetic reagent or disinfectant have been suggested. For example dialkoxyxymethane could be envisioned as a direct fuel for combustion engines or aqueous formaldehyde and paraformaldehyde may act as a liquid organic hydrogen carrier molecule (LOHC) for hydrogen generation to be used for hydrogen fuel cells. To turn these new perspectives in feasible approaches, it requires also new less energy-intensive technologies for the synthesis of formaldehyde. This perspective article spreads light on the recent directions towards the low-temperature reductive synthesis of formaldehyde and its derivatives and low-temperature formaldehyde reforming for hydrogen generation. These aspects are important for the future demands on modern societies’ renewable energy management, in the form of a methanol and hydrogen economy, and the required formaldehyde-feedstock for the manufacture of many formaldehyde-based daily products.

Introduction

Formaldehyde is widely abundant in nature and the anthropogenic environment owing to multiple natural and artificial decomposition pathways of both biological and artificial organic matter.1–3 Currently, these formaldehyde production

Leo E. Heim is a PhD student at the Prechtl Lab and has been researching since his Master's thesis on catalytic formaldehyde decomposition. Since 2012 he has served as a contracted student research assistant in the same lab. Previously he worked on his Bachelor's thesis with Axel Jacobi von Wangelin and served as chair of the Student Representatives of the Department of Chemistry. He is a co-inventor for a patent on hydrogen generation, and the first and co-author of six articles published for example in Nat. Commun. and Angew. Chem.

Hannelore Konnerth is a PhD student as a Manchot-Fellow at the Prechtl Lab and works on catalytic hydrogenation in multiphase-systems. She performed research on biomass conversion in water for her Master's thesis at the NU Singapore in collaboration with Ning Yan. She has been granted with a competitive Contact-Singapore/A-Star-Fellowship for her research at the NUS. Since 2012 she has served as a contracted research assistant in the Prechtl Lab. Previously she worked on her Bachelor's thesis with Axel Jacobi von Wangelin. She is the first and co-author of six articles and published her most recent results in Chem. Commun. (Emerging Investigator Issue 2016).


Martin H. G. Prechtl

Martin Prechtl (FRSC), named Humbolditian and Heisenbergian, received the NRW Returnee Award 2009 (1.25 M€) and works at the University of Cologne as Privatdozent. He is the editor for Wiley, RSC, DeGruyter and Elsevier. Besides other awards, he holds the Ernst-Haage-Prize 2014 (MPH-CEC) for his contribution to hydrogen storage (Nat. Commun., 2014, PCT-patent). His group develops molecular and nanoscale (de) hydrogenation catalysts and is known for H₂-generation from methanol/formaldehyde at room temperature. Before Cologne he performed research in Wuppertal, Bridgetown, Sao Paulo, Aachen, Muelheim/Ruhr, Porto Alegre and Berlin.

context, formaldehyde impurities also play a role in terms of safety and storage issues for aqueous nuclear waste treatment owing to the observation that formaldehyde-containing nuclear waste generates flammable mixtures of H₂ and N₂O. In this regard, formaldehyde decontamination technologies would be desirable for the safe pre-treatment of contaminated and potential flammable waste previous to storage or further processing. In another perspective, formaldehyde itself is a hydrogen-rich molecule containing 6.7 wt% H₂ in the gaseous phase, and in aqueous media this value rises to 8.4 wt% owing to the favourable equilibrium towards methanediol. Thus, it provides potential to become suitable as a liquid organic hydrogen carrier (LOHC) molecule for the delivery of hydrogen in high-purity for hydrogen fuel cell technologies. In this regard, it might be even more attractive than the hydrogen-richer methanol (12.5 wt%) of the C₁-family owing to the different thermodynamic properties. In vast contrast to methanol which needs a larger energy input during the endergonic methanol reforming process, the formaldehyde reforming process is exergonic, thus more feasible for a self-sustaining hydrogen delivery pathway. In combination with a low-temperature formaldehyde synthesis, the formaldehyde reforming would result in a rechargeable hydrogen battery suitable for hydrogen fuel cell technologies (Scheme 1).

In this perspective article the recent progress and efforts towards more sustainable formaldehyde synthesis by the reduction of CO₂ and CO are described, as well as the approaches for low-temperature formaldehyde reforming. New formaldehyde production methods are also required to feed the potential future application in the energy sector on a large scale because the currently produced formaldehyde is already reserved for the established synthetic applications. Likewise the current annual global methanol production capacity (~110 Mt) cannot serve
soley the energy sector owing to the requirements for methanol (~80–90 Mt per year) in the chemical and pharmaceutical industries.

