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CO₂-based hydrogen storage – Hydrogen generation from formaldehyde/water

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Abstract:

Formaldehyde (CH₂O) is the simplest and most significant industrially produced aldehyde. The global demand is about 30 megatons annually. Industrially it is produced by oxidation of methanol under energy intensive conditions. More recently, new fields of application for the use of formaldehyde and its derivatives as, i.e. cross-linker for resins or disinfectant, have been suggested. Dialkoxymethane has been envisioned as a combustion fuel for conventional 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. For the realization of these processes, it requires less energy-intensive technologies for the synthesis of formaldehyde. This overview summarizes the recent developments in low-temperature reductive synthesis of formaldehyde and its derivatives and low-temperature formaldehyde reforming. These aspects are important for the future demands on modern societies' 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.

Keywords: formaldehyde, methanol, carbon dioxide, reforming, hydrogen storage, hydrogen generation

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1 Introduction

Formaldehyde (CH₂O) is the simplest and most significant industrially produced aldehyde. Since the discovery in 1855 by Butlerow and early synthesis by von Hofmann in 1867, the potential applications of this compound underwent a rapid headway. In the early twentieth century, formaldehyde became an industrially produced chemical. When combined with phenol, it formed the first successful derivative, "Bakelite", which introduced mankind to the "plastic age" [1]. The work by Haber, Bosch, and others in the 1920s marked a turning point. Synthesis gas manufactured from coal became a source of ammonia, methanol, and urea on an industrial scale. In 1926, I.G. Farben introduced Kaurit glue to the market, a polymer based on formaldehyde and urea. The suitability of the low-cost urea–formaldehyde resins for bonding wood significantly contributed to the popularity of particle board and launched a revolution in the construction and furniture industries. Several types of

formaldehyde-based resins have exhibited exceptional heat and chemical resistance, which make them particularly important in the automobile and aerospace industries. The properties as a preservative and disinfectant were also documented by Blum at the end of the nineteenth century [2]. Due to its ability to cross-link primary amino groups and other nucleophilic functional groups in proteins, formaldehyde is a common fixative used to preserve tissue for histology. Driven by new discoveries in science and technology which see formaldehyde as useful for a wide range of applications, the demand for formaldehyde has risen steadily in the past decades. Nowadays, it is one of the most important industrial organic chemicals and the worldwide production capacity surpasses 30 million tons per year [3].

Formaldehyde is ubiquitous in the atmosphere, where is released *via* photochemical oxidation and incomplete combustion of hydrocarbons. It is a well-known pollutant, since is contained in car exhaust and tobacco smoke and therefore significant concentrations have been observed in polluted urban air [4]. Moreover, formaldehyde was one of the first "complex" organic molecules detected in the interstellar medium [5]. New research shows that the organic or carbon-containing materials (including amino acids) were likely made from formaldehyde in the primitive solar system – thus formaldehyde is one of the key molecules that are relevant to the origin of life.

Formaldehyde is gaseous at ambient conditions but typically available as aqueous solutions known as formol or formalin. A saturated water solution of formaldehyde (37 wt%) is commercialized as 100 % formalin. Pure aqueous solutions contain mainly the formaldehyde hydrate, methylene glycol (HOCH₂OH) in equilibrium with mixtures of oligomeric poly(oxymethylene) glycols [HO-(CH₂O)_n-H, n = 1-8], where the degree of polymerization depends on the temperature, concentration and pH. The non-hydrated form (H₂CO) is present at room temperature, below 0.1 wt%, instead the major species is the hydrated form methanediol (K $\approx 2*10^3$). Paraformaldehyde is the solid polymerization product of formaldehyde (mp = 120°C) with an average degree of polymerization of 8–100 units, which is depolymerized to the monomer upon heating or under slightly acidic conditions (e. g. pH 5–6), which leads to opening of the poly-acetal. A more expensive alternative to paraformaldehyde is trioxane which is much more stable, and therefore the acetal opening requires much harsher and more acidic conditions.

The formaldehyde molecule is relatively stable, with a heat formation of -115.9 kJ mol⁻¹ (see Table 1 for a selection of physical properties). Decomposition by direct heating occurs at temperatures above 423 K, forming methanol and carbon dioxide (CO₂). The selectivity in the decomposition seems to be dependent on the temperature. Higher temperatures (>623 K) provoke the formation of synthesis gas (H₂/CO) [7]. At lower temperatures, transition metal catalysts (rhodium, iridium, ruthenium, or cobalt) can promote the decarbonylation of the molecule and allow the use of formaldehyde as surrogates of syngas in hydroformylation reactions [8].

Molar mass	30.026 a.u.
Vapor pressure (295 K)	470 kPa
Boiling point	254 K
Flash point	358 K
Ignition temperature	697 K
Standard heat of combustion	570.7 kJ mol ⁻¹
Ionization energy	$10.88 \text{ eV} = 87793.3 \text{ cm}^{-1}$
Dipole moment	2.33 D
Heat of formation (298 K)	-115.9 ± 6.3 kJ mol ⁻¹
Gibbs energy (298 K)	$-109.9 \text{ kJ mol}^{-1}$
Heat of combustion (298 K)	$-561.5 \text{ kJ mol}^{-1}$
Specific heat capacity (298 K)	$35.425 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$

Table 1: Physical properties of formaldehyde [6].

Formaldehyde is becoming a promising energy carrier for on-demand hydrogen generation. Some of the most recent research focusses on hydrogen production by decomposing formalin at low temperatures by employing catalysts with only CO_2 as by-product. The latter could be recycled resulting in a carbon-neutral fuel cycle. Related liquid-phase chemical hydrogen storage C1 materials such as methanol /water mixtures and formic acid have been intensively studied in the past years. Figure 1 shows a comparison of the gravimetric H_2 content and corresponding thermodynamic data for the complete dehydrogenation of each of these liquid organic fuels (LOF). This data show that formaldehyde is a good compromise between hydrogen content and energy required for the hydrogen release reaction. Although the MeOH/H₂O system has a higher hydrogen content (12 wt%), the higher energy required for complete dehydrogenation makes methanediol a competitive and equally attractive C1 energy carrier.

Reaction	wt% H ₂	∆H _r (kJ mol⁻¹)	∆G ⁰ (kJ mol⁻¹)
$MeOH + H_2O \rightarrow CO_2 + 3H_2$	12.0	38.8	8.8
$H_2CO + H_2O \rightarrow CO_2 + 2H_2$	8.3	-35.8	-47.4
$HCO_2H \rightarrow CO_2 + H_2$	4.3	-14.9	-31.8

 $LOF-H_2 \leftrightarrows LOF + H_2$

Figure 1: Comparison of gravimetric H₂ content of C1 liquid organic fuels (LOF) and thermodynamic data for the dehydrogenation reaction. Data obtained from http://webbook.nist.gov.

