# REVIEW

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# Advances in CO<sub>2</sub> circulation hydrogen carriers and catalytic processes



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# Abstract

Hydrogen serves as a renewable, clean energy carrier, and the critical development of technologies for safer and simpler storage and transportation is imperative for addressing global warming. There is also a growing demand for efforts to capture and utilize CO<sub>2</sub> to tackle similar issues. Consequently, considerable attention has been drawn to carriers that chemically store hydrogen. Hydrogen can be stored and released through hydrogenation and dehydrogenation. Notably, the storage and release of hydrogen via CO<sub>2</sub> hydrogen economy, rendering it an appealing option as a CO<sub>2</sub> circulation hydrogen carrier (CCHC). To leverage CCHC for various applications, a catalytic process enabling the reversible storage and release of hydrogen is essential. This review focuses on CCHC candidates, such as methanol (MeOH), dimethyl ether (DME), and formic acid (FA), summarizing recent catalytic approaches for hydrogen gen production through pivotal dehydrogenation processes within the CCHC cycle.

**Keywords** Hydrogen, Carbon dioxide, Carrier, Hydrogenations, Dehydrogenations, Circulation, Methanol, Dimethyl ether, Formic acid

# Introduction

In recent years, the spotlight has shifted toward the impacts of global warming, sparking interest in energy supply. Anomalous climate patterns stem from rising greenhouse gas concentrations, making emission reduction a pivotal solution to combat global warming (Chang et al., 2011). Hydrogen energy stands out as an effective method for this endeavor. Yet, hydrogen, existing as a gas under standard conditions, necessitates novel technologies for its storage, transportation, and utilization. Its low-density mandates either liquefaction at incredibly

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low temperatures or compression at high pressures for storage and transit. Safety concerns surrounding hydrogen highlight the urgent need for the safety of hydrogen technologies to address these challenges. The practical utilization of hydrogen fuel remains unattainable until the development of these technologies (Behroozsarand et al., 2010).

Hydrogen is highly abundant in various natural sources such as seawater, rain, river water, and biomass. Industrially, hydrogen can be extracted from water, fossil-derived sources, and hydrogen sulfide. The production of hydrogen from these sources typically falls into four categories: electrical, thermal, biochemical, and photonic (Agency, 2023; Dincer, 2012).

Currently, several industrial methods produce hydrogen through thermal processes, but they pose problems due to the substantial emissions of greenhouse gases, primarily  $CO_2$ , which contribute significantly to global warming. For instance, over 95% of the roughly 70 million tons of H<sub>2</sub> produced annually come from petrochemical fuels (75% natural gas and 23% coal) using



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steam methane reforming (SMR) (Hurtubia & Sauma, 2021; Pade & Guimaraes, 2007). Although an efficient process, SMR emits high concentrations of  $CO_2$ , leading to the classification of this hydrogen as "gray hydrogen", which is considered to be carbon neutral. Hydrogen generated incidentally during other chemical processes is referred to as "white hydrogen" (Aimikhe & Eyankware, 2023; Hermesmann & Müller, 2022). Conversely, advancements in technology for capturing and storing the high-concentration  $CO_2$  generated during hydrogen production have led to the emergence of "blue hydrogen" (Monkman & MacDonald, 2017). Projects implementing SMR while capturing and storing  $CO_2$  have been underway in Canada and the United States since mid-2017.

A small fraction, approximately 4%, of hydrogen production methods involve water electrolysis, a method increasingly utilized in various locations (Kirchofer et al., 2012). When hydrogen is produced via electrolysis using electricity sourced from renewable energy, it is termed "green hydrogen" (Hren et al., 2023). The efficiency of hydrogen production through electrolysis exceeds 80% (higher heating value HHV). Primary methods encompass alkaline electrolysis (AEL), proton exchange membrane (PEM) based electrolysis, and electrolysis in solid oxide electrolyzer cells (SOECs). Notably, AEL and PEM systems are commercially available and widely adopted, whereas SOEC is currently in the developmental phase, showing promise for co-electrolysis applications (such as direct synthesis, gas production, and Fischer-Tropsch synthesis), thus presenting an attractive option for  $CO_2$ conversion (Kirchofer et al., 2012). Additionally, ongoing developments focus on reusing the CO<sub>2</sub> generated from blue hydrogen production processes and the CO<sub>2</sub> captured via direct air capture (DAC), with increasing research on CO<sub>2</sub> as a renewable carbon resource (Dimitriou et al., 2015; Dorner et al., 2010; Saeidi et al., 2014; Sakakura et al., 2007). Methods for CO<sub>2</sub> conversion encompass thermocatalytic (TC), (Galadima & Muraza, 2019) electrochemical (EC), (Lin et al., 2020) photochemical (PC), (Kuramochi et al., 2018), and biological (Bio) (Barin et al., 2018) processes. These technologies facilitate the transformation of CO<sub>2</sub> into methane, methanol (MeOH), dimethyl ether (DME), formic acid (FA), alkanes (such as ethane), and alkenes (such as ethylene) using carbon monoxide (CO) as an intermediary substance. This review centers on exploring the potential applications of such liquid organic hydrogen carriers (LOHCs) (Bourane et al., 2016; Catizzone et al., 2021; Chatterjee et al., 2021; Crabtree, 2017; Eppinger & Huang, 2017; Guo et al., 2021; Hren et al., 2023; Kawanami et al., 2017; Li & Kawanami, 2023; Niermann et al., 2019; Preuster & Albert, 2018; Preuster et al., 2017; Sang et al., 2023; Teichmann et al., 2011, 2012, 2016; Zhong et al., 2018a, b) sourced from  $CO_2$  as hydrogen carriers, specifically designated as  $CO_2$  circulation hydrogen carriers (CCHC), within the framework of carbon neutral hydrogen storage and release (CNHSR) systems (Fig. 1).

LOHCs are recognized for their cost-effectiveness, safety, and long-term stability, qualities that make them ideal for hydrogen storage and transportation under ambient conditions. These compounds are characterized by their ability to undergo reversible dehydrogenation and hydrogenation processes, and they possess a substantial hydrogen capacity, making them well-suited for use in CNHSRs. Key examples of LOHCs include benzene/ cyclohexane pairs (Biniwale et al., 2008; Saito and Okada, 2016) and various organic heterocycles with a particular focus on nitrogen-containing aromatic compounds, which have undergone extensive study (Crabtree, 2017; Stark et al., 2015). The potential applications of a range of LOHCs, such as N-ethylcarbazole, dibenzyltoluene, toluene, and 1,2-dihydro-1,2-azoline, are being actively explored. These applications encompass diverse areas such as energy storage in buildings (Adamtz et al., 2017), energy transportation (Preuster et al., 2017), vehicle fuel, and even innovative adaptations for cement plants.

In a CNHSR system employing CCHCs, there is no release of CO<sub>2</sub> into the environment during the storage, transport, and production of hydrogen. However, to materialize this system in practice, a technology for recovering the CO<sub>2</sub> produced post-hydrogen generation from organic hydrogen storage materials is necessary. CCHC requires a technology capable of selectively capturing and re-generating CO2 from exhaust gases produced during hydrogen production. The CO<sub>2</sub> recovery technologies used in post-combustion and pre-combustion methods in fossil fuel-based thermal power plant can be applied. For instance, in the case of post-combustion, the Cansolv® CO<sub>2</sub> Capture System by Shell (Campbell, 2014) or the KS-1 (or KS-21) & KM CDR Process by Mitsubishi Heavy Industries (Miyamoto et al., 2017) can be utilized. These systems absorb CO<sub>2</sub> gas using an aqueous organic amine solution and re-generate liquid  $CO_2$  with a 90% capture yield from 13.4% of the  $CO_2$  gas. In the pre-combustion method, for example, the Selexol process by UOP LLC recovers CO<sub>2</sub> using absorbents (dimethyl ether and propylene glycol), producing liq. CO<sub>2</sub> with a 90% capture yield from 42% of  $CO_2$  (Bui et al. 2018; Hanifa et al., 2023; Osman et al., 2021; Peu et al., 2023). The capture costs for  $CO_2$  are approximately \$45/ton for post-combustion and \$53/ton for pre-combustion, which are relatively similar. In contrast, the  $CO_2$  capture cost by Direct Air Capture is estimated to be between \$500 and \$700 per ton of  $CO_2$ . Therefore, in the CCHC process, it is preferable to select a method with a CO<sub>2</sub> capture yield as close to 100% as possible.

Hence, reversible dehydrogenation/hydrogenation at mild temperatures is desirable. Hydrogenation reactions are typically exothermic and thermodynamically favorable, whereas dehydrogenation reactions are endothermic and necessitate high temperatures. Therefore, the development of efficient catalysts for dehydrogenation holds crucial importance. This review delves into the potential of MeOH and DME, derivatives of MeOH, and FA, as CCHCs, at room temperature and atmospheric pressure.

# Methanol

# Production of methanol from CO<sub>2</sub>

Methanol (MeOH) serves as an important raw material that is widely used in various applications, including as a fuel, a chemical feedstock, and as a non-corrosive, easy-to-handling solvent for chemical reactions. Therefore, there has been and is an active pursuit of the direct synthesis of MeOH via CO<sub>2</sub> hydrogenation (Alvarez et al., 2017; Li & Chen, 2019; Rodriguez et al., 2015). In addition, MeOH acts as a reactive intermediate in other processes, such as its conversion to gasoline (methanol to gasoline process; MTG) (Bjorgen et al., 2008; Olsbye et al., 2012) or to olefins (MeOH to olefines; MTO), (Plessow & Studt, 2017; Tian et al., 2015; Van Speybroeck et al., 2014), yielding hydrocarbons and olefins. Consequently, the conversion of CO<sub>2</sub> to MeOH offers the opportunity to significantly reduce CO<sub>2</sub>. The direct hydrogenation of CO<sub>2</sub> to MeOH is a simple and favorable process (Eq. 1). (Pérez-Fortes et al., 2016) However, as shown in Eq. 1, both  $\Delta H$  and  $\Delta S$  are negative, limiting the conversion of CO<sub>2</sub> to MeOH as the reaction temperature increases. Alongside CO, numerous byproducts such as hydrocarbons, FA and ethanol can be formed. (Bulushev & Ross, 2018; Chen et al., 2015) Thus, there is



\*CCHC: CO<sub>2</sub> Circulation Hydrogen Carriers

Fig. 1 Carbon dioxide circulation hydrogen carriers (CCHCs) of liquid organic hydrogen carriers (LOHCs)

a pressing need to develop catalysts with a high selectivity for MeOH (Saeidi et al., 2021).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
  $\Delta H = -49.5 \text{ kJ/mol}$ 
(1)

In heterogeneous catalysis, significant attention has focused on metal-based catalysts, particularly Cu-based ones. (Saeidi et al., 2021) Other catalysts, including Pd or bimetallic systems, have also been utilized for CO<sub>2</sub> hydrogenation to MeOH. In homogeneous catalysis, noble-metal-based (such as Ru or Ir) complex catalysts demonstrate high activity in producing MeOH from CO<sub>2</sub>. (Kothandaraman et al., 2016; Sordakis et al., 2016; Wesselbaum et al., 2015) Additionally, Co, Mn, and Fe complexes among non-noble metals have been reported to catalyze the hydrogenation of CO<sub>2</sub> to MeOH. (Schneidewind et al., 2017) Homogeneous catalysts play an important and crucial role in deciphering new routes to get MeOH from CO<sub>2</sub>. Milstein reported hydrogenation of CO<sub>2</sub> and CO to methanol using dearomatized PNN Rupincer complexes from pyridine- and bipyridine-based tridentate ligands (Balaraman et al., 2011). In the same year, Huff and Sanford et al. reported methanol synthesis in the presence of homogeneous Ru catalysts (Ru-1 and Ru-2) and Lewis acid (Sc(OTf)<sub>3</sub>, OTf=1,1,1-trifluoromethane sulfonate) at low temperature. (Huff & Sanford, 2011) To achieve methanol production from  $CO_2$ , they introduced three different catalysts for cascade reactions: (a) hydrogenation of  $CO_2$  with **Ru-1**, (b) esterification to generate a formate ester with  $Sc(OTf)_3$ , and (c) hydrogenation of the ester to release methanol with Ru-2 (Fig. 2). These include Hu's first homogeneous catalysts for hydrogenation of CO<sub>2</sub> derivatives (Hu et al., 2014). The Huff and Sanford's alcohol and amine-assisted pathways, and several other homogeneous systems that perform well at 100-140 °C. Same catalysts show low turnover numbers at 50-70 °C below 100 °C. (Huff & Sanford, 2011; Rezayee et al., 2015).