Direct formaldehyde synthesis

Since the early commercialisation of formaldehyde its production is based on an energy-intensive gas phase process via partial oxidation and/or dehydrogenation of methanol \( (\text{i.e. Formox process}) \).\textsuperscript{3,14,23} Interestingly already in the late 19th century, at least since the 1870s there are early reports about chemical, photochemical, and especially electrochemical and high-temperature attempts described to reduce CO and CO\textsubscript{2} to formaldehyde; the high-temperature decomposition of formaldehyde to syngas \( (\text{CO/H\textsubscript{2}}) \) can be found in the literature.\textsuperscript{24–29} These early attempts have been fallen in oblivion for about 80 years owing to thermodynamic disfavours.\textsuperscript{30,31} Still nowadays, when methanol production from CO\textsubscript{2} has been already realised, and Carbon Recycling International (CRI) installed even a CO\textsubscript{2} methanol plant in Iceland (covering about 3% of Iceland’s energy demands),\textsuperscript{32} the Formox process and related methanol oxidation processes remain the technical state of the art for the formaldehyde production. Thus, even so the more sustainable production of methanol can be realised, the production of formaldehyde remains energy \( (300–400 \degree\text{C}) \) and cost intensive on a large scale. Currently >35% of the world methanol production is used to cover the global formaldehyde demands, which turns formaldehyde to the number one product derived from methanol. The conventional formaldehyde production includes a highly energetic three-step process line to formaldehyde consisting of steam reforming of natural gas \( (700–1100 \degree\text{C}) \) to syngas, followed by methanol synthesis \( (200–300 \degree\text{C}) \) and finally partial oxidation/dehydrogenation of methanol \( (300–400 \degree\text{C}) \) to yield formaldehyde as the major product (Scheme 2).

The mentioned energy-related drawbacks owing to the high temperature required for this process line are accompanied by further energy-intensive compression and purification steps which results in economic and ecological deficiencies.\textsuperscript{3} Today’s modern societies are largely based on C\textsubscript{1}-molecules and their derivatives in many daily life products.\textsuperscript{2,4,5,7} To sustain the status quo of modern life, it urgently requires more sustainable processes for the interconversion of those molecules. Owing to the massive global demands of methanol, the efforts focus on the substitution of the traditional oxidative methanol synthesis from natural gas by a reductive process utilizing abundant CO\textsubscript{2}.\textsuperscript{33–35} Taking into account studies about the life-cycle assessment for the conversion of CO\textsubscript{2} to methanol, this approach is promising in the case that the required hydrogen is delivered from renewables or plain water.\textsuperscript{36} In vast contrast, conventional hydrogen derived from fossil sources leads to the so-called CO\textsubscript{2}-paradoxon owing to the fact that the total CO\textsubscript{2}-production is superior in comparison to the required hydrogen for the CO\textsubscript{2} reduction to methanol.\textsuperscript{37} Interestingly, the research about improved methanol syntheses is much more advanced than the progress for the formaldehyde synthesis, even so that most of the methanol (35%) is simply produced to produce formaldehyde. Over 80 years the valorisation of syngas has quite developed and is widely used for example for hydroformylation,\textsuperscript{4,38} or synthetic fuels (Fischer–Tropsch synthesis).\textsuperscript{39,40} However, it was not considered for the formaldehyde synthesis because of thermodynamic disfavours in gas phase reactions and low yields (~0.2%).\textsuperscript{30,31} In comparison to the classical formaldehyde synthesis, a direct conversion of syngas to formaldehyde would eliminate two energy intensive steps (methanol synthesis and oxidation) and most recently this has been proven as an elegant alternative.\textsuperscript{5} Surprisingly, the direct catalytic hydrogenation of carbon dioxide to formaldehyde or formalin has rarely been reported. In vast contrast, many reports on CO\textsubscript{2} hydrogenation to formic acid and methanol are available, likewise reports where methanol and formic acid are described as a hydrogen source.\textsuperscript{1,14,15,34,35,37,41–51} However, there are reports of trapping formaldehyde in the form of derivatives such as acetals. An overview about those chemical transformations is given in another section of this article. Moreover, a more general review article by Klankermayer and Leitner is of interest for those who want to gain a general overview about the interconversion of C\textsubscript{1}-molecules in general.\textsuperscript{32}