Figure 2 summarizes the thermodynamic data for two possible dehydrogenation pathways of formaldehyde in water: Pathway (A) sequential hydration/dehydrogenation/decarboxylation and pathway (B) decarbonylation of H₂CO followed by a water gas shift reaction (WGS). The potential "fuel energy", ΔE_F , which can be gained in the overall process through the combustion of the produced H₂ with O₂, is given as $\Delta E_F = [n \Delta H_R(H_2 + \frac{1}{2}O_2) - \Delta Hr]$ with n = number of equivalents liberated in the dehydrogenation step. In the pathway A, the hydration of formaldehyde and the first dehydrogenative step of methanediol is an exergonic process overall (-20.9 kJ mol⁻¹), as is the second dehydrogenation step forming CO₂ (-14.9 kJ mol⁻¹). In the alternative pathway B, aldehyde decarbonylation is thermodynamically less favored than this hydration/dehydrogenation sequence because the first step is endergonic although only slightly by 5.4 kJ mol⁻¹ (298 K). Depending on the individual activation barriers, which determine the kinetics of each reaction step, the formation of carbon monoxide as intermediate has to be taken into account (vide infra Section 2.2.2.).

Pathway B

$$\begin{array}{c} 0 \\ H \end{array} \begin{array}{c} -H_2 \\ H_2 \end{array} \begin{array}{c} -H_2 \\ -H_2 \end{array} \begin{array}{c} 0 \\ -H_2 \end{array} \begin{array}{c} H_2 + C \\ -H_2 \end{array}$$

	Pathway A	Pathway B		
	Hydration/Dehydrogenation	Decarboxylation	Decarbonylation	WGS
ΔH_r	-20.9	-14.9	5.4	-41.2
ΔG^0	-15.5	-31.8	-27.2	-20.2
$\Delta {\rm E}_{\rm F}$	-262.7	-256.7	-236.6	-243.2

Figure 2: Reaction pathways of formaldehyde reforming. WGS = Water gas shift. Comparison of thermodynamic data (ΔH_r) standard Gibbs free energy (ΔG^0) and overall "fuel energy" gain in the process (ΔE_F) in kJ mol⁻¹. Data obtained from webbook.nist.gov/chemistry.

New strategies for the catalytic reforming of H_2CO under mild conditions have raised expectations of this affordable compound as an alternative fuel. Herein, we discuss mainly catalyzed processes using heterogeneous or homogeneous systems. Most of the presented work is very much in its early stages, compared with other organic fuels (methanol or formic acid), especially the selective reversible conversion of CO_2 back to formaldehyde.

2 Production of formaldehyde and related technologies

2.1 Formaldehyde production and metabolism by biological systems

Formaldehyde (H_2CO) exists globally in the natural atmosphere as an oxidation product of CH_4 . It is also a naturally occurring biological compound present in all tissues, cells, and biological fluids. Most formaldehyde is produced as the oxidation product of methanol [9]. Bacteria utilize three classic mechanisms for methanol metabolism: the Calvin cycle, the ribulose monophosphate cycle, and the serine cycle (Figure 3). First, the most energetically costly pathway of methanol metabolism begins with the sequential oxidation of methanol to formaldehyde, further to formate and then to carbon dioxide, which is then incorporated into the Calvin cycle as a carbon source.



Figure 3: Formaldehyde production and metabolism. Overview of the pathways to convert sequentially methanol to formaldehyde and CO₂. NAD+/NADH, oxidized, and reduced form of nicotinamide adenine dinucleotide; ADH, Alcohol dehydrogenase; FDH, formaldehyde dehydrogenase; cytosolic (ALDH1A1) and a mitochondrial (ALDH2) aldehyde dehydrogenases. Figure adapted from reference [8].

This first oxidative step from methanol to formaldehyde can be executed *via* one of at least three different pathways: the catalase-H₂O₂ system, the cytochrome P450 (CYP2E1), and the zinc-based alcohol dehydrogenase I (ADH1) *via* NAD⁺-dependent oxidation. The bulk of the formaldehyde is exported to the cytoplasm where it is further oxidized. The oxidation of formaldehyde to formate occurs by several separate pathways with the participation of P450 monooxygenases, mitochondrial aldehyde dehydrogenase 2 (ALDH2), and formaldehyde dehydrogenase (FDH). Under certain conditions, some formaldehyde may be oxidized to formate in the peroxisomes, either by methanol oxidase, which possesses dual substrate specificity, or by the reaction of hydrogen peroxide and catalase. The formate generated by formaldehyde oxidation can undergo further oxidization to carbon dioxide. These metabolic pathways involve catalase, 10-formyltetrahydrofolate dehydrogenase also known as ALDH1L1, or ALDH1L2, its mitochondrial isoform. Another endogenous source of formaldehyde is the oxidative deamination of methylamine by semicarbazide-sensitive amine oxidases (SSAOs), according to eq. (1).

$$CH_3NH_2 + O_2 + H_2O \xrightarrow{SSAO} HCOH + H_2O_2 + NH_3$$
(1)

Beside the oxidation of methanol, formaldehyde is also formed by the conversion of glycine to serine in the presence of tetrahydrofolate (serine cycle) [10]. Furthermore, formaldehyde is part of the C1-carbon pool, which is utilized for the biosynthesis of purines, thymidine, and several amino acids, which are incorporated into DNA, RNA, and proteins during macromolecular synthesis.

2.2 Industrial production of formaldehyde

The large-scale production of formaldehyde involves a sequence of three reactions: (i) steam reforming of natural gas producing synthesis gas, a mixture of CO and H_2 . (ii) Conversion of CO/ H_2 to methanol, and (iii) finally partial oxidation and/or dehydrogenation of methanol to formaldehyde eqs (2) 2 (3) [11].

$$CH_3OH \rightleftharpoons CH_2O + H_2 \ \Delta Hr = 84kJ \ mol^{-1}$$
⁽²⁾

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \Delta Hr = -159kJ mol^{-1}$$
 (3)

The industrial production of formaldehyde from methanol is based on two major processes: (a) The air-deficient process or silver contact process. In this process methanol air mixtures are dehydrogenated eq. (2) and partially oxidized by O_2 eq. (3) to formaldehyde at atmospheric pressure and in a temperature range of 600–720°C. Under these conditions, the liberated H_2 is oxidized with O_2 to water (BASF, Borden, Bayer, Degussa, Imperial Chemical Industries (ICI), Celanese, DuPont, Mitsubishi, and Mitsui) [12]. This process can be further classified into two types: the methanol ballast and the water ballast process (or BASF process). In the second large-scale process, the Formox process, partial oxidation of methanol takes place in the presence of an excess of air (Lummus, Montecatini, Hiag/Lurgi, and Perstorp/Reichold). Due to the higher stability of the catalyst (iron/molybdenum or vanadium oxide) and lower temperatures (250–400°C), the Formox process attracts more attention than silver-based catalytic process [13].