Then in 2012, Wesselbaum et al. reported, with water as a medium, additive-free  $CO_2$ -to-methnaol reaction has been achieved using Ru-Triphos catalyst **Ru-4** (Triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane. (Wesselbaum et al., 2015) After these initial studies, extensive mechanistic investigations and DFT modeling helped understand hydrogenation catalytic routes and rationally tune molecular catalysts. Homogeneous catalysts have enabled integrated  $CO_2$  capture and use recently. Kothandaraman et al. have shown amineassisted systems that recycle  $CO_2$  from air into carbonneutral methanol. (Kothandaraman et al., 2016) The same group recently created the first hydroxide-based integrated system. (Sen et al., 2020) Homogeneous catalysis has pioneered green and energy-efficient transformations



Fig. 2 Cascade reaction for the methanol synthesis and the Ru homogeneous catalysts and Lewis acid (Reprinted with permission from Huff, C.A. et al. Copyright 2011, American Chemical Society)

like  $CO_2$  and CO to methanol and will continue to help realize sustainable, green, carbon-neutral processes.

As a route to produce MeOH from  $CO_2$ , there is also generation by the disproportionation of FA. Initially, FA is produced from  $CO_2$  and  $H_2$ , and then MeOH is generated from the produced FA by disproportionation (reactions 2 and 3). However, the competitive reaction 4 occurs, so improving selectivity is a challenge.

$$CO_2 + H_2 \rightarrow HCOOH + H_2O$$
 (2)

$$3\text{HCOOH} \rightarrow \text{CH}_3\text{OH} + 2\text{CO}_2 + \text{H}_2\text{O}$$
(3)

$$HCOOH \rightarrow CO_2 + H_2$$
 (4)

In 2013, Miller et al. reported the generation of methanol by FA disproportionation in the presence of [Cp\*Ir(BPY)H<sub>2</sub>O](OTf)<sub>2</sub> Ir-1 in aqueous solution (BPY = 2, 2'-bipyridine,OTf=trifluoromethane sulfonate). (Miller et al., 2013) FA was converted to MeOH with 34 of TON and 1.4 h<sup>-1</sup> of TOF in a sealed vessel at 80 °C for 24 h, but the yield of MeOH did not exceed 1.9% because the dehydrogenation of formic acid was preferentially proceeding. In 2014, Savourey et al. reported formic acid disproportionation using a Ru catalyst. (Savourey et al., 2014) They were successful in achieving a methanol yield of 50.2% from formic acid by adding methylsulfonate to [Ru(COD)(methylallyl)<sub>2</sub>] (COD: cyclooctadienyl) and a supporting ligand (Triphos). DFT calculations have stated that disproportionation is promoted under high pressure. In 2015, Parkin et al. reported methanol disproportionation from formic acid using a non-precious metal molybdenum complex (CpMo(PMe<sub>3</sub>)<sub>2</sub>(CO)H) Mo-1 with a TOF of 54  $h^{-1}\!.$  (Neary & Parkin, 2015) In 2021, Alberico et al. also reported a methanol selectivity of 30% and TON 69 using a Mo complex under 6 MPa of hydrogen pressure. (Alberico et al., 2021) In 2016, Sordakis and Tsurusaki were successful in obtaining methanol with a selectivity of 97% from FA using catalysts such as [Cp\*Ir(4-DHBP)  $H_2O$ SO<sub>4</sub> Ir-2 (4-DHBP: 4,4'-dihydroxy-2,2'-bipyridyl)

under high-pressure conditions of 10 MPa of hydrogen pressure with sulfuric acid as an acid catalyst. (Sordakis et al., 2016, 2017; Tsurusaki et al., 2017) Furthermore, by raising the hydrogen pressure to 20 MPa, they confirmed the conversion of 99% of formic acid and the production of 1.22 mmol of methanol from 10 mmol of formic acid. Additionally, by using  $[Cp*Ir(5-DMBP)H_2O]SO_4$ (5-DMBP: 5,5'-dimethyl-2,2-bipyridine), they improved the TON to 1314 and methanol selectivity to 47.1%. In 2021, Fujita et al. reported a formic acid conversion rate of 100%, methanol yield of 28%, and TON 191 by performing formic acid disproportionation at 185 °C using a dinuclear Cp\*Ru complex generated from SnO and Ru complex **Ru-6**. (Fujita et al., 2021) (Fig. 3).

# Hydrogen production from methanol

MeOH has a high H-to-C ratio of 4:1 and can undergo conversion to  $H_2$  at a relatively low temperature of around 250 °C, according to Eq. 5. (Palo et al., 2007) This sets it apart from methane, given MeOH's ease of activation at lower temperatures.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H_{298K} = +49.7 \text{ kJ/mol}$$
(5)

Recently, the MeOH dehydrogenation reaction has garnered significant attention in research. However, several of the reported catalysts tend to generate only one hydrogen molecule from a single methanol molecule. The complexity arises in achieving high-purity H<sub>2</sub> due to the byproduct CO, impacting MeOH dehydrogenation suitability for use in fuel cells and similar applications. To tackle this issue, diverse catalysts have been developed. The most prevalent heterogeneous catalysts rely on Cu due to their high activity and selectivity. The Cu/ZnO catalyst employed in MeOH synthesis is also widely used in dehydrogenation reactions due to its operation at relatively low temperatures. However, this catalyst poses a high risk of spontaneous ignition (Lindstrom & Pettersson, 2001). Zn in Cu/ZnO is recognized for its role in preventing the sintering of Cu,

2+

SO₄<sup>2-</sup>



Fig. 3 Selected Ir, Ru, Mo homogeneous catalysts for methanol synthesis

thereby enhancing the catalyst's performance (Xu et al., 2017). Although the influence of ZnO on the active site's morphology has been suggested (Hadden et al., 1997; Ovesen et al., 1997), the complete understanding of the mechanism behind reaction promotion remains elusive (Rameshan et al., 2012).

In the case of a heterogeneous catalyst, Yao et al. (2006) and Zhou et al. (2016) used  $ZrO_2$  as a support to enhance the MeOH dehydrogenation reaction on the Cu catalyst. Other researchers explored MeOH dehydrogenation reactions using SiO<sub>2</sub>, barium oxides, and Al<sub>2</sub>O<sub>3</sub>, among others. Qing et al. studied catalyst deactivation after prolonged operation using Cu/SiO<sub>2</sub>, attributing it to Cu coking and SiO<sub>2</sub> degradation of SiO<sub>2</sub> during the reaction. Agrell et al. (2003), Jeong

et al. (2006) and Qing et al. (2019) compared the catalyst activity of Cu/ZnO with and without the addition of zirconia and alumina. In both studies, the Cu/ZnO/ $ZrO_2/Al_2O_3$  catalyst exhibited the highest MeOH conversion rate at the lowest tested CO concentration. This outcome is believed to stem from Zr promotion Cu dispersion and particle formation on the catalyst surface.

Numerous reports focused on MeOH dehydrogenation using heterogeneous Cu catalysts. However, precious metal catalysts such as Pd and Pt have been assessed to mitigate deactivation and achieve enhanced activity and stability. A majority of these catalysts are supported on silica or alumina and demonstrate notable activity. Nevertheless, unlike Cu-based catalysts, these variants function at elevated reaction temperatures, favoring the

Table 1 Selected list of catalysts for methanol dehydrogenation

Catalyst	Solvent	Additive	<b>Temp.</b> (°C)	Time (h)	TON	TOF $(h^{-1})$	Refs.
Ru-7	H <sub>2</sub> O	8 M KOH	72	552	350,000	200	(Nielsen et al., 2013)
Ru-8	Toluene	KOH <sup>(a)</sup>	100	720	29,000	40	(Hu et al., 2014)
Ru-9	Dioxane/H <sub>2</sub> O	8 M KOH	82	4.5	-	55	(van de Watering et al., 2016)
Ru-10/Ru-11	H <sub>2</sub> O	Triglyme	93.5	192	4200	21	(Monney et al., 2014)
Ru-12	H <sub>2</sub> O/THF	_	90	10	2500 <sup>(b)</sup>	24,000 <sup>(c)</sup>	(Rodriguez-Lugo et al., 2013)
lr-3	H <sub>2</sub> O	NaOH <sup>(d)</sup>	100	150	10,510	70	(Fujita et al., 2015)
Ir-4	H <sub>2</sub> O	0.5 M KOH 8 M KOH	94	16 60	1400 1900	326 <sup>(e)</sup> 31	(Prichatz et al., 2017)
Fe-2	H <sub>2</sub> O	8 M KOH	91	46	9834	644	(Alberico et al., 2013)
Mn-1	H <sub>2</sub> O	8 M KOH Trialvme	92	>720	>20,000	-	(Anderez-Fernandez et al., 2017)

(a) The reaction was conducted in autocleave made of glass

 $^{(b)}$  The TON value was obtained from the results of 1 g of MeOH, 10  $\mu mol$  of Ru-12, 80% of conversion after 10 h

<sup>(c)</sup> Initial TOF value using 0.01 mol% of **Ru-12** 

<sup>(d)</sup> The reaction was conducted in autocleave

 $^{\rm (e)}$  The TOF value was the initial TOF within 1 h

production of syngas from MeOH (Li et al., 2012; Palo et al., 2007), consequently increasing CO selectivity.