In the mid-1980s Gambarotta and co-workers reported a stoichiometric stepwise reduction of carbon dioxide to formaldehyde and methanol using the zirconium metalloocene \([\text{Cp}_2\text{Zr(H)(Cl)}]_n\) as a reducing agent.\textsuperscript{52} The authors fully characterised the corresponding complexes formed in the course of the metal hydride transfer to CO\textsubscript{2}. In the first step an oxo-bridged dimeric complex \([\text{Cp}_2\text{Zr(Cl)}]_2\text{O}\) is formed, indicating a C–O bond cleavage of CO\textsubscript{2}. In a second step \([\text{Cp}_2\text{Zr(H)(Cl)}]\) reacts with formaldehyde, yielding \([\text{Cp}_2\text{Zr(OMe)(Cl)}]\) (Scheme 3).

Corriu and co-workers reported a few years later the insertion of CO\textsubscript{2} in the Si–H bonds of a hypervalent organosilane in the presence of a tertiary amine (Scheme 4).\textsuperscript{53} In the first step a silyl formate is formed which is stable at room temperature. The silyl ester decomposes at 65–85 °C under argon within two

Scheme 2  Classical high temperature gas phase process line to formaldehyde: (I) natural gas reforming, (II) methanol synthesis, and (III) partial methanol oxidation.

Scheme 3  Stoichiometric reaction of CO\textsubscript{2} to formaldehyde at room temperature.\textsuperscript{52}
hours yielding a trimeric siloxane and formaldehyde. The formaldehyde was trapped and characterised as a hydrazone using 2,4-dinitrophenylhydrazine.

In an enzymatic approach Liu and co-workers demonstrated the NADH-coupled reduction of CO$_2$ to formaldehyde using formate dehydrogenase (FDH) and formaldehyde dehydrogenase (FADH) as catalysts (Scheme 5).$^{54}$ The optimised reactions have been performed at 37 °C in phosphate buffer (pH 6) with 1 mL of 100 mmol L$^{-1}$ NADH solution under 5 bar of CO$_2$ yielding about 0.901 mmol L$^{-1}$ HCHO for example after 12 h.

In contrast to the above mentioned molecular approaches, there is a report on the direct formation of free formaldehyde starting from CO$_2$ using solid catalyst materials. Lee and co-workers reported a pronounced selectivity even for the hydrogenation of CO$_2$ to formaldehyde at 150 °C under a total pressure of 6 bar with a H$_2$ : CO$_2$ ratio of 20 : 1. They used a PtCu/SiO$_2$ (Pt/Cu = 0.03) catalyst and obtained 0.87 × 10$^{-4}$ mmol min$^{-1}$ Ru: 1 NADH solution under 5 bar of CO$_2$ yielding about 0.901 mmol L$^{-1}$ HCHO for example after 12 h.

In a photocatalytic approach using ruthenium(II)-complex/carbon nitride hybrid photocatalysts (with cis-[Ru(bipy)$_2$Cl$_2$(CO)$_2$] as a precursor), the authors reported the formation of HCHO (380 nmol) in the course of the conversion of CO$_2$ into CO and formaldehyde. In another photocatalytic method, the authors used a dye-sensitized TiO$_2$ film with bis(tetrabutylammonium)-cis-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) for the reduction of CO$_2$ to formaldehyde and methanol. At pH 10 they observed for example the formation of 0.0835 mmol cm$^{-2}$ formaldehyde, 0.1292 mmol cm$^{-2}$ formaldehyde and 0.1781 mmol cm$^{-2}$ methanol after visible light illumination for 5 h (Scheme 7). In other reports about photocatalytic reduction of CO$_2$ typically a mixture of formic acid, formaldehyde, methanol or even methane has been observed on either a low conversion level and/or with low selectivity for formaldehyde.$^{59-63}$