2.3 Related technologies for formaldehyde synthesis

Processes for converting hydrocarbons or ethers (e. g., dimethyl ether) [14] into formaldehyde are not of major industrial importance for economic reasons. Additionally, other processes that employ partial hydrogenation of CO [15] or oxidation of methane cannot compete with methanol conversion methods due to the lower yields obtained in these processes. Formaldehyde production from CO_2 itself would be advantageous due to the usage of non-fossil fuel sources and the possibility of recycling CO_2 formed in large amounts by burning fossil fuels. The chemical recycling of CO_2 may give formalin as a renewable, carbon-neutral, almost unlimited source for transportation fuels, as medium for storing and transporting energy, as well as a convenient feedstock for the production of fine chemicals. Recent studies focused on developing alternatives to the oxidative synthesis of methanol from natural gas based on reductive processes using CO_2 as raw material. Although there are many studies on the hydrogenation of CO_2 to formic acid and methanol, the selective catalytic hydrogenation to formaldehyde has been scarcely investigated although in the formation of CH_3OH from CO_2 , theoretical calculations suggest the transient formation of formaldehyde as intermediate [16].

Lee et al. presented the first report on the direct formation of formaldehyde from CO₂ by a heterogeneous catalyst. An optimum atomic ratio of Pt : Cu = 0.03 : 1 supported on SiO₂ gives a catalytic system which allows the production of 0.87×10^{-4} mol min⁻¹ g⁻¹ catalyst and a selectivity of *ca*. 80 % with MeOH as side product. The H₂ : CO₂ ratio of 20 : 1 is essential to achieve a high selectivity (Figure 4a) [17].

Heterogeneous systems PtCu/SiO₂ a) $CO_2 + 2 H_2$ $H_2CO + H_2O$ 150°C NiRu H₂CO $CO + H_2$ b) <100°C <100 bar or H_2O 100% selectivity idem $H_{2}CO + H_{2}O$ $CO_2 + 2 H_2$ BBD/Pt c) $CO_2 + 4H^+ + 4e^{-1}$ $H_{2}CO + H_{2}O$ Enzymatic systems FDH-TiO₂/FADH

Figure 4: Heterogeneous or enzymatic catalytic reduction of CO₂ to formaldehyde. BDD (boron-doped diamond electrode). FDH (formate dehydrogenase) and FADH (formaldehyde hydrogenase)

H₂CO + 2 NAD⁺ + H₂O

 $CO_2 + 2 \text{ NADH} + 2 \text{ H}^+$

An alternative production of formaldehyde by hydrogenation of CO or CO_2 has been reported by Tanksale and co-workers in 2015, respectively in 2017 [18, 19]. In their proof-of-concept study they demonstrated that the thermodynamically disfavored conversion of syngas to formaldehyde in the gas phase (Gibbs energy is positive) can be indeed successfully performed by simply conducting the reaction in the aqueous phase (Gibbs energy is negative). When the conversion level reached 19 %, aqueous formaldehyde is formed with 100 % selectivity at temperatures as low as 80°C in water under 100 bar with a NiRu catalysts (Figure 4b). In the continuation of this research line, these authors demonstrated that under fairly similar conditions, CO can be substituted by carbon dioxide, resulting in a catalytic system which is capable to convert CO_2 into aqueous formaldehyde at temperatures below 100°C and at low pressure (70 bar) (Figure 4b) [19].

The authors considered two possible mechanistic pathways through two-reaction step which involve CO or formic acid as intermediates, respectively. In the first proposed route (a), CO₂ is initially hydrogenated to formic acid ($\Delta H_{298} = -7.5 \text{ kJ mol}^{-1}$), which consecutively undergoes hydrogenation to the formaldehyde hydrate ($\Delta H_{298} = -1.2 \text{ kJ mol}^{-1}$). In the second pathway (b), CO is formed *via* reverse water gas shift reaction (RWGS) (endothermic by $\Delta H_{298} = 11.2 \text{ kJ mol}^{-1}$) which in turn is hydrogenated to H₂CO (exothermic by $\Delta H_{298} = 19.9 \text{ kJ mol}^{-1}$). The authors did not find any experimental evidence for the formation of formic acid or CO during the course of the reaction. However, in experiments with formic acid as substrate, the authors found that the molar yield of formaldehyde was lower than the corresponding consumption of formic acid, indicative of competing reactions. Hence, it is stated that route b is a more plausible pathway.

Nakata et al. described the electrocatalytic sequential reduction of CO_2 to first formic acid and then formaldehyde using a boron-doped diamond (BDD) electrode with a p-type surface and a Pt counter electrode under ambient conditions. This method overcomes the usual limitation of a narrow potential window and low electrochemical stability of other electrodes (Cu, Sn, Ag), achieving high Faradaic efficiency (74%) for the production of formaldehyde. Either methanol, aqueous NaCl, or seawater can be used as the electrolyte. [20] Although photoreduction of CO_2 shows great potential, at present only low conversion rates are achieved. The main key factors which limit the efficiency are the low solubility of CO_2 in water, reverse reaction, the reduction of water to hydrogen as competing reaction, and poor charge carrier separation efficiency [21].

Enzymatic systems have been scarcely explored for CO_2 conversion to formaldehyde. They involve several consecutive reductions catalyzed by two different dehydrogenases, FDH (formate dehydrogenase) and FADH (formaldehyde hydrogenase). One of the few successful examples was reported by Zhang et al. who entrapped formate dehydrogenase during the formation of titania nanoparticles (NPs) through bio-inspired titanification. After *in situ* surface functionalization of NPs with pre-polymerized dopa (oligodopa, dopa = 3,4-dihydroxy-L-phenyl-alanine), formaldehyde dehydrogenase is immobilized on the surface of these NPs through an amine-catechol adduct reaction. Formaldehyde yields of up to 81 % and initial specific activity (1.87 U mg⁻¹ of active enzyme) (enzyme unit (U) = 1 μ mol min⁻¹) were achieved by reducing the particle size down to 75 nm. After storing for 20 days at 4°C, this multi-enzyme system was able to retain up to 70 % of its initial activity [22].