Homogeneous catalysts, as reported in 2013 by Nielsen et al., utilized a Ru-pincer complex (Ru-7) to dehydrogenate MeOH under mild conditions (Table 1). (Nielsen et al., 2013) The reaction achieved a turnover number (TON) of 350,000 within 23 days at a relatively low temperature (<100 °C), employing a MeOH–water mixture. CO<sub>2</sub> was captured as carbonate, with minimal byproducts such as CO or  $CH_4$  (<10 ppm). Hu et al. investigated the dehydrogenation of MeOH catalyzed by a Ru-PNN pincer complex (Ru-8) in the presence of KOH. (Hu et al., 2014) The catalyst effectively promoted dehydrogenation in a MeOH and water-toluene mixture, displaying exceptional durability and sustained reactivity even after MeOH re-addition. Eventually, it exhibited a TON of 29,000 after approximately 30 days. Similarly, Watering et al. (2016) reported a Ru complex with a salen ligand (Ru-9) using KOH for reactions in a 1,4-dioxane/H<sub>2</sub>O solution. The turnover frequency (TOF) for MeOH dehydrogenation was 55  $h^{-1}$ , with no detection of CO but observed production of H<sub>2</sub>, FA, and carbonates. Monney et al. introduced a dual-catalyst system composed of  $[Ru(H)_2(dppe)_2]$  (**Ru**-10) and a Ru-PNP pincer complex [Ru-MACHO-BH] (**Ru-11**), for MeOH dehydrogenation in the absence of a base. (Monney et al., 2014) While the Ru-10 catalyst exhibited the necessary catalytic activity for MeOH dehydrogenation, FA generation occurred under nonbasic conditions, diminishing its effectiveness. To address this, the author combined another catalyst (Ru-10) to develop a method for FA dehydrogenation. This approach sustained activity for 8 days, achieving H<sub>2</sub> production at a TON 4,200. Rodriguez-Lugo et al. reported a **Ru** complex [K(dme)<sub>2</sub>][Ru(H)(trop<sub>2</sub>mad)] (Ru-12), featuring a chelating bis(olefin) diazadiene ligand, which fully dehydrogenated MeOH with an approximately 85% conversion rate in the absence of a base (Rodriguez-Lugo et al., 2013).

Based on the Ir complex catalyst, Fujita et al. an efficient Cp\*Ir catalyst (**Ir-3**), which promotes dehydrogenation in MeOH/H<sub>2</sub>O (Fujita et al., 2015). Continuously adding MeOH using a syringe pump and investigating the robustness of the catalyst, they observed that it maintained its activity for 150 h, ultimately exhibiting a TON of 10,510. Prichatz et al. synthesized an Ir pincer complex (**Ir-4**) by transitioning the metal base from Ru to Ir (Prichatz et al., 2017). Under 0.5 M KOH in MeOH/H<sub>2</sub>O at 70 °C, the reaction achieved a TOF of 326 h<sup>-1</sup> and a maximum TON of 1,400. Increasing the base concentration to 8 M resulted in a longer reaction time despite a decrease in the initial reaction rate, yielding a TON of 1900 in 60 h.

While precious metal-based complex catalysts exhibit high activity, there has been a push to develop cost-effective non-precious metal-based ones. Alberico et al. conducted MeOH dehydrogenation using a Fe pincer complex (**Fe-2**) with a similar structure to Ir complex (Alberico et al., 2013). Under 8 M KOH in MeOH/H<sub>2</sub>O at 91 °C, the TON after 43 h was 6,270, with an initial TOF of 702 h<sup>-1</sup>. Reducing the amount of catalyst from 4.16 to 1 mmol resulted in a TON of 9,834 after 46 h, with a TOF of 644 h<sup>-1</sup>, confirming improved catalytic activity. However, the stability of the catalyst remained inferior to that of the Ru-pincer complex.

Anderez-Fernandez et al. also reported that a Mnbased complex catalyst (**Mn-1**) demonstrated MeOH dehydrogenation activity (Anderez-Fernandez et al., 2017). Building on prior research highlighting the efficiency of pincer ligands in MeOH dehydrogenation, the Mn-pincer complex underwent examination. Under conditions of 8 M KOH in MeOH/H<sub>2</sub>O at 92 °C, the TON was 54. Through optimization of reaction parameters and the addition of triglyme and 10 molar equivalents of PNP-*i*Pr ligand, the activity of the catalyst remained stable for at least one month, boasting a TON exceeding 20,000. This complex exhibited superior stability in comparison to the analogous Fe pincer complex.

# **Dimethyl ether**

Dimethyl ether (DME) stands out as a viable alternative clean fuel (Marchionna et al., 2008; Song, 2006). Its unique chemical characteristic lies in having solely CH and CO bonds without any C=C bonds. Furthermore, the combustion of DME does not yield any toxic byproducts. DME proves to be an economically feasible circular  $H_2$  carrier, holding significant potential as an alternative fuel (Catizzone et al., 2021). Notably, it serves as an intermediary in the production of dimethyl sulfate, methyl acetate, light olefins, and gasoline (Sun et al., 2014). However, while several natural sources can be tapped for synthetic DME, recent attention has veered toward its production from CO<sub>2</sub> (Catizzone et al., 2018). Specifically, the direct hydrogenation of CO<sub>2</sub> for DME production has garnered increasing interest. Utilizing renewable H<sub>2</sub> and CO<sub>2</sub> to generate DME could represent a sustainable route for a green energy provision (Fleisch et al., 2012). Hence, harnessing DME as a carbon source for fuel and chemical production becomes crucial in curbing  $CO_2$  emissions. Within this context, one must consider the following aspects of DME:

- (i) Hydrogen storage in DME.
- (ii) Hydrogen release from DME.

This section delves into the catalyst's role in the conversion process from  $H_2$  to DME and vice versa.

## **DME production**

DME is typically generated through either a two-step process or an indirect method. In the two-step method: (i) MeOH is initially produced from  $CO_2$  in one reaction chamber (Eq. 6), and (ii) the subsequent step involves the dehydration of MeOH into DME in a secondary reactor (Eq. 7) (Catizzone et al., 2021).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H^0_{298K} = -49.5 \text{ kJ/mol}$$
(6)

 $2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad \Delta H^0_{298K} = -23.4 \text{ kJ/mol}$ (7)

In addition to reactions (6) and (7), the reverse water– gas shift (RWGS), which is a significant competitive reaction, leads to the development of  $CO_2$ , thereby hindering the production of DME (Eq. (8)).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
  $\Delta H^0_{298K} = 41.2 \text{ kJ/mol}$ 
(8)

The overall production is limited by the decomposition of MeOH and/or DME, along with potential sidereaction pathways. The thermodynamic characteristics of DME synthesis closely align with those of MeOH synthesis when  $CO_2$  serves as the initial raw material; DME formation occurs sequentially through MeOH formation. To mitigate the thermodynamic constraints of  $CO_2$  conversion and elevate the reaction pressure, efficient conversion of MeOH to DME can be employed by continually removing MeOH from the product side of Eq. (7).

For DME production to become a reliable and costeffective method for  $CO_2$  hydrogenation (Chen et al., 2016), synthesizing MeOH and dehydrating DME need to occur in a single step (Eq. 9) (Shen et al., 2000). These reaction processes entail synthesizing MeOH and dehydrating DME simultaneously.

$$2\text{CO}_2 + 6\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \qquad \Delta H^0_{298\text{K}} = -122 \text{ kJ/mol}$$
(9)

The impact of temperature and pressure on the conversion of  $CO_2$  to DME differs between the one-step and two-step procedures. In the one-step process, these factors bear more significance due to MeOH consumption through the dehydration reaction (Eq. 9), particularly noticeable at low temperatures and high pressures (Chen et al., 2012). Even though the two-step process yields exceptionally clean DME without water-related issues, the one-pot method is considered a more cost-effective  $CO_2$  conversion technique. Developing a suitable catalytic system to support both MeOH production and MeOH dehydration is an ongoing issue in one-pot synthesis. Current research primarily concentrates on:

- i. Developing an efficient multi-functional catalyst capable of simultaneous MeOH synthesis and dehydration,
- ii. Enhancing catalyst performance for increased DME production,
- iii. Improving catalyst stability under specific reaction conditions, and
- iv. Enhancing CO<sub>2</sub> utilization efficiency.

DME and other greener fuels offer substantial economic benefits, especially considering the rising demand for their low-cost production.

## Catalytic activity for one-step synthesis of DME

The direct CO<sub>2</sub>-to-DME hydrogenation method requires catalysts capable of efficiently synthesizing and dehydrating MeOH while minimizing side reactions such as CO production and secondary product generation via the RWGS, akin to hydrocarbon production at high temperatures (Mondal & Yadav, 2019). Bifunctional and hybrid catalysts are distinguished by effectively combining mixed-oxide(s) and acid site activities for MeOH synthesis and dehydration, respectively. An effective catalyst, balancing active metals and acidic sites, is crucial for the one-step CO<sub>2</sub>-to-DME process, producing MeOH and dehydrating it into DME while minimizing CO formation via RWGS (Wang et al., 2011; Ye et al., 2019). These catalysts must exhibit high activity for CO<sub>2</sub> hydrogenation to MeOH at low temperatures and be water-resistant. Additionally, low acidity is essential to prevent extra dehydration reactions leading to other by-products. Zeolites appear suitable for these purposes due to their numerous acidic sites, water stability, and shape selectivity. To optimize the synergy between both functionalities and prevent their partial deactivation, controlling the balance and distance between the metal and acid sites is vital (Mota et al., 2021; Zecevic et al., 2015).

Copper (Cu) can independently activate  $CO_2$  as a catalyst. When combined with zinc oxide (ZnO), their catalytic activity often increases. ZnO serves multiple functions, primarily associated with metal dispersion or Cu–ZnO interfaces. Moreover, the creation of  $Cu^{\delta+}$  sites activate  $CO_2$  (Catizzone et al., 2021). Incorporating an additional component, such as  $Al_2O_3$ , into the basic Cu/ZnO composition results in a traditional ternary composition with enhanced thermal and chemical stability (Wang et al., 2011). Furthermore, the inclusion of ZrO<sub>2</sub>, instead of  $Al_2O_3$ , enhances catalyst stability during direct  $CO_2$ -to-DME hydrogenation due to Zr's superior water tolerance compared to alumina (Catizzone et al., 2018). In the preparation method, Cu/Zn molar ratio,

calcination, reduction temperature, and duration can significantly affect Cu particle size and dispersion. Solid acid catalysts for the metal-oxide phases encompass alumina, alumino-silicates, and molecular sieves. Due to its acidity and extensive surface area,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is often recommended for the atmospheric pressure MeOH-to-DME dehydration conversion. However, under high reaction pressure, water inhibits the activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Naik et al. reported a hybrid catalyst of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZSM-5 for MeOH synthesis through mechanical mixing (Naik et al., 2011). At 260 °C and 5 MPa in a fixed-bed reactor, ZSM-5 demonstrates superior activity to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is unsuitable as an acid catalyst for the one-pot CO<sub>2</sub>-to-DME process.