In 2014 a promising electrocatalytic method converting CO$_2$ into formaldehyde even in seawater has been presented by Nakata and Einaga (Scheme 8).$^{16}$ The authors used boron-doped diamond (BDD) electrodes with p-type surfaces and a platinum counter electrode in the range from −1.0 V to −1.9 V vs. Ag/Ag$^+$. In a methanol electrolyte. They reported a maximum Faradaic efficiency for formaldehyde of 74% at −1.7 V vs. Ag/Ag$^+$, the efficiency is maintained between 1 h and 20 h. The efficiency at −1.5 V, and H$_2$ is formed with 1.1% below −1.7 V. The reduction of formic acid, instead of CO$_2$ as the starting material, yielded formaldehyde with 85% at −1.5 V. After optimization of the set up with artificial electrolytes they tested seawater as a natural electrolyte successfully yielding 36% formaldehyde, and 7.5 × 10$^{-3}$ M per hour. As a reference they tested also 0.1 M aq. NaCl yielding 62% formaldehyde. The lower activity in seawater is attributed to natural impurities. Other electrochemical approaches gave Faradaic efficiencies between 0.08% and 25% for formaldehyde derived from CO$_2$ using polyoxometalate as a catalyst material.$^{64}$

Again in 2014, the first direct conversion of syngas (CO : H$_2$ = 1 : 1) to formaldehyde has been realized in aqueous media (Scheme 9, patent filed).$^5$ The driving force to push the equilibrium into the desired direction was the performance of the reaction in the liquid rather than in the gaseous phase.

Scheme 4 Stoichiometric reaction of CO$_2$ to formaldehyde via decomposition of a silyl formate.$^{55}$

Scheme 5 Sequential reduction of CO$_2$ by means of FDH and FADH enzymes and NADH co-factor.$^{54}$

Scheme 6 Hydrogenation of CO$_2$ with a PtCu catalyst.$^{55}$

Scheme 7 Photocatalytic conversion of CO$_2$ into HCHO.$^{57}$

Scheme 8 Electrocatalytic reduction with boron doped-diamond electrodes with highest efficiency for formaldehyde at −1.7 V.$^{16}$

Scheme 9 Elimination of two energy and cost intensive synthesis steps towards low temperature formaldehyde synthesis from syngas in aqueous solution.$^5$
Indeed, this reaction requires a protic environment to stabilise formaldehyde in the form of methanediol or (hemi)acetals and prevent over-reduction to methanol. In contrast to the performance in the aqueous phase, the gas phase hydrogenation of CO to formaldehyde with a solid catalyst is thermodynamically very limited (vide infra). In consequence to these observations, considering the reactivity of formaldehyde towards water, water has been used as a solvent. Formaldehyde is known to form methanediol as the major product in aqueous solution. This low-temperature approach has the potential to save costs and energy owing to the elimination of two high-temperature reaction steps.

The hydrogenation of CO to methanediol in water was then thermodynamically favourable and highly selective (100%) for methanediol at a conversion level of 19% in a slurry reactor, pointing out that formic acid, methanol or methane was not formed. Subsequent work has demonstrated that formic acid (14%), methanol (1.4%), and methane (0.2%) were the main products formed, with pinacol borane with \( [\text{RuH}_2(\eta_2\text{H}_2)(\text{PCy}_3)_2] \) (Cy = cyclohexyl; 10 mol%) as the catalyst precursor (Scheme 10). The key step for the CO\(_2\) reduction goes via the insertion of CO\(_2\) into the ruthenium hydride bond. Later the authors showed that an iron catalysed pathway involving a metal hydride catalyst is also feasible for the generation of borylmethylene derivatives with good selectivities. Likewise most recently in 2016, Cantat and Berthet showed that besides iron, also copper and cobalt phosphine complexes are active for the borylation of CO\(_2\) yielding mixtures of bisboryl acetal and methoxy borane with a broad range of selectivity for these two products.

In their ongoing research they focussed on the generation of free formaldehyde and achieved this with a slightly modified protocol. Using this catalyst precursor \( [\text{RuH}_2(\eta_2\text{H}_2)(\text{PCy}_3)_2] \) (Cy = cyclohexyl; 1–10 mol%) they achieved the formation of 22% formaldehyde by reduction of CO\(_2\) with pinacol borane besides the above mentioned borylmethylene acetals (6 and 12%). For further improvement of the formaldehyde yield, they added bulky diisopropyl aniline to the starting material resulting in the corresponding formyl imine (74%) and upon addition of aqueous methanol, the imine is hydrolysed yielding aqueous formaldehyde and paraformaldehyde (Scheme 11). Interestingly, in a study with phosphineborane catalysts about hydroboration of CO\(_2\) yielding methoxy-