Unfortunately, a catalytic system for the selective hydrogenation of CO_2 to formaldehyde with only molecular H_2 still remains very rare. There are, however, other approaches where formaldehyde is trapped in the form of acetals by reduction with metal hydrides, boranes, silanes or H_2 /alcohol mixtures. Soluble transition metal hydride complexes have emerged catalysts capable of the reduction of CO_2 . The work by Floriani et al. [23]. exemplified the stepwise reduction of CO_2 to formaldehyde and methanol using the Schwartz's reagent, $[Cp_2Zr(Cl)H]_n$. This study was followed by mechanistic investigations to elucidate the CO_2 reduction pathways using metal hydrides [24]. Experimental evidence for a dinuclear complex with a bridging diolate L_nM — OCH_2O — ML_n as intermediate has been initially presented by Berger et al. [25]. The authors applied successfully DOSY NMR spectroscopy to detect the extremely unstable diolate intermediate in the reaction of $[Cp_2Zr(Cl)H]$ with CO_2 (Figure 5a). A recent report by Cummins et al. describes the isolation and structural characterization of a tantalum methylene diolate complex. This compound could be the key to develop an efficient molecular hydrogenation catalyst if the $[H_2CO_2]^{2^-}$ ligand could be liberated by heterolytic splitting of hydrogen regenerating the tantalum hydride species (Figure 5b) [26].



Figure 5: Carbon dioxide reduction by metal hydrides. Detection and isolation of bridging methylene diolate complexes [ref 24, 25].

Significant progress has been made with homogeneous catalysts and boranes or silanes as reductants, where acetals (E-OCH₂-E, E = SiR₃, BR₂) are the direct product from the reaction. Sabo-Etienne et al. achieved the hydroborylation of CO₂ (1 bar) with pinacol borane (HBPin) in a reaction catalyzed by complex $[RuH_2(H_2)_2(PCy_3)_2]$ (Cy = cyclohexyl) at ambient conditions [27]. The formation of several boryl compounds from CO₂ and pinacol borane could be observed as intermediates on the pathway to formic acid and methanol.

One of the intermediates was identified as a C2-boron compound derived from formaldehyde formed *in situ* (Figure 6a). A slight modification of the phosphine ligand from cyclohexyl to cyclopentyl (= Cyp) gives the catalyst $[RuH_2(H_2)_2(PCyp_3)_2]$ and thereby enables the synthesis and isolation of formaldehyde. This reaction involves a reduction with borane in the presence of a sterically hindered aniline. This has the purpose of trapping $H_2C = O$ forming a formyl imine intermediate, which is then hydrolyzed to formaline or paraformaldehyde [28].



Figure 6: Reduction of CO₂ to acetals by boranes and silanes catalyzed by metal complexes.

Oestreich et al. have described the ruthenium-catalyzed reduction of CO_2 to bis(silyl)acetal or methyl silyl ether by adjusting the reaction temperature [29]. The groups of Berke [30], Parvez [31], and Rodriguez [32] applied the frustrated Lewis pair (FLP) concept to the selective hydrosilylation of CO_2 , employing rhenium, scandium, and nickel complexes, respectively, in combination with a Lewis acid (Figure 6b).

Khan et al. described the use of K[Ru(EDTA-H)Cl] (EDTA = ethylenediamine tetraacetic acid disodium salt) for the homogeneous catalytic reduction of carbon dioxide by hydrogen to give formic acid and formaldehyde as the initial reaction products, which they decompose to give CO and H_2O . The decomposition of formaldehyde was faster than its formation, thus imposing an important obstacle for the practical application of this catalytic system to the production of formaldehyde [33]. The ruthenium complex [Ru(triphos)(tmm)] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, tmm = trimethylenemethane) was employed successfully by Klankermayer for the first documented reduction of CO₂ to formaldehyde using H_2 . The reaction achieved TON up to 200 and formaldehyde was trapped in form of dialkylmethylene ethers, which were formed in a tandem reaction in the presence of alcohols (Figure 7) [34].



Figure 7: Hydrogenation of CO₂ to acetals in the presence of alcohols catalyzed by [Ru(triphos)(tmm)].

3 Aqueous formaldehyde as hydrogen and energy carrier

3.1 Base promoted dehydrogenation

Since the Cannizzaro reaction was discovered in 1853 [35], the release of very small quantities of hydrogen was noticed from aqueous solutions of formaldehyde and NaOH. In the past decades, this hydrogen evolution re-

action has become of great concern because it can cause the detonation of storage solution from nuclear waste, particularly mixtures containing ethylenediaminetetraacetic acid (EDTA) in highly basic media. Formaldehyde is one of the products formed in the photolysis, radioIysis, and thermal degradation of EDTA and therefore could be an important intermediate in the release of H_2 during its storage. In order to control this process, a fundamental understanding of the reaction responsible for the formation of hydrogen was carried out independently by Sauer, Ashby, and Kapoor et al. [36]. An initial explanation of hydrogen evolution is shown in the proposed mechanism in Figure 8 [36a]



Figure 8: Reactivity of formaldehyde in aqueous basic solutions.

When formaldehyde reacts with an excess of base, it generates a dianionic Cannizzaro acetal, which serve as hydride donor to reduce another molecule of formaldehyde to form methoxide (CH_3O^-) and formate (HCO_2^-) (Cannizzaro disproportionation pathway, Figure 8). It was initially calculated that the same intermediate could react with water to form H_2 and a second molecule of formate (Methanediol dehydrogenation pathway, Figure 8). The authors found experimentally that high concentrations of base (16 M) and low concentrations of formaldehyde (1.5 mM) give quantitative formation of H_2 (98 % yield) at 60°C. No methanol was observed. The reaction is found to be first order in substrate, which implies that only one molecule of formaldehyde participates in the rate-determining step. A primary isotope effect was observed in experiments with deuterated formaldehyde (D₂CO) indicating that the cleavage of the C-H bond likely determines the rate of the reaction.

3.2 Metal catalyzed dehydrogenation

3.2.1 Heterogeneous catalytic processes

Several reports have shown that nanometallic catalysts, especially Cu, Ag, Au, Pd, Pt, and Zn can significantly accelerate the rate of hydrogen production from formaldehyde/water mixtures. Most of them are able to operate under thermal, electrochemical, or photochemical conditions. However, metal nanoparticles suffer from the intrinsic problem to agglomerate into larger particles over time, which greatly decreases the amount of active sites and consequently reduces the catalytic performance. Therefore, more recent investigations mainly focus on the prevention of this agglomeration by immobilizing the nanoparticles on different supports. In some cases, a synergetic interaction between the metal and support was observed and hence the type of the support and the dispersity of the metal nanoparticles play an important role in the catalytic performance of the catalysts.