In this regard, zeolites appear to offer the greatest variability in terms of a greater number of acidic sites, water resistance, and shape-selectivity regarding the needed component, as above mentioned (Bonura et al., 2016; Busca, 2017; Gackowski & Datka, 2020). For one-step synthesis of DME, a hybrid catalyst can be combined in two ways. The first one is a physical mixture (PM) in which a solid acid catalyst and a MeOH synthesis catalyst are merely combined, keeping the spatial functions of the two processes distinct. The second is an integrated mixture, where the catalytically active elements for the two processes are positioned purposefully close together to assist the desired DME synthesis. Table 2 provides a summary of some of the findings related to the direct  $CO_2$  hydrogenation to DME.

The current focus of research lies in developing and optimizing catalysts and reactors for direct DME production from CO<sub>2</sub> and H<sub>2</sub>, aiming to sustain high selectivity and stability under high-pressure, and high-temperature conditions (Ateka et al., 2022; Banivaheb et al., 2022). However, despite these efforts, CO<sub>2</sub> conversion and DME yield values remain low, typically less than 30% CO<sub>2</sub> conversion (Bonura et al., 2021), due to significant kinetic and thermodynamic constraints caused by the production of water as a side product. Water deactivates both the MeOH and acid catalyst centers, underscoring the importance of maintaining a dry reaction chamber by eliminating water from the reaction environment (Frusteri et al., 2015; Li et al., 2021). As a result, the most effective approach to attain the necessary dry reaction environment and significantly enhance the efficiency of direct DME synthesis from CO<sub>2</sub> and H<sub>2</sub> involves utilizing a dehydration membrane capable of selectively removing water in situ while preserving other reaction components within the reaction system.

Table 2	Recent investiga	ted catalysts	for one-pot CC	-to-DME process
				/

Catalyst	Preparation method	Metal-acid phase ratio (wt/wt)	GHSV (mLg <sup>-1</sup> <sub>cat</sub> h <sup>-1</sup> )	T <sub>R</sub> ; P <sub>R</sub> (°C; bar)	X <sub>CO2</sub> (%)	Y <sub>DME</sub> (%) S <sub>DME</sub> (%)	Refs.
6CuO-3ZnO-1Al <sub>2</sub> O <sub>3</sub> / HZSM-5	Precipitation by Na <sub>2</sub> CO <sub>3</sub> + mechani-	1.5:1	3000	260;30	29	$S_{\rm DME} = 65$	(Naik et al., 2011)
6CuO-3ZnO-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	cal mixing	1.5:1	3000	260;30	14	$S_{\text{DME}} = 57$	
CuZnAl/Al–Zr–SBA-15	Hydrothermal + physi- cal mixing	1:1	1500	240;30	22.5	S <sub>DME</sub> =73 Y <sub>DME</sub> =16.5	(Mondal & Yadav, 2022)
CuZnAl/HZSM-5		1:1	1500	240;30	23.5	S <sub>DME</sub> =66.5 Y <sub>DME</sub> =15.7	
CZA/HZSM-5	Stepwise precipita-	Not reported	1440	240;28	25.6	$Y_{\rm DME} = 17.2$	(Fan et al., 2023)
ZrO <sub>2</sub> -CZA/HZSM-5	tion + slurry mixing					$Y_{\rm DME} = 18.4$	
CuO-Fe <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HZSM-5	Co-precipitation	1:1	1500	260;30	28.4	$Y_{\rm DME} = 18.3$	(Liu et al., 2013)
CuO–ZnO–Al <sub>2</sub> O <sub>3</sub> –La <sub>2</sub> O <sub>3</sub> / HZSM-5	Coprecipita- tion + grinding	2:1	3000	250;30	43.8	Y <sub>DME</sub> =31.2	(Gao et al., 2013)
(CuO–ZnO–Al <sub>2</sub> O <sub>3</sub> + HZSM- 5)/ MWCNT	Coprecipitation in urea/CNT solution	1:1	1800	262; 30	46	Y <sub>DME</sub> =21	(Zha et al., 2013)
(CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> ) Amorphous silica–alumina	Coprecipita- tion + Core–shell encapsulation		8800	240;30	47.1	$Y_{\rm DME} = 19.9$	(Zha et al., 2012)
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /SAPO-18	Physical mixing	2:1	Not reported	275:30	10	S <sub>DME</sub> =68.9 Y <sub>DME</sub> =14.5	(Ateka et al., 2017)
Hyb–pwd–CuO–ZnO-ZrO <sub>2</sub> / MFI	Co-precipitation + 3D printing	1:1	1000	260;30	23.6	S <sub>DME</sub> =42.6	(Bonura et al., 2023)
Hyb-3D–CuO–ZnO–ZrO <sub>2</sub> / MFI					22.8	S <sub>DME</sub> =36	
Cu/Zn/Al/ZSM-5	Co-precipitation		7500	275;40	35	$Y_{\rm DME} = 23$	(Ereña et al., 2005)
Cu/Zn/Al/γ-Al2O3					40	Y <sub>DME</sub> =10	

Notably, one-step CO<sub>2</sub> hydrogenation to DME has yielded intriguing results in the literature (Azizi et al., 2014; Catizzone et al., 2021; Ereña et al., 2005). However, there is a pressing need to develop bifunctional catalysts that enable large-scale DME production without deactivation. The deactivation of hybrid catalysts primarily from the presence of water and the mobility of metal sites, inducing sintering and/or ion exchange with acid sites. Future advancements in one-pot CO<sub>2</sub>-to-DME production should prioritize the creation of novel catalytic systems capable of operating at lower temperatures and with increased stability for industrial-scale production. While the Cu-ZnO catalyst is expected to maintain its prominence in the industrial CO2-to-MeOH step due to its superior catalytic activity, stability, and economic benefits, the use of FER-type zeolites as acid catalysts in MeOH dehydration revealed acceptable water resistance albeit deactivation during the one-pot CO<sub>2</sub>-to-DME process (Bonura et al., 2016, 2017). Enhancing hydrophobic sites at high temperature might not resolve the issue; instead, an in situ water removal approach is necessary for a highly stable system. Li et al. (2021) demonstrated a notable increase in MeOH formation and dehydratioin activity by employing Na<sup>+</sup>-gated water-conducting membranes (WCM), resulting in a 4- and 10-fold increase. Achieving DME yields of up to 54.5% and single-pass CO<sub>2</sub> conversion rates of up to 73.4% at 250 °C and 35 bar pressure, surpassing the thermodynamic equilibrium of the bare MeOH synthesis, has been observed. Addressing catalyst deactivation caused by coke accumulation from carbonaceous substances is another critical challenge. The blockage of zeolite pores due to coke production renders them inaccessible. Innovative and stable hybrid catalysts are imperative to transition from laboratory-scale experiments to industrial operations.

# Hydrogen production from dimethyl ether

Various methods have been explored to produce  $H_2$  from DME, including partial oxidation, autothermal reforming, and steam or dry reforming. Among these, steam reforming (SR) stands out as the most efficient method releasing  $H_2$  (Gao et al., 2013; Naik et al., 2011). Due to DME's chemical properties, it facilitates easier reforming at relatively low temperature, typically ranging from 250 to 450 °C, and reformation takes place at low pressure. The SR process for DME occurs in two-steps as shown in Eqs. 10 to 12.

The first step involves the hydrolysis of DME into MeOH:

$$CH_3OCH_3 + H_2O \rightleftharpoons 2CH_3OH \qquad \Delta H^o = +37kJ/mol$$
(10)

The second step is MeOH SR:

$$CH_3OH + H_2O \rightleftharpoons 3H_2 + CO_2 \qquad \Delta H^o = +49 \text{ kJ/mol}$$
(11)

The overall SR of the DME reaction is expressed by:

$$CH_3OCH_3 + 3H_2O \rightleftharpoons 6H_2 + 2CO_2 \qquad \Delta H^o = +135 \text{ kJ/mol}$$
(12)

To favor hydrogen release in the endothermic reaction of DME SR, employing high temperatures and low pressures is essential from a thermodynamic perspective due to the increase in the number of moles (Ledesma et al., 2019). The rate-determining hydrolysis step (Eq. 7) relies on an acid-catalyzed mechanism and demand higher pressures, while SR step (Eq. 8) is metal-catalyzed. Besides potential additional side reactions that may occur during DME SR, various side reactions, including RWGS and DME decomposition, occur based on catalyst characteristics and reaction conditions such as temperature and pressure, affecting H<sub>2</sub> production.

Attaining high-yield  $H_2$  necessitates a catalyst that prevents CO, hydrocarbons (HC), and coke formation (Gul et al., 2023). Both purity of the produced gas and catalyst stability play critical roles in advancing this technology, especially for high-purity hydrogen production crucial in PEM fuel cells. Given the two-step nature of DME SR, effective bifunctional catalysts are vital for achieving high DME conversion,  $H_2$  selectivity, and minimizing CO (Eq. 13) and HC by-products such as  $CH_4$  (Eq. 14). As DME hydrolysis occurs at solid acid catalyst sites, acidic surfaces like alumina or zeolite are necessary, whereas metallic catalysts (Cu-, Pd-, and Pt-based catalysts) function as MeOH reformers.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
 (13)

$$CH_3OCH_3 \rightleftharpoons CH_4 + CO + H_2$$
 (14)

#### DME SR procedure parameters and catalysts

Bifunctional catalysts comprise metallic sites for MeOH reforming and acidic sites for DME hydrolysis (Kim et al., 2017). Typically, the two types of acid catalysts, alumina, and zeolite, are used for DME hydrolysis, while MeOH reforming occurs over various metallic sites like Cu, Pd, Pt, and Ru (Catizzone et al., 2021; Mota et al., 2021). Enhancement of catalytic performance is achieved through metal doping, including Ni, Ce, and Fe. The bifunctional catalyst determines the DME's SR process (Cui et al., 2022). To consolidate the DME SR results, we considered the reaction process, diverse catalysts, varying reaction conditions, and catalyst stability. Table 3 summarizes the selected DME SR processes using different

Catalyst	Experimental condition	Х <sub>DME</sub> (%)	H <sub>2</sub> production	References
xCu/y-Al <sub>2</sub> O <sub>3</sub>	350–400 °C, 1 atm	95	Y <sub>H2</sub> =74.08%,	(Kim et al., 2022)
xCu/γ-Al <sub>2</sub> O <sub>3</sub>	300–600 °C, 1 atm	100	YH2=72%,	(Kim et al., 2020)
Cu–Ni/γ-Al <sub>2</sub> O <sub>3</sub>	350 <sup>0</sup> C, 1 atm	100	$V_{\rm H2} = 55 - 70 \text{ mmol g}^{-1} \text{ h}^{-1}$	(Wang et al., 2010)
CuMn <sub>2</sub> O <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	350 °C, 1 atm	71	V <sub>H2</sub> =23-24 mL/min	(Faungnawakij et al., 2008)
Cu/SiO <sub>2</sub> -HPA/γ-Al <sub>2</sub> O <sub>3</sub>	290 °C,1 atm	100	Y <sub>H2</sub> =74%,	(Galvita et al., 2001)
CuFe <sub>2</sub> O <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	375 °C,1 atm	56.8–99.6	Y <sub>H2</sub> =48-97.6	(Faungnawakij et al., 2009)
CuNiFe/γ-Al <sub>2</sub> O <sub>3</sub> /Al	400 oC, 1 atm	100	Y <sub>H2</sub> =97%,	(Deng et al., 2019)
CuFe <sub>2</sub> O <sub>4</sub> / γ-Al <sub>2</sub> O <sub>3</sub>	350–425 °C, 1 atm	70–95	$V_{\rm H2}$ = 55–95 mmol g <sup>-1</sup> h <sup>-1</sup>	(Faungnawakij et al., 2006)
CuZnAlZr/γ-Al <sub>2</sub> O <sub>3</sub>	350–425 °C,1 atm	90–95	Y <sub>H2</sub> =85-95%,	(Sun et al., 2012)
CuZnAl <sub>2</sub> O <sub>3</sub> /HZSM-5	275 <sup>0</sup> C,1.2 atm	40-44	Y <sub>H2</sub> =35-43%,	(Arteta et al., 2014)
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> 1.55% ZSM-5	200–300 °C,1 atm	570-100	Y <sub>H2</sub> =65-96%	(Long et al., 2019)
Pd/ZrO <sub>2</sub>	360–550 °C,1 atm	50-100	$Y_{\rm H2} = 31 - 65$	(Ledesma et al., 2011)

Table 3 Effect of different catalysts and process parameters on DME steam reforming

catalysts under varied conditions, and their impacts on DME conversion and  $\rm H_2$  production.