### Table 1  Thermodynamic data of CO hydrogenation to formaldehyde

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( X ) [%]</th>
<th>( \Delta G ) [kJ mol(^{-1})] (K [mol(^{-1})])</th>
</tr>
</thead>
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<td>4.38 \times 10^{-3}</td>
<td>34.565 (8.760 \times 10^{-7})</td>
</tr>
<tr>
<td>323</td>
<td>4.67 \times 10^{-3}</td>
<td>37.297 (9.348 \times 10^{-7})</td>
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<tr>
<td>373</td>
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<tr>
<td>423</td>
<td>4.86 \times 10^{-3}</td>
<td>48.705 (9.711 \times 10^{-7})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( X ) [%]</th>
<th>( \Delta G ) [kJ mol(^{-1})] (K [mol(^{-1})])</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.40</td>
<td>-7.071 (17.332)</td>
</tr>
<tr>
<td>18.42</td>
<td>-5.648 (8.186)</td>
</tr>
<tr>
<td>3.86</td>
<td>-1.297 (1.519)</td>
</tr>
<tr>
<td>5.84 \times 10^{-4}</td>
<td>4.853 (2.52 \times 10^{-1})</td>
</tr>
</tbody>
</table>

**Formaldehyde derivatives**

In 2013 Sabo-Etienne and Bontemps trapped formaldehyde as bis(boryl)methylene acetal in the course of the CO\(_2\) reduction with pinacol borane with \( [\text{RuH}_2(\eta_2\text{H}_2)(\text{PCy}_3)_2] \) (Cy = cyclopentyl; 1–10 mol%) as the catalyst precursor (Scheme 10). The key step for the CO\(_2\) reduction goes via the insertion of CO\(_2\) into the ruthenium hydride bond. Later the authors showed that an iron catalysed pathway involving a metal hydride catalyst is also feasible for the generation of borylmethylene derivatives with good selectivities. Likewise most recently in 2016, Cantat and Berthet showed that besides iron, also copper and cobalt phosphine complexes are active for the borylation of CO\(_2\) yielding mixtures of bisboryl acetal and methoxy borane with a broad range of selectivity for these two products.

In their ongoing research they focussed on the generation of free formaldehyde and achieved this with a slightly modified protocol. Using this catalyst precursor \( [\text{RuH}_2(\eta_2\text{H}_2)(\text{PCy}_3)_2] \) (Cy = cyclohexyl; 1–10 mol%) they achieved the formation of 22% formaldehyde by reduction of CO\(_2\) with pinacol borane besides the above mentioned borylmethylene acetals (6 and 12%). For further improvement of the formaldehyde yield, they added bulky diisopropyl aniline to the starting material resulting in the corresponding formyl imine (74%) and upon addition of aqueous methanol, the imine is hydrolysed yielding aqueous formaldehyde and paraformaldehyde (Scheme 11). Interestingly, in a study with phosphineborane catalysts about hydroboration of CO\(_2\) yielding methoxy-

![Scheme 10 Reduction of CO\(_2\) with pinacol borane yielding borylmethylene acetal](image)

![Scheme 11 Reduction of CO\(_2\) with pinacol borane in the presence of aniline, followed by hydrolysis yielding aqueous formaldehyde and paraformaldehyde](image)
boranes, formaldehyde borane adducts have been postulated as catalytically active species.\(^\text{18}\)

Oestreich and Metsänen reported a ruthenium-catalysed hydroxylation of CO\(_2\) with Et\(_3\)SiH yielding silylated formaldehyde or methanol.\(^\text{19}\) Here the key step is the formation of the bis(silyl)methylene acetal which gives high selectivities (81–99%) at moderate to very high conversions (33 to >99%; Scheme 12) at 80 °C. Silylated methanol can be obtained after 7 days at 150 °C with 75% selectivity and 69% conversion.

Under similar conditions, Serrano and Rodriguez evaluated a nickel PBP-complex for the formation of bis(silyl)methylene acetal from CO\(_2\) in the presence of Et\(_3\)SiH with high selectivities (78 to >99%) and moderate to high conversion (41–91%) at 70 °C.\(^\text{17}\) Already in 2013, Berke and co-workers reported the hydrosilylation of CO\(_2\) using a Frustrated Lewis Pair (FLP) consisting for example of a rhenium hydride and B(C\(_6\)F\(_5\))\(_3\) (Scheme 12) at 80 °C.\(^\text{21}\) Here the authors reported yields of ~90%. Piers and co-workers reported a scandium complex for the above described reaction.\(^\text{20}\) In general, it should be underlined that the interest in the synthesis of boryl and silyl methylene acetals from CO\(_2\) is of fundamental academic nature, and this might stimulate interest in the preparation of inorganic/organic hybrid materials incorporating formaldehyde derived from CO\(_2\). Contrarily, the above described approaches seem unsuitable for their application to generate organic combustion fuels or liquid organic hydrogen carrier molecules for energy storage and hydrogen storage systems based on CO\(_2\)-derived formaldehyde.