3.2.1.1 Cu catalysts

In an early example, Bi et al. achieved the production of pure hydrogen with no detectable content of CO from aqueous formaldehyde solutions in a reaction catalyzed by various nano-sized metal particles (Pt, Au, Ni, and Cu) at room temperature and atmospheric pressure. In particular, a nano-Cu catalyst exhibited a high activity toward formate and H₂ formation at 60°C under basic conditions (140 mL min⁻¹ g⁻¹ catalyst). In the absence of base, hydrogen could not be detected. Moreover, at higher concentrations of base (NaOH) and formaldehyde, the Cannizzaro reaction occurred, which resulted in the retardation of hydrogen generation [37]. Preti et al. reported that the aerobic oxidation of alkaline H₂CO to formate catalyzed by CuO microparticles was selective, quantitative, and accompanied by the generation of fuel cell grade hydrogen (8 mL min⁻¹ g⁻¹ catalyst) [38]. Using MgO as a sacrificial agent, Cu₂O microcrystals can generate hydrogen from formaldehyde at room temperature. The authors explored the formation of paramagnetic oxygen deficient Cu(I) oxide and hydroxyl

radicals as principal reagents for the formaldehyde degradation [39]. The anodic oxidation in alkaline media of H₂CO can be also promoted by Cu metal or Cu-based amorphous alloys (CuTi, CuZr) as electrocatalysts, especially when treated with HF. High current densities (*ca.* 40 mA cm⁻²) were observed at a potential as low as 0.2V (NHE) [40]. CuO-Ag₂O nanowires, prepared on the surface of a ternary AgCuZn alloy, displayed an efficient electrocatalytic oxidation of formaldehyde to hydrogen and formate at room temperature [41]. The authors proposed a mechanism based on the electro-oxidation of a highly electroactive Cu₈O species as intermediate, which is produced in the reduction of CuO by formaldehyde. This complex catalyst provides a convenient gas sensor to monitor formaldehyde at the ppb level (52.40 mA ppm⁻¹ cm⁻² with a detection limit of ca 21 ppb) and generates much more hydrogen (70 mL min⁻¹ g⁻¹) than previous CuO microparticles.

3.2.1.2 Ag catalysts

Lu et al. demonstrated that Ag nanocrystals could catalyze the quantitative conversion at room temperature of formaldehyde in alkaline aqueous solution into hydrogen and formate, and no CO could be detected. The reaction conditions were very mild and there was a hydrogen production rate of up to 164 mL min⁻¹ g⁻¹ catalyst. The hydrogen can be detected immediately both in high and in low concentrations of H_2CO . Hence, Ag nanocrystals can be used to degrade formaldehyde on large scale and also to detect formaldehyde [42]. As mentioned above, nanoparticles as such inevitably tend to agglomerate to larger particles. To circumvent this defect, Ag nanocrystals were dispersed on the surface of γ -Al₂O₃ and indeed showed much higher catalytic activities (414 mL min⁻¹ g⁻¹ catalyst) and allowed the use of a lower amount of metal by weight [43]. In a recent report, Zou et al. introduced a heterogeneous catalyst based on Ag nanoparticles supported on MgO (AgNPs/MgO), which promoted the hydrogen evolution from aqueous formaldehyde with TOF up to 6000 h^{-1} . The TOF reported by the authors is an apparent TOF value considering the surface number of Ag atoms in the catalyst, calculated by the equation: TOF = $(n_{\text{H2}}/n_{\text{Ag}} \times t) \times (d/1.3)$, $(n_{\text{H2}} = \text{molar amount of evolved H}_2,$ n_{Ag} = molar amount of Ag catalyst, d = average diameter of Ag NPs and 1.3/d is the empirical surface atom dispersion) [44]. In this case, molecular oxygen was used as a promoter of the reaction. The reaction kinetics depend almost linearly on the oxygen partial pressure. As the temperature increases from 0 to 50°C, the steady-state hydrogen release rate increases from 100 to 120 mmol $h^{-1}g^{-1}$ catalyst (ca. 48 mL min⁻¹g⁻¹ catalyst). The authors proposed, based on EPR spin-trapping experiments and calculations, that a surface stabilized MgO/Ag-•OOH complex is probably a catalytically active species. Bimetallic nanoparticles may exhibit advantages over their monometallic counterparts, since it is possible to tailor the electronic and geometric structures of the particles to enhance their catalytic activity and selectivity. Bimetallic AgPd particles supported on Vulcan XC-72 (AgPd@C-72) – a conducting carbon support – exhibit high catalytic activity and good stability, and the hydrogen generation rates reached up to 237 mL min⁻¹ g⁻¹ catalyst [45].

3.2.1.3 Au Catalyst

An Au-SrTiO₃ composite was used by Jia et al. in the H₂ evolution from aqueous formaldehyde solutions without any additives at low temperature. The support plays an important role in the activation of formaldehyde, which is further transformed into formate as intermediate and later decomposed into hydrogen and carbon dioxide. However, the catalyst exhibits low efficiency for H₂ evolution (<1 μ mol min⁻¹ g⁻¹ catalyst) compared with Cu- and Ag-based catalysts [46]. Formaldehyde aqueous solutions (10 %v/v) were degraded to H₂ and CO₂ on supported titanium dioxide (TiO₂) nanotubes (NTs), which were loaded with Au or Pt nanoparticles (NPs). The TiO₂–NTs were produced by an oxidation process at an anode (anodization). Compared with Pt-loaded TiO₂-NTs, hydrogen production was superior with Au NPs. Using this catalyst, H₂ evolved steadily (0.06 μ mol h⁻¹ cm⁻²) after many hours of continuous UV-Vis irradiation without decrease in the photocatalytic activity. When Au NPs/TiO₂ NTs were used, hydrogen was also produced using only visible light irradiation (λ >400 or 450 nm) [47].