Kim et al. studied the DME reforming by the catalyst  $xCu/\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different cu loading (x=5-15%) allowing H2 production 72-74.08% at 300-375 °C (Kim et al., 2020, 2022). Wang et al. (2010) reported the Cu-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> based catalyst for inhibition of sintering Cu particle by the modified catalyst using Ni. These catalysts exhibited improved dispersion of Cu and supressed the RWGR. Using physical mixing, Sobyanin et al. found 100% DME conversion at 290 °C with heteropoly acid (HPA,  $H_4SiW_{12}O_{40}$ ) supported over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu/ SiO<sub>2</sub>. (Galvita et al., 2001) Faungnawakij et al. tested the composite of  $CuFe_2O_4$  spinel and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for catalytic hydrogen production from SR of DME. (Faungnawakij et al., 2009) The spineloxides with less reducible Cu species had more Cu<sup>1+</sup> species in the reducing atmosphere, indicating higher DME SR activity. Cu clusters highly dispersed in iron oxide matrix were reduced from the spinel structure, and their strong interaction should result in high activity and durability. After adding Fe to CuNi/y-Al<sub>2</sub>O<sub>3</sub>/Al, CO concentration decreased. CuNiFe/g-Al<sub>2</sub>O<sub>3</sub>/ Al catalysts with 12.5% Fe content converted DME 100% and yielded over 97% H<sub>2</sub> in the microreactor and fixedbed reactor (Deng et al., 2019). They also reported that SR of DME activity was affected by acidic catalyst acid amount, strength, and site type. With optimal reforming temperature at 350–375 °C,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mixed with CuFe<sub>2</sub>O<sub>4</sub> produced high yeild H<sub>2</sub>.and activity was stable and durable for 25 h (Faungnawakij et al., 2006). Sun et al. examined that Al and Zr greatly affect catalyst performance, including DME conversion, H<sub>2</sub> yield, and CO/CO<sub>2</sub> selectivity. The catalyst CuZnA<sub>10.8</sub>Zr<sub>0.2</sub>O achieves the highest DME conversion and  $H_2$  yield across 300-425<sup>o</sup>C reaction temperatures. Long et al. (2019) showed that over 90% DME conversion and  $H_2$ yield were achieved after 50 h of TOS with 2.17 wt% MgO-modified HZSM-5 and Cu/ ZnO/Al<sub>2</sub>O<sub>3</sub>.

The cases emphasize the necessity of gaining a deeper understanding of the underlying processes and interactions among the active ingredients in both mixed and bifunctional catalysts. Moreover, additional research should explore the role that the catalyst's composition and the fundamental factors that govern both activity and stability of the catalysts.

## **Reactor development**

Several reactor concepts have been proposed for the independent and efficient direct synthesis of CO<sub>2</sub> to DME and DME to H<sub>2</sub> (Azizi et al., 2014; Tavan et al., 2013). The direct production of DME gives priority to the microstructural and membrane reactor. Microstructural reactors, often with dimensions around  $10^{-3}$  m, aim to enhance heat and mass transport characteristics (Ateka et al., 2022). While microstructure reactor designs involve either stacking prefabricated foils or utilizing additive manufacturing techniques. Two primary concepts for implementing a catalyst in microstructures involve packing the catalyst and coating the microchannels to improve heat transfer. Alternatively, entire reactors can be manufactured from catalytically active materials (Peláez et al., 2018). A membrane reactor combines chemical reactions and product separation in a single unit, boosting conversion rates (Hamedi & Brinkmann, 2022) and optimizing thermodynamic equilibrium by extracting by-products and achieving higher purity.

Nonetheless, the integration of porous, organic, or inorganic membranes into reactors poses challenges, often necessitating tubular or planar systems to achieve highly selective and defect-free membranes.

# Future perspectives on DME as a H2 carrier

Direct  $CO_2$  hydrogenation using renewable  $H_2$  to produce DME is a key technique for integrating renewables into the chemical and fuel production processes. In recent years, significant attention has been directed toward developing new catalytic systems for one-pot  $CO_2$  hydrogenation to DME, as well as cost-reducing approaches such as designing a single reactor unit for MeOH synthesis and dehydration.

The direct synthesis of DME usually occurs within the temperature range of 200-300 °C and a pressure range of 10-50 bar. Optimal operational conditions for CO<sub>2</sub> to DME conversion are at 30 bar pressure and temperatures between 270–275 °C (Merkouri et al., 2022). Understanding the differences between bifunctional and hybrid catalysts is crucial for advancing one-pot CO<sub>2</sub> hydrogenation. Bifunctional catalysts combine metal and acid active sites, whereas hybrid catalysts lack distinct catalytic functions. The preparation methods and choice of metal/acid precursors significantly impact the catalytic performance of the hybrid grains during the one-pot CO<sub>2</sub>-to-DME process (Mota et al., 2021). Future advancements in the one-pot CO<sub>2</sub>-to-DME process should concentrate on developing new catalytic systems operating at lower temperatures and exhibiting higher stabilities. The mobility of metal sites and the presence of water are the primary causes of hybrid catalyst deactivation. Innovative methods can help inhibit metal mobility and enhance the anchoring of metal particles while maintaining metal/acid spatial proximity. Cu-based catalysts (such as Cu-ZnO) are anticipated to remain the standard for the CO<sub>2</sub>-to-MeOH step due to their superior activity, stability, and economic advantages. Water contributes to the deactivation by promoting metal particle mobility instead of competitive adsorption. Increasing hydrophobicity may not solve this issue, particularly at high temperatures, where adsorption is less favorable. Exploring unconventional technologies for in situ water removal, such as membrane reactors, might lead to more stable systems.

However, numerous challenges persist in optimizing catalysts for the one-pot  $CO_2$  hydrogenation to DME, necessitating new laboratory-scale studies to develop more innovative and stable hybrid materials. Overall, optimizing catalysts for one-pot  $CO_2$  hydrogenation to DME remains a considerable challenge requiring further research. Laboratory-scale studies are essential for developing innovative and stable hybrid materials suitable

for industrial applications. Considering DME's use as a replacement for LPG, especially in China, its storage and transport must be feasible.

At a laboratory scale, researchers are studying the enhancement of the catalyst performance for releasing  $H_2$  from DME via the SR process. The first DME SR was described in the early 2000s, utilizing a catalyst at atmospheric pressure and temperatures ranging between 200 and 400 °C.

The focus has been on developing a bifunctional catalyst achieved by physically combining metal-based (Cu) components with acid-based ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or zeolite) catalysts. The presence of Cu-based spinal-like structures significantly influences the DME SR process. Maintaining the catalytic properties of DME SR relies heavily on the quantity of the doping species. Additionally, the selection of acid functional sites is crucial in the hydrolysis of DME. Zeolite-based acid sites offer the potential for developing bifunctional catalysts by optimizing both chemical and physical properties. Therefore, it is imperative to conduct laboratory-scale investigations to assess the performance of hybrid systems under high-pressure conditions, given the need for high-pressure  $H_2$  and the ease of separating  $CO_2/H_2$ in such conditions.

Presently, the existing catalyst systems have not shown sufficient progress in the industrial production of  $CO_2$ -to-DME and DME-to-H<sub>2</sub>. However, a more detailed understanding of the reaction mechanism and identification of active or spectator species involved in the processes of  $CO_2$ -to-DME and DME SR are required. Despite uncertainties about these processes, it is clear that several parameters can be addressed to enhance the efficiency of renewable hydrogen storage and release.

# **Formic acid**

Formic acid (FA), the smallest carboxylic acid molecule, is a colorless, low-toxicity liquid at room temperature and atmospheric pressure. With a melting point of 8 °C and a boiling point of 102 °C under atmospheric pressure, FA possesses physical properties that facilitate easy handling on the ground, allowing safe transportation as a liquid through pipelines and tanker trucks (Pérez-Fortes et al., 2016; Tian et al., 2015). Industrially, FA is obtained as a byproduct of acetic acid production (Yoneda et al., 2001), or it can be acquired by hydrolyzing methyl formate, which is produced by carbonylation of MeOH with carbon monoxide in the presence of a strong base, or by acidolysis of alkali formates (Reutemann & Kleczka, 2003). FA is renowned for its high hydrogen storage capacity and the low energy required for hydrogen production. Being a liquid under ambient conditions, it is simpler to transport and store than molecular hydrogen. Thanks to these characteristics, FA is considered a safe and cost-effective hydrogen carrier for transportation and storage.

# Formic acid dehydrogenation

Extensive research has focused on developing catalysts for  $H_2$  production from FA. Two potential pathways for the catalytic breakdown of FA have been explored. The first pathway involves FA dehydrogenation, yielding  $H_2$ and CO<sub>2</sub> (Eq. 15). This process is thermodynamically favorable, endothermic, and exergonic, reducing the risk of thermal runaway. Conversely, the gas-generating dehydrogenation process is easily facilitated owing to the significant entropy change.

$$\begin{array}{ll} \text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2 & \Delta H = +31.2 \text{ kJ/mol} \\ \text{(15)} \\ \text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} & \Delta H = +29.2 \text{ kJ/mol} \\ \text{(16)} \end{array}$$

FA can undergo another decomposition reaction through dehydration, resulting in the production of CO and  $H_2O$  (Eq. 16). In applications involving hydrogen carriers, it is preferable to employ a catalyst that produces  $H_2$ selectively while inhibiting CO formation. Considerable research has focused on developing both homogeneous and heterogeneous selective dehydrogenation catalysts to prevent CO production. Therefore, the need persists for catalysts capable of selectively yielding  $H_2$  while minimizing CO output (Kawanami et al., 2017).