Following the above described efforts on trapping formaldehyde in the form of boryl and silyl methylene acetals (Schemes 11 and 12), most recently in 2016, Klankermayer \textit{et al.} demonstrated for the first time the catalytic conversion of CO\(_2\) (20 bar) and H\(_2\) (60 bar) in the presence of alcohols into dialkoxymethane ethers (oxymethylene ethers) in a multi-step reaction using a molecular ruthenium-triphos catalyst and aluminium triflate as a Lewis acidic co-catalyst (Scheme 13).\(^\text{8}\) The reaction has been validated for a wide range of linear and branched aliphatic alcohols (C\(_1\)–C\(_{10}\)) and benzyl alcohol. The achieved turnovers reached about 200 TONs for methanol and varied for the higher aliphatic alcohols between 50 and 120, showing a dependency of the chain-length, with an activity increase for long-chain alcohols. The Klankermayer protocol gives direct access to dimethoxymethane and higher oxymethylene ethers which are considered to be potential fuels or fuel additives\(^\text{10}\) using abundant CO\(_2\) and renewable hydrogen.

### Formaldehyde as hydrogen source

In contrast to the above described obstacles and challenges for the synthesis of formaldehyde under reductive conditions starting from CO\(_2\) and CO\(_2\), the dehydrogenative decomposition of aqueous formaldehyde and paraformaldehyde to H\(_2\) and CO\(_2\) is much more straightforward,\(^\text{14}\) even so, in contrast to long-investigated hydrogen evolution from formic acid or methanol,\(^\text{69,70}\) it has been rarely considered and investigated.

Recently, we showed that water in the presence of C\(_1\)-entities like (para)formaldehyde (6.7 wt% per unit) is suitable for molecular hydrogen-storage as these molecules can be easily and selectively dehydrogenated forming pure H\(_2\) and CO\(_2\) (Scheme 14).\(^\text{14}\) A theoretical efficiency of 8.4 wt% of H\(_2\) concerning 1 equiv. H\(_2\)O and H\(_2\)CO is possible owing to the favourable equilibrium constant for methanediol in aqueous solution. In this regard, the incorporation of water into the formaldehyde molecule yielding methanediol can be interpreted as a chemical indirect water-splitting reaction, where water acts as a proton source and formaldehyde as a hydride source. The H\(_2\)-content is higher than for formic acid (4.4 wt%), even when technical aqueous H\(_2\)CO is used, the solution has a minimum efficiency of 5.0 wt%. This catalytic decomposition of H\(_2\)CO can be envisioned as a novel approach for simultaneous H\(_2\) production and decontamination treatment of wastewater with formaldehyde impurities as a waste to value approach.\(^\text{5,13}\)

The dehydrogenation reaction of aqueous formaldehyde proceeds under mild conditions in the temperature range between room temperature and 95 °C using a molecular ruthenium catalyst under base-free, respectively pH neutral
conditions, without any prevention to exclude air.\textsuperscript{1,14,15} As catalyst precursors a wide range of [Ru(arene)Cl\textsubscript{2}]\textsubscript{2} complexes are suitable (arene = benzene, toluene, \textit{p}-cymene, etc.). The catalyst is \textit{in situ} transformed into a cationic ruthenium hydride formiato species [Ru(arene)[\mu-H][\mu-Cl][\mu-HCO\textsubscript{2}]Ru(arene)]\textsuperscript{X\textsuperscript{–}}\textsuperscript{−} (X: Cl, BF\textsubscript{4}) which plays a major role in the catalytic cycle.\textsuperscript{1} The hydrogen evolution is solely accompanied by CO\textsubscript{2} formation without any carbon monoxide present. In regard to the hydrogen production yields of 85\% of pure H\textsubscript{2} using concentrated formaldehyde solutions have been obtained within 60 minutes of reaction time. Additionally, the capability for the wastewater purification has been proven with diluted formaldehyde solutions. Those tests gave conversions of \textgtrsim 99.95\%, and the residual amount of formaldehyde in solution was as low as 10\textsuperscript{–}40 ppm. These values are in the range for the tolerance of formaldehyde in wastewater, where the highest reported TOF was 3142 h\textsuperscript{–}1 using [Ru(\textit{p}-cymene)Cl\textsubscript{2}] as the precatalyst.\textsuperscript{1}