3.2.1.4 Pd catalysts

Hollow Pd nanotubes serve as a highly efficient and convenient catalyst for inhibiting the Cannizzaro reaction and facilitating hydrogen generation from alkaline formaldehyde solutions at room temperature. Pd nanotubes show significant higher catalytic activity (up to 170 mL min⁻¹ g⁻¹ catalyst) compared with Pd nanoparticles (40 mL min⁻¹ g⁻¹ catalyst). The kinetics of the reaction are highly dependent on the temperature, concentration of formaldehyde and base. The dehydrogenation process was successfully extended to higher aldehydes, such as acetaldehyde, propanal and benzaldehyde [48]. Ultra-thin TiO₂ nanosheets containing Pd quantum dots were used recently as catalyst (250 mL min⁻¹ g⁻¹ catalyst) for hydrogen generation from aqueous formaldehyde solutions at room temp, which is much more efficient than the previous Pd nanostructures [49]. Perovskite LaCoO₃ was found to be an efficient photocatalyst and displayed promising photocatalytic activity for H₂ production. The low efficiency to keep photogenerated electrons and holes separated and poor adsorptive performance could be improved with the p-type semiconductor PdO. Because of the resulting PdO/LaCoO₃ heterojunction, this photocatalysts shows an optimal activity in H₂ production from aqueous formaldehyde solution under irradiation with visible light which exceeds the one of LaCoO₃ alone (0.5 mL min⁻¹ g⁻¹ catalyst) by ten times [50].

3.2.1.5 Zinc catalysts

ZnO is well-known as a support and co-catalyst for methanol or formaldehyde steam reforming [51]. Fan et al. presented recently a Lewis acid-base combination as strategy to design a new heterogeneous catalysts for hydrogen formation (0.75 mL h⁻¹) from aqueous formaldehyde without additional additives [52]. The system is based on a core-shell structured ZnO@Bi(NO₃)₃ composite (BN-ZnO-X) with a strong electronic interaction at the interphase between both components. Several experiments were performed to correlate the catalytic activity of BN-ZnO to the interface between ZnO and Bi(NO₃)₃. First, the authors evaluated of the H₂ evolved as a function of the percentage of upshifted Zn 2p (Zn^{2+δ}), considered as a descriptor for the number of interfacial sites in different BN-ZnO samples. In a second experiment, annealing a BN-ZnO sample at 550°C, provoked the decomposition of Bi(NO₃)₃ into Bi₂O₃. The treated sample had the same Zn 2p signal with ZnO and the 3.3 eV upshift disappeared, suggesting that the interfacial electronic interaction between ZnO and Bi(NO₃)₃ is destroyed. Destroying the interfacial electronic interaction leads to a fast deactivation while increasing interfacial sites proportionally enhances the activity, indicating that they are in fact the active sites. DFT calculations confirmed that the catalyst composites greatly lower the activation barrier for H₂ formation from two adsorbed H atoms and thus promote the H₂ production (Figure 9).



Figure 9: H_2 evolution from aqueous formaldehyde catalyzed by ZnO@Bi(NO₃)₃. Reproduced with permission of Ref. 49. Copyright 2017 ACS.

The activities and efficiency of the heterogeneous catalysts developed so far for formaldehyde reforming are shown in Table 2. The highest catalytic activities up to date are achieved by Ag nanocrystals dispersed on the surface of γ -Al₂O₃ (ref 43). Based on the amount of generated hydrogen (1230 mL H₂ g⁻¹), this system has theoretically a potential energy density of up to 13 MJ/Kg (3,700 Wh/Kg), assuming that the produced H₂ is completely combusted of with O₂ ($\Delta H = 242$ kJ mol⁻¹) which leads potentially to a power density of 369 W/Kg. Compared to conventional Li-ion batteries (energy density 100 to 250 Wh/kg; power density 300 to 1500 W/kg), energy storage devices based on formalin may have a considerably higher energy density and acceptable power density values.

Table 2: Heterogeneous	catalysts for the f	formaldehyde/water	dehydrogenation reaction.
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Entry	Catalyst	Additives	Conditions	Average rate of H_2 production (mL min ⁻¹ g ⁻¹) ^a	Products	Ref.
1	Nano-Cu	NaOH	60°C	140	HCO ₂ Na	37
2	CuO microparticles	NaOH	25°C	8	HCO ₂ Na	38
3	Cu ₂ O microcrystals	MgO	hu	<2	$Mg(HCO_2)_2$	39
4	CuO-Ag ₂ O nanowires	КОН	electrocatalytic	70	HCO ₂ K	41

5	Ag	NaOH	25°C	164	HCO ₂ Na	42
6	Ag nanocrys- tals/ γ -Al ₂ O ₃	NaOH	25°C	414	HCO ₂ Na	43
7	Ag NPs/MgO	O ₂	50°C	48	HC(OMe) ₃ (from HCO ₂ H and MeOH), MgCO ₃	44
8	AgPd@C-72	NaOH	25°C	237	HCO ₂ Na	45
9	Au-SrTiO ₃	-	35°C	< 0.02	CO ₂	46
10	Pd NTs	NaOH	25°C	170	HCO ₂ Na	48
11	Pd NPs	NaOH	25°C	40	HCO_2Na	48
12	Pd/TiO ₂	NaOH	25°C	250	HCO ₂ Na	49
13	Pd/LaCoO ₃	-	hυ	0.5	CO ₂	50

^a Activities are given in mL per minute and gram of catalyst.

At present, the catalytic activities of heterogeneous catalyst do not compare favorably with those achieved with homogeneous systems. A strong limitation of the heterogeneous systems is the fact that most of them are only capable to liberate one equivalent of H_2 rather than two from a H_2CO/H_2O mixture because formic acid or formate salt, respectively, remains unconverted after the first dehydrogenation step in the reaction mixture (Table 2). At present, those heterogeneous systems are unsuitable for a complete formaldehyde reforming and lower the theoretically accessible hydrogen capacity of formaldehyde to the one of formic acid. Moreover, the mechanism of a catalytic reaction promoted by a heterogeneous catalyst is in general more difficult to investigate. Especially under this aspect, the application of a homogeneous catalytic system has its advantages because the core structure of a molecular complex as catalyst can be more easily modified such that electronic and steric factors, which are important for the catalytic activity become evident. Even if in the end a heterogeneous catalyst is the better choice for large-scale conversions given economic and technical constraints.

3.2.2 Homogeneous catalysts and mechanistic insights

Very recently, the first clean low temperature dehydrogenations of aqueous methanol to H_2 and CO_2 were reported, which were catalyzed by well-defined group 8 or 9 metal complexes (1–4) (Figure 10) [53]. In these reactions, water serves as an oxygen transfer reagent and in any case no trace of CO contamination was observed. The three dehydrogenation steps, which allow complete methanol reforming are shown in Figure 10 and each requires a catalyst. The first H_2 release originates from the dehydrogenation of methanol to formaldehyde. The subsequent reaction with water gives methandiol from which a second equivalent of H_2 is liberated upon dehydrogenation to formic acid. Final dehydrogenation of HCOOH to CO_2 releases the third H_2 molecule.