Figure 4 displays the standard reaction enthalpies and Gibbs free energies for the dehydrogenation and dehydration of FA across different temperatures. In the case of dehydration, the reaction enthalpy remains constant across various temperatures, whereas the Gibbs energy increases with rising temperature. For dehydrogenation, the reaction enthalpy ( $\Delta H$ ) decreases slightly at higher temperatures, but the Gibbs energy exhibits an increase. Dehydrogenation is endothermic, while dehydration is exothermic. Although both reactions share similar enthalpy values, dehydrogenation displays higher temperature dependence and greater energy content. Therefore, performing the reaction near the FA boiling point maximizes the attainable thermodynamic energy. This substantial difference in the Gibbs energy mainly arises from one of the products of dehydration products being liquid water (Fig. 5).

# Formic acid dehydrogenation by homogeneous catalysts

FA dehydrogenation (FAHD) using homogeneous systems began in 1967 with the development of  $IrH_2Cl(PPh_3)_3$  by Coffey (Coffey, 1967). Since then, numerous complex catalysts, primarily based on transition metals, such as Ir (Forster & Beck, 1971), Ru (Johnson et al., 2010; Rodriguez-Lugo et al., 2013), Pt (Paonessa & Trogler, 1982; Yoshida et al., 1978), Rh (Forster & Beck, 1971), and Pd (Wiener et al., 1986), have been reported.



Fig. 4 Homogeneous catalysts are used for methanol dehydrogenation



**Fig. 5** The reaction enthalpies and Gibbs energies of dehydrogenation and dehydration of formic acid across various temperatures

In 2008, Loges et al. used commercially available [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (Fig. 3, Ru-13) to perform FADH and achieved a high TOF of 417  $h^{-1}$  after 2 h. (Loges et al., 2008) This catalyst's activity was further enhanced by pretreating it with a small amount of DMF, reaching a TON of 891 and an initial TOF of 2688 h<sup>-1</sup> after 2 h. Fellay et al. used hydrophilic Ru-based catalysts generated in situ by adding  $[Ru(H_2O)_6]^{2+}$  (**Ru-14**) or commercially available RuCl<sub>3</sub> with mTPPTS (*m*-trisulfonated triphenylphosphine: L1) (Fellay et al., 2008). With the former catalyst system, a continuous system that continuously fed FA achieved a TOF of 460 h<sup>-1</sup>. These reports have spurred remarkable progress in the development of Ru catalysts for FADH. In 2009, Johnson et al. investigated a series of organometallic complexes and reported that commercially available [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] (**Ru-15**) exhibited very high activity for FADH (> 200 ppm CO byproduct), showing a TOF of 18,000  $h^{-1}$  at 120 °C (Johnson et al., 2010). In 2013, Sponhol et al. (2013) reported a system capable of decomposing FA into H<sub>2</sub> and CO<sub>2</sub> with excellent activity (TON 1,000,000) using a catalyst formed in situ from commercially available  $[RuCl_2(C_6H_6)]_2$  (**Ru-16**) and 1,2-bis(diphenylphosphino)ethane (dppe: L2). In 2016, Pan reported a Ru-PNP pincer complex coordinated with a pyridine pincer ligand (Ru-17) (Pan et al., 2016). This catalyst showed high activity in DMSO under relatively mild conditions, achieving a TON of 95,000. Furthermore, the presence of amines in the reaction solution allowed the catalyst to maintain its activity over the long term, achieving a TON of 1,000,000 over 150 h. In 2009, Himeda et al. reported Cp\*Ir complex catalysts with 4,4-dihydroxy-2,2'-bipyridine, (Ir-which is NN'-bidentate ligand, sparking many subsequent reports on Ir catalysts for FADH (Himeda, 2009). They noted a significant increase in catalytic activity upon the introduction of electron-donating substituents (Ir-2) such as hydroxyl and methoxy groups) into 2,2'-bipyridine. The Cp\*Ir-4DHBP complex (Ir-2) efficiently catalyzed the reaction in water, completely converting FA into H<sub>2</sub> and CO<sub>2</sub>, without generating CO (less than 10 ppm) or requiring additives. Additionally, they synthesized an Ir complex with an imidazoline ligand (Ir-5) (Wang et al. 2015a; b). Under reflux conditions, Ir-4 exhibited a TON of 68,000 and a TOF of 322,000  $h^{-1}$  after a 30-min reaction. Wang et al. recently developed an Ir complex with a bisimidazoline ligand (Ir-6), demonstrating exceptional catalytic performance with a TOF of 487,500  $h^{-1}$  in water. (Wang et al., 2015c) In 2020, Kawanami developed a series of Ir complexes (Ir-7) with amino-substituted 2,2'-bipyridine ligands for high-pressure hydrogen production. (Kawanami et al., 2020) Notably, the Cp\*Ir-4DMABP complex (Ir-7) substituted with dimethylamino groups, displayed outstanding activity even under high-pressure conditions, generating gas pressures exceeding 150 MPa. This method of high-pressure hydrogen production from hydrogen carriers eliminates the need for mechanical compression when utilizing hydrogen gas.

Recently, there has been a surge in reports focusing on nonprecious metal-based complex catalysts for FADH. Although they typically exhibit lower activities than precious metal-based complexes, they are gaining attention due to their abundance and cost-effectiveness. In 2010, Boddien et al. developed an Fe-phosphine catalyst in situ by combining  $Fe_3(CO)_{12}$  (Fe-3), 6,6'-phenyl-2,2':6',2"terpyridine (L3), and PPh<sub>3</sub> (L4), yielding hydrogen with an initial TOF of 200  $h^{-1}$  under visible light irradiation for 1 h (Boddien et al., 2010). The following year, their group reported FADH using a complex derived from  $Fe(BF_4)_2 \cdot 6H_2O$  and the tetradentate ligand PP<sub>3</sub> (Fe-3+L5) (Boddien et al., 2011). In 2013, Zell et al. (2013) reported an Fe-based pincer complex (Fe-4) that catalyzes FADH under mild conditions in the presence of Et<sub>3</sub>N, achieving a TON of 100,000. Ni-based metal complexes have also been reported by Enthaler et al. (2015) , who developed a Ni catalyst with a PCP pincer ligand (Ni-1) and achieved a TON of 626 after 3 h in the presence of propylene carbonate (PC) and dimethyl-n-octylamine (*n*-OctNMe<sub>2</sub>). Effective homogeneous catalysts for the dehydrogenation of FA are generally categorized as iridium and ruthenium complexes with ligands like phosphine, bipyridine, N,N'-bidentate ligands, Cp\*, and pincers. Notably, there has been a recent development in immobilized catalysts containing homogeneous complexes on various substrates have been reported.

Compared with other H<sub>2</sub> carriers, the unique production of H<sub>2</sub> from FA is attributed to its negative Gibbs free energy of dehydrogenation, driving the reaction to yield gaseous H<sub>2</sub> and CO<sub>2</sub> from liquid FA owing to its substantial reaction enthalpy (Iguchi et al., 2016a, b). Currently, high pressures can be produced from the generated gas; the maximum pressure, determined by the Gibbs energy, reaches 225 MPa (Iguchi et al., 2016a, b). There have been various reports on producing high-pressure gases through FA dehydrogenation. In 2008, Fellay et al. utilized a high-pressure NMR tube and reported the generation of a high-pressure gas at 75 MPa from FA using  $[Ru(H_2O)_6]^{2+}$  (Ru-14) or a RuCl<sub>3</sub> complex with tris(metasulfonate phenyl) phosphine (*mtppms*) as the ligand (Fellay et al., 2009). Subsequently, in 2016, Czuan et al. () employed IrCl<sub>3</sub> and *N*,*N*-bidentate ligands, achieving high-pressure gas production up to 15 MPa with  $IrCl_3 + IndH$  (**Ir-IndH**). In the same year, Papp et al. also reported the production of 14 MPa of high-pressure gas from FA using the *cis-mer*-[IrH<sub>2</sub>Cl(*m*tppms)<sub>3</sub>] (*m*tppms=monosulfonated triphenylphosphine Na-salt) (Papp et al., 2016). In 2017, Broicher et al. (2017) reported the production of 6 MPa at 160 °C in the presence of iridium catalyst with bipyridine-based conjugated microporous polymer (CMP), whereas the CO concentration increased to 152 ppm in the generated gas. Guan et al. (2017) generated 25.8 MPa of high-pressure gas using arene-Ru (II) catalysts in 2017. In 2018, Boncella et al., reported the high-pressure gases 19 MPa of high-pressure gas in the presence of Ru complex with <sup>tBu</sup>PONOP (tBuPONOP = 2,6-bis(ditert-butylphosphinito)pyridine)) pincer ligand (Nickolas et al., 2017), and Geri et al. (2018) also reported the production of 19 MPa from FA using various Ru complexes with N,N', and N-bispyridylisoindoline as ligands (Ru-Ind-OTf). Kawanami published several reports on the generation of high-pressure gas from FA. In 2016, they first achieved 120 MPa of highpressure gas from 20 M FA using a Cp\*Ir complex containing a 4,4'-2,2'-bipyridine ligand (Cp\*Ir-4DHBP), etc. (Iguchi et al., 2016a, b). Moreover, they observed a decrease in the pressurization rate during gas production under high pressure, indicating catalyst degradation via ligand detachment under high-pressure reductive conditions. They later updated this report by generating a maximum pressure of 157 MPa using Cp\*Ir complexes (Cp\*Ir-4DMABP) (Fig. 6) (Kawanami et al., 2020). They also reported Ir complexes with ortho-substituted bipyridine ligand (Cp\*Ir-6DHBP) can generate high-pressure gas, but rapid decomposition compared to the Ir complex with para-substituted one was occur under high-pressure conditions (Iguchi et al., 2017). The achieved pressure by formic acid generation using various reported catalyst is summarized in Figs. 7 and 8.

The dehydrogenation of FA generates high-pressure gas, functioning as a chemical pump for releasing hydrogen from liquid-phase hydrogen carriers at elevated pressures. The use of FA can bypass the hydrogen compression process at stations, leading to cost reductions by eliminating multiple steps compared to compressorbased methods (Dutta et al., 2022; Müller et al., 2017).



Fig. 6 Selected Ru, Ir, Fe, and Ni complexes as catalysts for FADH



**Fig. 7** Example of the time course of generated pressure by FADH in the presence of Cp\*Ir-4DMABP at 80 °C using Cp\*Ir complexes. (Kawanami et al., 2020). (Reprinted from Kawanami et al. Copyright 2023, American Chemical Society



**Fig. 8** Reaction temperature vs. achieved pressure from the formic acid dehydrogenation using selected catalysts. Selected data are shown as follows: red filled circles referred from (Iguchi, et al., 2016a, b; Kawanami et al., 2020), blue filled diamond referred from (Fellay et al., 2009), green filled triangle referred from (Papp et al., 2016), yellow square is referred from (Czaun et al., 2016), and black crosses are referred (Broicher et al., 2017; Zhong et al., 2017)

However, some drawbacks arise from the simultaneous production of hydrogen and carbon dioxide during FA dehydrogenation, necessitating their separation to attain high-purity hydrogen, especially in hydrogen fuel cell vehicles, which require hydrogen purity above 99.97% with minimal impurities, maintaining CO content below 0.2 ppm. (Standardization, 2019) Several gas separation methods exist, including temperature swing adsorption (TSA), pressure swing adsorption (PSA), membrane separation, and amine-based carbon dioxide separation. Yet, TSA and PSA result in substantial hydrogen loss, membrane separation lacks feasibility under high pressure, and amine-based separation risks contaminating hydrogen, reducing its purity. Notably, catalyst-driven processes exclusively yield high-pressure gases of hydrogen and carbon dioxide from FA, enabling deep cryogenic separation methods under high pressure to achieve hydrogen purification up to 96% and a recovery rate exceeding 99% for liquefied carbon dioxide, preventing any loss (Figs. 9, 10) (Iguchi et al., 2016a, b).