An extension of aqueous formaldehyde as LOHC has been further investigated with regard to room-temperature methanol reforming.\textsuperscript{15} The room temperature reforming of methanol follows a bio-inspired approach using a multi-catalytic system consisting of enzymes and a biomimetic formaldehyde dehydrogenase (Scheme 15). The limitations of this approach are related to the compatibility of the metal complex and the enzymes which might be overcome with metal–protein technologies,\textsuperscript{71} and it is also related to the reaction conditions.\textsuperscript{72} The catalyst modification and also slightly modified reaction conditions turn the catalytic formaldehyde dehydrogenation into an efficient biomimetic dismutase reaction pathway.\textsuperscript{72}

Besides the above described ruthenium catalysed hydrogen generation from formaldehyde in water, Fukuzumi and co-workers showed that a water-soluble iridium complex is suitable for hydrogen generation from paraformaldehyde in water at room-temperature, however so far with TONs <100 depending on the basicity (pH 6–10) of the solutions (Scheme 16).\textsuperscript{22} Yamaguchi and colleagues demonstrated the formaldehyde dehydrogenation with an iridium complex carrying a cooperative ligand-site, resulting in conversions up to 89\% (TON = 178).\textsuperscript{73} In both cases it has been shown that pH has an influence on the catalyst structure in solution and on the activity and yield. Both reactions show better performance under basic conditions.

**Summary & outlook**

In this decade, major progress has been achieved towards the low-temperature synthesis of formaldehyde and its derivatives starting from CO and CO\textsubscript{2}. For the first time a promising direct formaldehyde synthesis from syngas has been realized. Likewise the first synthesis of dialkoxymethane \textit{via} catalytic reduction of CO\textsubscript{2} has been demonstrated. Moreover an electrocatalytic conversion of CO\textsubscript{2} to formaldehyde using sea water as the electrolyte shows a further promising direction. These
novel pathways in the C1-chemistry puzzle open new windows of opportunities towards more sustainable cost and energy saving production chains with formaldehyde as the platform reagent. The methods may become independent of fossil sources if the future hydrogen production processes will use renewables or plain water. The same efforts will be required for the future production of syngas using biomass or organic waste as the feedstock. The scenario of the stabilization of formaldehyde in solution with water and alcohol will play a key role to further improve these reductive syntheses because the thermodynamic parameters caused by the reactive protic solvents have a tremendous influence on the all over reaction pathways and the reactivity of all solute species and intermediates: methanediol, (di)alkoxymethane in the formaldehyde case or carbonic acid and carbonates in the CO2 case as dominant species in solution. Other approaches for the stabilization of formaldehyde in solution included the formation of bis(silyl) or bis(boranyl)methylene acetals, which might generate further interest for inorganic materials with formaldehyde as a cross-linker. Still the selective hydrogenation of CO2 to formaldehyde is a missing piece of the C1-puzzle. In analogy to the CO hydrogenation in water, the key for a selective CO2 hydrogenation will be probably the application of water as the solvent to trap formaldehyde in its form as methanediol, hence formalin solution. Notably, free formaldehyde can be also obtained in sequential enzyme catalysis applying FDH and FADH in the presence of NADH as a co-factor. This clearly shows that also the biotechnology pathway might be promising one day to complement the global demands for the large amounts of formaldehyde already required nowadays for established application.

Considering new potential fields for the application of formaldehyde in the energy sector for new combustion fuels or as liquid hydrogen carrier molecules for hydrogen fuel cell technologies, consequently this will require further efforts to enhance significantly the global production of formaldehyde. Thus, one needs to consider also biomass- and waste-based formaldehyde production. In this regard also the hydrogen production from wastewater containing residual formaldehyde might become an interesting aspect to complement the hydrogen production. The realization of a formaldehyde-based hydrogen battery requires the immobilization of the catalyst. In terms of long-term stability the system seems quite promising, also taking into account the usual limitations of battery life-time issues and the superior energy content of hydrogen and LOHC in comparison to conventional batteries.

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Notes and references