Figure 10: (A) Sequence of catalyzed dehydrogenation steps of methanol/water system. (B) Molecular catalyst for the dehydrogenation of methanol/water (1–4) or formaldehyde/water mixtures **3–6**.

Although in previous work on methanol reforming, formaldehyde hydrate or its oligomers were not observed, it has been repeatedly proposed as logical intermediate in the dehydrogention of methanol. A priori, it seems trivial that any of the previously studied catalysts must be considered for the reforming of formaldehyde. However, the dehydrogenation of aqueous formaldehyde and paraformaldehyde to H₂ and CO₂ catalyzed by a molecular catalyst has been scarcely investigated [54, 55, 57, 58]. In fact, few reports have described the conversion of aldehyde/water mixtures to hydrogen and carboxylate derivatives. An early study from Maitlis et al. showed that a series of half-sandwich complexes of Rh, Ir, and Ru were able to catalyze the disproportionation of aliphatic aldehydes under neutral conditions to a mixture of alcohols and acids. Because the acids were obtained as main products, substantial amounts of H₂ must have been produced in the reaction. In particular, the water-soluble hydroxocomplex [Ru₂(C₆Me₆)₂(OH)₃Cl] gave a 5:1 ratio of acetic acid/ethanol in the disproportionation of aqueous acetaldehyde with TONs of up to 2,400 at 45°C [56].

In 2014, homogeneous formaldehyde reforming was reported for the first time by Prechtl et al. [57]. The airstable and easily accessible ruthenium catalyst $[(Ru(p-cymene))_2(\mu-Cl)_2Cl_2]$ (5) catalyzed the formation of H₂ from aqueous solutions at temperatures between 25°C and 95°C [54, 55, 57, 58]. The decomposition of formaldehyde (37 wt%) and paraformaldehyde proceeded preferably in the pH range of 5.5 to 7.0, with conversions up to 85 % within 60 minutes [57]. Note that the catalyst itself is active in over a rather broad pH range between 2.0 and 9.0. The best catalytic performance was observed at 95°C, where hydrogen was obtained with acceptable TONs (188) and turn over frequencies (TOFs) of up to 170 h^{-1} . This catalytic process tolerates oxygen and gives pure mixtures of CO₂ and H₂ without detectable traces of CO. Water is clearly involved in the reaction and labelling experiments with H₂¹⁸O indicate that water acts as the oxygen donor in the formation of the methanediol intermediate and is also the proton source to form H_2 and final product (CO₂). The authors were able to identify and isolate $[(Ru(p-cymene))_2(\mu-H)(\mu-HCO_2)(\mu-Cl)]^+$ as active species and hydroxocomplexes (i. e. $[(Ru(p-cymene))_2(\mu-OH)_3]^+)$ were detected as intermediates on course of the formation of the active species in this reaction [57]. In a diluted solution (5 wt%), the catalyst was able to reduce the content of formaldehyde to levels below 45 ppm. Quantitative conversion was achieved within 24 h giving a TON of up to ca. 1000 and initial TOFs of $>3000 h^{-1}$ [55]. More recently, Prechtl, Deska et al. merged the catalytic activity of this ruthenium complex with the alcohol oxidase Candida Boidinii. This system allowed the sequential conversion of aqueous methanol to formaldehyde (catalyzed by the enzyme) and then the dehydrogenation of methanediol (catalyzed by the Ru complex) to H₂ yielding 15.3 μ mol mL⁻¹ and CO₂ at room temperature (Figure 11). [58] In addition,



the authors demonstrated that aqueous formaldehyde undergoes dismutation in presence of an organometallic formaldehyde dismutase mimic [59], and is suitable for redox self-sufficient reductive N-methylation [60].

Figure 11: Chemoenzymatic methanol reforming [58] in presence of the formaldehyde dehydrogenase mimic [(Ru(p-cymene))₂(μ -H)(μ -HCO₂)(μ -Cl)]⁺ [54, 55, 57, 58].

Fukuzumi et al. showed that the water-soluble aqua complex $[Ir^{III}(Cp^*)(4-(1H-pyrazol-1-yl-kN^2)benzoic acid-kC^3)(H_2O)]_2SO_4$ is able to produce H₂ and CO₂ in a 2:1 ratio from paraformaldehyde solutions (Figure 10). Although with very low TONs (<24), the reaction proceeded at room temperature and the rate of H₂ production increased with increasing pH [61]. The optimal H₂ production is obtained at pH 11, at which the hydroxocomplex **6** is the actual catalyst that reacts with paraformaldehyde to form formate and an iridium hydride complex. The formation of metal hydride species led to the proposition of a classical mechanism in which the substrate is activated and converted at the metal center (Figure 12). The reaction of formalin to CO₂/H₂ mixtures was also catalyzed using a similar Ir complex **4** (Figure 10). In this system, the cooperative α, α' -bipyridonate ligand participates as a proton acceptor in the activation step and the intramolecular reaction of hydride on the metal with protic hydrogen on the resulting α -hydroxypyridine-based ligand leads to the formation of molecular hydrogen (Figure 13) [62]. The system operates using catalytic amounts of base and achieves a TON of 178. The protonated aqua complexes showed very low catalytic activities.



Figure 12: Proposed pathway for dehydrogenations of formaldehyde/water mixtures catalyzed by iridium complex **6** (classical metal-centered mechanism).



Figure 13: Proposed pathway for dehydrogenations of formaldehyde/water mixtures catalyzed by iridium complex **4** (metal ligand cooperative mechanism).