The unique properties of high-pressure gas facilitate the exclusive use of FA, not only for producing high-pressure hydrogen but also for recovering liquefied carbon dioxide. However, despite the advantages of high-pressure gases, challenges have emerged. While the dehydrogenation rate of gaseous FA remains independent of pressure, the reaction rate for liquid or aqueous FA solutions is pressure sensitive. For instance, at 0.1 MPa, 10 MPa and 30 MPa conditions, the reaction rate drops to 1/4 when using a 8 M aqueous FA solution (Iguchi et al., 2016a, b). Consequently, measures like increasing catalyst amounts or enlarging the reaction vessel become necessary to maintain the space velocity in FA dehydrogenation.

# Formic acid dehydrogenation by heterogeneous catalysts

Research into the decomposition of FA using heterogeneous catalysts commenced in the 1930s. Early studies did not focus much on optimizing catalysts or considering byproducts such as CO (Grasemann & Laurenczy, 2012). Initially, the reaction was studied in the gas phase, above the boiling point of FA (>101 °C). Hence, there is a pressing need for liquid-phase FADH heterogeneous catalysts, leading to an ongoing search for optimal catalysts (Zhong et al., 2018a, b; Zhu & Xu, 2015).

Pd-based catalysts exhibit the highest activity for FADH. Pd demonstrates greater resistance to CO production than other metals, exhibiting high hydrogen conversion rates and selectivity. Pd/C, a widely used catalyst, can be industrially synthesized on a large scale. However, the performance of Pd/C in FADH is affected by the preparation method and Pd particle size (Jeon & Chung, 2017; Kim & Kim, 2019). Alloy catalysts incorporating a second metal to enhance heterogeneous and core–shell catalyst performance have also been reported. Wang et al. (2018) reviewed numerous bimetallic, trimetallic, and core–shell catalysts.

The activation energies for FA dehydrogenation using bimetallic and acid-metal heterogeneous catalysts are generally low, facilitating reactions at room temperature with these catalysts (Zhong et al., 2018a, b). For instance, by alloying Pd with Ag, and Au, its activity is maintained



Fig. 9 Selected Ru and Ir catalyst for the high-pressure generation by FADH



Fig. 10 Phase behavior of the generated gas from FADH at each temperature. a 0.1 MPa and 35 °C, b 30 MPa and 35 °C, c 30 MPa and -10 °C (Iguchi et al., 2016b) (Reprinted with permission from Kawanami et al. Copyright 2023, John Wiley and Sons)

while CO-induced catalyst poisoning is prevented. Xing et al. synthesized a series of Pd–Au/C catalysts with various atomic ratios, demonstrating exceptional activity (TOF of 6634 h<sup>-1</sup>) for Pd<sub>0.69</sub>Au<sub>0.31</sub>/C at room temperature (Xing et al., 2019). Lu et al. developed a catalyst featuring Pd–Cr(OH)<sub>3</sub> nanoparticles on amine-functionalized mesoporous silica supports, achieving a 100% FA conversion rate and a TOF of 3112 h<sup>-1</sup> (Ding et al., 2023). In a trimetallic system, Jiang et al. reported a CoAuPd alloy supported on carbon exhibiting a TOF of 80 h<sup>-1</sup> under ambient conditions without additives (Wang et al., 2013).

In the midst of these advancements, Zhong et al. (2017) utilized Pd/PDA- $\gamma$ GO (PDA=phenylenediamine) as a catalyst in the dehydrogenation of FA, producing high-pressure gas up to 36 MPa by employing an aqueous

solution of FA and sodium formate in a 1:1 ratio. As far as our knowledge extends, this stands as the sole record of high-pressure gas generation from FA using a solid catalyst. However, the more active PdAu/PDA- $\gamma$ GO, while capable of generating high-pressure gas, exhibits a drawback: the amines supported on the  $\gamma$ GO surface convert into amides or carbamic acid in the presence of high-pressure carbon dioxide, consequently reducing its activity (Zhong et al., 2018a, b). Hence, adapting it to a high-pressure hydrogen/ carbon dioxide separation process becomes challenging. The activation energy required for the dehydrogenation of FA using solid catalysts is lower than that using homogeneous catalysts. Nonetheless, solid catalysts prove unsuitable for generating high-pressure gas.

## CO<sub>2</sub> hydrogenation into formic acid

FA is produced via the two-electron reduction of  $CO_2$  during hydrogenation reduction (Eq. 17). Homogeneous complex catalysts for this process have been reported since 1976 when Inoue et al. utilized phosphine-based complexes of Ni, Ru, Rh, Pd, and Ir (Inoue et al., 1976).

$$CO_2(g) + H_2(g) \rightarrow HCOOH(l) \quad \Delta G^{\circ}298K = 32.0 \text{ kJ/mol}$$
(17)

This gas-phase reaction is entropically unfavorable. However, in a solvent, the thermodynamics of the reaction change, making the reaction slightly exergonic in solvents such as water (Eq. 18).

$$CO_2(aq) + H_2(aq) \rightarrow HCOOH(aq) \quad \Delta G^{\circ}298K = -4 \text{ kJ/mol}$$
(18)

The inclusion of a base further amplifies the exergonic nature of the reaction. Several studies have documented the creation of formate salts by employing bases in  $CO_2$  hydrogenation. This has led to reversible cycles involving the storage and release of H<sub>2</sub> using bases (Sordakis et al., 2015). Yet, when bases are employed, the resulting formate salts necessitate neutralization with an acid to produce FA, adding extra steps to the process. Consequently, achieving FA directly from  $CO_2$  is preferred. However, there are limited reports on the synthesis of FA without utilizing bases.

An enormous number of reports about FA synthesis using transition metal complexes are published, and the FA and formate synthesis from H<sub>2</sub> and CO<sub>2</sub> have been reviewed by many research groups (Alvarez et al., 2017; Johnson et al., 2010; Leitner, 1995; Wang et al., 2015a, b) In 1989, Khan et al. (1989) reported the hydrogenation of CO<sub>2</sub> at a rate of 62.5 mmol/min under 17 bar of H<sub>2</sub> and 3 bar of CO<sub>2</sub> using a 0.01 M aqueous solution of  $K[Ru(EDTAH)Cl]_2H_2O$  (EDTAH = ethylenediaminetetraacetic acid). However, they noted the formation of formaldehyde and CO owing to the decomposition of FA. Tsai and Nicholas et al. achieved the formation of FA at a maximum concentration of 0.18 M using [Rh(nbd)  $(PMe_2Ph)_3$ ]BF<sub>4</sub> (nbd = norbornadiene) as a catalyst under conditions of 96 bar  $H_2/CO_2$  (1:1) at 40±1 °C in wet tetrahydrofuran (THF) (Tsai & Nicholas, 1992). In 2004, Hayashi et al. reported a TON of 55 using a water soluble Ru catalyst,  $[(C_6(CH_3)_6)Ru(4,40-dmbpy)(H_2O)]SO_4$ (dmbpy=dimethoxy-2,2'-bipyridine), under 2.5 MPa CO<sub>2</sub>/5.5 MPa H<sub>2</sub> (Hayashi et al., 2004). Additionally, Moret et al. reported a TON of 74 and an FA concentration of 0.2 M in water under conditions of 20 MPa  $H_2/$  $CO_2$  (3:1) (Moret et al., 2014). They found that the use of DMSO as the solvent increased the TON to 750. Also, Lu et al. (2016) in 2016 reported a TOF of 13,000  $h^{-1}$  under 50 bar  $H_2/CO_2$  (1:1) using an Ir catalyst to hydrogenate CO<sub>2</sub> to FA in an aqueous medium. However, the FA concentration was low (0.005 M). Increasing the pressure to 76 bar exceeded the TON of 10,000, and the FA concentration reached 0.117 M. Tossaint et al. (2022) was achieved high TOF numbers of 1,100,000  $h^{-1}$  in the presence of Ru-PNP pincer complex and showed the activation energy of CO<sub>2</sub> hydrogenation of 65 kJ/mol. Rohmann et al. (2016) demonstrated that [Ru(acriphos)(PPh<sub>2</sub>)(Cl)-(PhCO<sub>2</sub>)] (acriphos: 4,5-bis(diphenylphosphino)acridine) catalyzes the hydrogenation of CO<sub>2</sub> to FA under 80 bar  $H_2/CO_2$  (1:1) at 60 °C in DMSO, reaching a TON of 1094 (0.09 M FA) after 16 h. Interestingly, a solvent mixture of 5 vol.% H<sub>2</sub>O/DMSO enhanced the TON to 4200 (0.33 M FA). The specific water concentration is crucial, as low or high concentrations adversely affect the yield. Density functional theory (DFT) calculations revealed the favorable effects of water molecules and suggested the thermodynamic stabilization of FA. Repeating this experiment in the presence of acetic acid buffer (CH<sub>3</sub>COOH/ CH<sub>3</sub>COONa 1:1, pH 4.75) nearly quadrupled the FA concentration to 1.27 M, achieving a TON of 16,310. Westhues et al. recently demonstrated that [Ru(N-triphosCy) (N-triphos = N, N, N-tris(dicyclohexyl-phosphi-(tmm)] nomethyl)amine, tmm=trimethylmethane), which contains a sterically demanding cyclohexyl group, catalyzes the hydrogenation of  $CO_2$  in the presence of Al(OTf)<sub>3</sub> (OTf=trifluoromethanesulfonate) as a Lewis acid additive (Westhues et al., 2019). Under 120 bar  $H_2/60$  °C in MeOH/dioxane (3:1) mixture saturated with CO<sub>2</sub>, FA was formed, which was then converted to methyl formate with a maximum TON of 9,542. ILs containing basic anions are beneficial for efficient CO<sub>2</sub> hydrogenation under base-free conditions. In 2020. Weilhard et al. (2020) reported the use of a Ru catalyst in 1-butyl-3-methylimidazolium acetate (BMIM-OAc) IL, serving as a buffering medium for CO<sub>2</sub> hydrogenation. The IL stabilized the pH and prevented catalyst deactivation, whereas the acetate counter anion improved the selectivity for FA synthesis. Using 5 vol.% H<sub>2</sub>O/DMSO as the solvent under 60 bar  $H_2/CO_2$  (1:1) at 70 °C, they reached a TOF of 4520 after 72 h. Additionally, in 2021, using the same IL as the solvent and a Ru-CNC pincer complex as the catalyst, with the addition of Sc(OTf)<sub>3</sub> as a cocatalyst, Weilhard et al. achieved a CO<sub>2</sub> hydrogenation TON of 126,000 and TOF of 22,000  $h^{-1}\!,$  with a final FA concentration of 0.36 M. (Weilhard et al., 2021) Similarly, in 2023, Hu et al. developed an immobilized catalyst for FA hydrogenation/dehydrogenation by supporting  $Ir(COD)Cl(PPh_3)$ (COD=cyclooctadienyl) on polymerized triphenylphosphine KAPs(Ph-PPh<sub>3</sub>) (KAPs=knitting aromatic polymers) (Hu et al., 2023). Hydrogenation/dehydrogenation was performed using KAPs(Ph-PPh<sub>3</sub>-Ir) as the dissolved



Fig. 11 Recycling of catalyst and ionic liquid in the  $CO_2$  hydrogenation. (Hu et al., 2023) Reprinted from Hu et al., (2023) with permission from Elsevier

homogeneous catalyst and 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as the solvent. Bases such as DBU are known for  $CO_2$  hydrogenation, yet ionic liquids have a similar effect. With BMIM-OAc, a maximum TON of 53,832 (21 h) was achieved. Firstly, ILs do not evaporate, facilitating easy distillation of the produced FA. Distillation with [EMIM]Cl resulted in 99.5% FA. Furthermore, no performance degradation was observed after 5 recycling (Fig. 11).