The catalyst $[K(dme)_2][Ru(H)(trop2dad)]$ (3) $(trop_2dad = 1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-bis(5H-diben$ diazabuta-1,3-diene) developed by Grützmacher, Trincado et al. was able to catalyze efficiently the dehydrogenation of both, methanol [53]f and formalin [63]. The ruthenium species was also able to promote the dehydrogenation of formic acid with one of the highest TOFs reported to date for a process without any additives $(24,000 h^{-1})$. In Yamaguchi's and Grützmacher's approaches, the metal center is coordinated by a cooperative ligand. The complex 3 contains a redox and chemically non-innocent diolefin diazadiene ligand which participates actively in the dehydrogenation reactions of all C1-susbtrates. Diazadiene ligands [64] behave as chemically "non-innocent" ligands, accepting up to 2 equivalents of H₂ forming the fully hydrogenated species 3(H4) (Figure 14), which is also an active catalyst. This particular metal-ligand cooperativity is illustrated in simplified form by the equilibria between the structures 3N and 3N' (redox non-innocence; either as resonance forms or distinctive electronic states) and the fully hydrogenated complex 3(H4) (chemical non-innocence) (Figure 14). The tetradentate, robust trop₂dad ligand contains no phosphanyl but two olefinic binding sites which can also behave as non-innocent ligands. Their electronic flexibility allows for the stabilization of low-valent metal centers by metal-to-ligand back donation of electron density. The most remarkable results were achieved in the reforming of aqueous solutions of paraformaldehyde ($c_0 = 0.47 \text{ M}$) at low reaction temperature (60°C) achieving high conversion to carbonate and H_2 (up to 90%). The catalyst was recycled up to six times without significant loss of efficiency (TOF₅₀ > 20,000 h⁻¹). The various reaction pathways A and B shown in Figure 2 for the conversion of formalin were taken into account. One of those involves the production of carbon monoxide as an intermediate from the reaction $H_2CO \rightarrow CO + H_2$, a molecule that frequently "poisons" the metal catalysts. Remarkably, the ruthenium catalyst **3** is able to operate in a carbon monoxide atmosphere, although with much lower activity. This observation may be taken as indication that 3 acts as a catalytic "chameleon" and actually catalyzes the conversion of aqueous formaldehyde along different pathways (decarbonylation/WGS and hydration/dehydrogenation and Cannizzaro/methanol dehydrogenation; see Figure 2).

Because the formaldehyde hydration/methandiol dehydrogenation path is the most likely one, this reaction sequence was calculated with DFT methods. Since **3** rapidly converts to the neutral species **3N**, the latter complex was set as starting point of the catalytic cycle. The theoretical data suggest that the first step is the exergonic formation of the methanediol complex **A**, followed by proton transfer from the alcohol to one of the iminic nitrogen atoms in the ligand backbone (Figure 15). The initially formed complex **B'** rearranges to a hydrogen-bond stabilized complex **B**, which by β -hydride elimination subsequently converts to the Ru hydride complex **C'**. The complex **C'** rearranges further to give intermediate **C** in which the Ru-H hydride unit is interacting with the proton of the hydroxyl group of the coordinated formic acid moiety. In **C** the formation of H₂ is pre-organized and indeed only a small activation barrier (3.2 kcal mol⁻¹) separates **C** from the H₂ complex **D** which loses H₂ in an essentially barrier-less reaction to produce formate complex **F** which contains loosely bound CO₂. The calculations imply that the transformation **E** \rightarrow **F'** may be the rate determining step (**TS-4**: E_a = 17.1 kcal mol⁻¹). Loss of CO₂ gives the amino hydride complex **F** which rearranges via the activated complex **TS-5** at E_a = 15.3 kcal mol⁻¹ to the diazadien hydrogen complex **G**, which readily loses H₂ to complete the cat-

alytic cycle. It is also possible that under the experimental conditions **3N** is hydrogenated to **3(H4)** [63] which was likewise considered as catalyst for formaldehyde dehydrogenation.



Figure 14: Redox- and chemically active metal-diazadiene-olefin system.



Figure 15: Proposed mechanism for H₂ production from formaline catalyzed by complex 3N.

Indeed, the DFT data show a comparable minimum energy reaction pathway (MERP) and indicate that it is quite likely that both, **3N** and **3(H4)**, are involved and contribute to the observed catalytic activity. In both pathways, hydride migration from the substrate to the metal are key steps in the catalytic cycle to produce H_2 , and in both mechanisms metal-ligand cooperativity plays an important role.

4 Future perspectives

In the last decade, major progress has been made with respect to the conversion of CO_2 to formaldehyde. This makes the use of formaldehyde as liquid organic hydrogen carrier (LOHC) promising, indeed. For the first time a promising direct formaldehyde synthesis from CO₂, respectively syngas, via RWGS (reverse water gas shift) has been realized and the synthesis of dialkoxyl methanes via catalytic reduction of CO_2 has been demonstrated. The electrocatalytic conversion of CO_2 to formaldehyde in sea water as electrolyte is another highly interesting concept. Such approaches have the potential to substitute old fashioned high-temperature oxidative production of formaldehyde from methanol. These novel pathways for conversion and generation of a C_1 -chemical feedstock open up new opportunities toward more cost and energy saving production chains with formaldehyde as a platform molecule. Carbon dioxide for the *in situ* generation of CO may turn the annual multi-megaton market of formaldehyde into a more sustainable chemical platform by eliminating fossil sources from the production chain. The stabilization of formaldehyde by water and alcohols will be the key to improve these syntheses due to the favorable thermodynamics in solution and the reactivity of all solute species and intermediates: Methanediol and (di)alkoxymethane, in the case of formaldehyde, or carbonic acid and carbonates in the case of CO_2 as hydrated species in solution. Moreover, the conversion of formaldehyde into bis(silyl) or bis(boryl) methylene acetals may generate further interest to use these compounds for inorganic materials with formaldehyde as cross-linker [54]. Notably, sequential enzyme catalysis applying FDH and FADH in presence of NADH as co-factor leads also to the selective formation of formaline from CO₂. This eventually brings biotechnological processes into the play for the production of formaldehyde under very mild conditions to complement the industrial procedures which are already established in order to meet the high global demands of formaldehyde.

New applications of formaldehyde in the energy sector for renewable combustion fuels (i. e. bio-derived methylene ethers) or as LOHCs for hydrogen fuel cell technologies require an enhanced global production of formaldehyde based on renewable resources and waste rather than fossil sources. 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.

Secondary batteries represent one of the biggest and most developed group of energy storage technologies. However, the research in this area is approaching the maximum energy density limits, under safe operational conditions. Electrochemical devices based on a direct or indirect formalin fuel cell could being considered as possible solutions to the limitations of conventional batteries. In terms of weight and volume, an electrochemical device with a liquid organic fuel (LOC) can offer a higher energy content. For example, the system based on formalin and a heterogeneous catalyst (Ag/Al₂O₃) [40] could store a ten-fold higher energy (3.39 KWh/Kg) than a Li-ion battery and gives a comparable power density (369 W/Kg) under the assumption that a complete oxidation occurs. On the other hand, the most efficient homogeneous system based on a ruthenium catalyst could also deliver an acceptable power density of 230.5 W/Kg. Further considerations (cost, safety, and convenience) will be also critical for the successful introduction of formaldehyde-fuel cells as replacements for batteries. The high prices for noble metal catalyst used up to now will not allow to make such a fuel cell competitive with established energy storage devices. Future research must concentrate on the development of system which contain earth-abundant and cheap metals from the fourth period of the periodic table. Recent work shows that this goal may be achieved as there are iron or manganese complexes which can be applied for the dehydrogenation of LOCs although the activities and stability are still rather low [65, 66].

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