#### Formic acid hydrogen storage and release system

In 1978, Williams et al. (1978) proposed a process for hydrogen storage and release that reversibly converts FA and CO<sub>2</sub>. Several researchers have pursued catalyst development to enable this theoretically feasible cycle; however, achieving a reversible cycle has proven elusive for many. In 2014, Lee et al. (2014) accomplished FA dehydrogenation at TON 106 and TOF 144 h<sup>-1</sup> at room temperature in water using a Pd/mpg-C<sub>3</sub>N<sub>4</sub> catalyst  $(mpg-C_3N_4 = mesoporous graphitic carbon nitride)$ . They also managed CO<sub>2</sub> hydrogenation in water by incorporating triethylamine at 150 °C, yet Pd/mpg-C<sub>3</sub>N<sub>4</sub> catalyst fell short in facilitating a successful reversible cycle integrating  $H_2$  storage and release. In 2017, Mori et al. (2017) explored FA dehydrogenation and CO<sub>2</sub> hydrogenation using a Pd/Ag-based catalyst supported on silica. This catalyst exhibited a TOF of 631 h<sup>-1</sup> for FA dehydrogenation and achieved catalytic activity of about 100 h<sup>-1</sup> for  $CO_2$  hydrogenation in a basic aqueous solution. Although three cycles of recycling were conducted for CO<sub>2</sub> hydrogenation without notable activity decline, tests encompassing H<sub>2</sub> storage and release, notably FA dehydrogenation, remained unexplored. Zhong et al. proposed a hydrogen carrier system for the mutual conversion of carbon dioxide and FA using graphene-supported Pd-Au catalysts. They reported FA dehydrogenation with a TOF of 7,180 h<sup>-1</sup>, producing over 85% potassium formate within 2 h of CO<sub>2</sub> hydrogenation, showcasing the potential of the FA cycle (Zhong, et al., 2018a, b). Nonetheless, actual recycling tests were not executed due to the technicalities involved in constructing a hydrogenation/ dehydrogenation cycle, which necessitates adept chemical engineering techniques. The separation of FA from the reaction solution post-hydrogenation, and the isolation of the catalyst from the reaction solution are pivotal, prompting numerous attempts to employ easily separable solid or immobilized catalysts. Despite these efforts, successful examples have remained scarce. On the other hand, reports have shown successful reversible H<sub>2</sub> cycles using homogeneous catalysts. In 2013, Hull et al. (2012) proposed a mild-condition reversible hydrogen storage system using a dinuclear Cp\*Ir complex catalyst. Ir, Rh, and Ru complexes, with proton-responsive ligands, facilitate system recycling by adding base (KHCO<sub>3</sub>) and acid (H<sub>2</sub>SO<sub>4</sub>) before conducting CO<sub>2</sub> hydrogenation and FADH, respectively, adjusting pH accordingly. Sordakis et al. (2015) reported an  $H_2$  storage and release cycle using bicarbonates in 2015. The catalyst, generated in situ with  $[RuCl_2(mTPPTS)_2]_2 + mTPPTS$  (mTPPTS=triphenylphosphine trisulfonate), displayed activity in producing formate salts via CO<sub>2</sub> hydrogenation and the dehydrogenation of formate salts. These reaction systems were tested for continuous H<sub>2</sub> storage and release cycles, completing five consecutive operations with conversion rates of approximately 95% for CO<sub>2</sub> hydrogenation and 62% for formate salt dehydrogenation.

Yamashita proposed a reversible H<sub>2</sub> production system using a Pd-Ag catalyst supported on mesoporous carbon (MSC) (Masuda et al., 2018). This catalyst exhibited a TOF of 5638 h<sup>-1</sup> for FA dehydrogenation and a TON of 839 for CO<sub>2</sub> hydrogenation, enabling three reversible H<sub>2</sub> storage and release cycles without significant loss of activity. Recently, Piccirilli et al. (2023) demonstrated that a Ru-PNP pincer complex was highly active in producing FA by CO<sub>2</sub> hydrogenation in the presence of an IL. They achieved a TON exceeding 32,000 under 60 bar  $(CO_2:H_2=1:1)$  at 80 °C for over 36 h. This catalyst was also effective for the dehydrogenation of FA under similar IL conditions, yielding a total TON of 11.8 million over 112 days. They illustrated that by controlling the pressure and temperature, the catalyst system equilibrium could shift between hydrogenation and dehydrogenation, achieving up to 13 cycles. In 2023, Verron et al. reported results for hydrogenation/dehydrogenation reactions under base-free conditions, with a TOF of 157  $h^{-1}$  for FA dehydrogenation and 5.4 h<sup>-1</sup> for carbon dioxide

(TON=92 for 17 h), using a *p*-coordinated phenoxy ruthenium dimer pre-catalyst (Verron et al., 2023). Verron et al. and Wei et al. successfully developed a CCHC system for storing hydrogen as formic acid at ambient temperature for several days, with the capability to regenerate hydrogen by heating at 90 °C repeatedly. However, as the catalyst remains in the formic acid solution, there is a risk that FADH process could gradually proceed, resulting in the conversion of the generated FA into  $H_2$ and CO<sub>2</sub>. Consequently, removing the catalyst from the solution is crucial for extended storage and ensuring safe transportation. Recently, Wei et al. also proposed a system that uses esters or amides of FA as CCHCs instead of FA. For instance, pincer-type Ru complexes have shown the capability of producing hydrogen with a relatively high TOF (8,376 h<sup>-1</sup>) under basic conditions from methyl formate. Moreover, under basic conditions, they established a hydrogen storage/production system from  $CO_2$  + amines or amino acids (morpholine, lysine, etc.) and FA amides using Mn and Fe pincer-type complexes, reporting a TOF value of 2,450  $h^{-1}$  (TON = 29,400 in 12 h) over 10 cycles (Wei et al., 2023). While hydrogen  $(H_2)$  is regulated by ISO 14687-2 and must be purified to exceed 99.97% with less than 0.1 ppm of amines and under 0.2 ppm of CO, the purity of regenerated  $H_2$ demands careful consideration. Furthermore, prolonged use of a catalyst can lead to its degradation and decreased activity, which in turn may increase CO production due to the reduced selectivity of the degraded catalyst. Although numerous studies have reported that catalysts do not produce CO, as analyzed by gas chromatography (GC-TCD) with a detection limit of a few ppm, it's still unclear whether the CO content stays below 0.2 ppm. For example, a homogeneous Ir catalyst (Cp\*Ir-4DABP), which is highly active for FADH, initially produces CO at a concentration of 1.6 ppm. However, this concentration gradually decreases to 0.2 ppm or lower after a few hours, as observed. (Sawahara et al., 2004) (Figs. 12, 13).



Fig. 12 Neutral carbon hydrogen storage and release in the presence of *p*-coordinated phenoxy ruthenium dimer pre-catalyst (Verron et al., 2023) (Reprinted with permission from Verron et al. Copyright 2023, American Chemical Society)



Fig. 13 Fe promoted partially reversible carbon neutral hydrogen stargate and release cycle using formamide. (Wei et al., 2023). (Reprinted with permission from Wei et al. (2023). Copyright 2023, Springer Nature)

Although practical applications of  $H_2$  carriers with FA or formate are still limited, there are emerging examples, such as DENS B.V. in the Netherlands, which is actively developing FA batteries. However, their system does not include a CO<sub>2</sub> capture system at the present time. Therefore, the development of an effective CO<sub>2</sub> capture process is essential to promote the use of FA as a  $H_2$  carrier worldwide. This could be the integration of systems such as Cansolv<sup>®</sup> CO<sub>2</sub> capture system or the KS-1 (or KS-21) & KM CDR process. In addition, a simple high-pressure gas–liquid separation process can be used to separate and purify  $H_2$  and CO<sub>2</sub>, although few catalysts are capable of extracting high-pressure gas from FA.

## Conclusions

In this review, we discussed MeOH, DME, and FA as organic compounds capable of undergoing repeated dehydrogenation/hydrogenation cycles, possessing substantial hydrogen storage capacities within organic hydrogen carrier systems (CCHC) that interchange with CO<sub>2</sub>. When considering CCHCs, it is essential to contemplate the CO<sub>2</sub> circulation process alongside the H<sub>2</sub> storage and H<sub>2</sub> production processes. Among MeOH, DME, and FA, MeOH exhibits a higher H<sub>2</sub> storage capacity per mole than FA, and its market price is lower than that of FA. However, FA requires a lower reaction temperature for CO<sub>2</sub> synthesis and dehydrogenation, making it seemingly more profitable. Moreover, FA's capacity to generate high-pressure gases during FA dehydrogenation is significant as it facilitates the subsequent cryogenic separation of H<sub>2</sub> and CO<sub>2</sub>. There is a wealth of reports on technology capable of regenerating FA by utilizing separated liquefied CO<sub>2</sub>, and currently, FA seems to hold advantages for use as a CCHC. Looking ahead, we anticipate that advancements in  $H_2$ energy technologies will lead to more practical applications, with reports suggesting MeOH and DME as commercially viable CO<sub>2</sub> circulation H<sub>2</sub> carriers.

#### Acknowledgements

The authors acknowledge the financial support by the Canon Foundation and the support by JST, establishment of university fellowships towards the creation of science technology innovation, Grant Number JPMJFS2106.

#### Author contributions

SO, DCS, RK, and HK prepared the original draft from the conceptualization guided by HK. All authors also reviewed and revised, and HK edited, proofread, and finalizing the manuscript.

#### Funding

This study was supported by Japan Science and Technology Agency (JPM-JFS2106); Canon Foundation

#### Availability of data and materials

No datasets were generated or analyzed during the current study.

# Declarations

### **Competing interests**

The authors decleare that they have no competing interests.

Received: 14 December 2023 Accepted: 30 January 2024 Published online: 24 February 2024

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