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Carbon Dioxide to Methanol: the Aqueous Catalytic Way at Room Temperature

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Abstract: Carbon dioxide may constitute a source of chemicals and fuels if efficient and renewable processes are developed that directly utilize it as feedstock. Two of its reduction products are formic acid and methanol, which have also been proposed as liquid organic chemical carriers in sustainable hydrogen storage. Here we report that both the hydrogenation of carbon dioxide to formic acid and the disproportionation of formic acid into methanol can be realized at ambient temperatures and in aqueous, acidic solution, with an iridium catalyst. The formic acid yield is maximized in water without additives, while acidification results in complete (98%) and selective (96%) formic acid disproportionation into methanol. These promising features in combination with the low reaction temperatures and the absence of organic solvents and additives are relevant for a sustainable hydrogen/methanol economy.

The catalytic reduction of atmospheric carbon dioxide with "green" hydrogen gas can provide a pathway for the transformation of a troublesome, yet inexpensive and widely available carbon source into value-added chemicals.^[1,2] Among potential products, formic acid's (FA) significance lies in its broad range of applications, while methanol (MeOH) serves as an indispensable platform molecule in various chemical processes and constitutes the primary fuel of a methanol economy.^[3,4] In addition, both FA and MeOH may be utilized as easy-to-handle H₂ storage media.^[5] The group of Sasaki firstly obtained methanol, methane and CO from homogeneous CO₂ hydrogenation with Ru₃(CO)₁₂ at 240 °C.^[6] In recent years, a number of groups has investigated the conversion of CO₂ derivatives or CO₂ to methanol in the presence of homogeneous catalysts.^[7–14] Common features of these works were high temperatures (over 100 °C), the employment of organic solvents and, in certain cases, low selectivities. Alternatively, MeOH can be obtained from a stepwise approach, comprising CO₂ hydrogenation to formic acid (Equation 1) and disproportionation reaction report a MeOH yield of 50% (with 50% competing dehydrogenation) in THF at 150 °C, in the presence of a ruthenium-phosphine catalyst and a methanesulfonic acid additive.^[16]

Himeda et al. have studied the $[(Cp^*)Ir(dhbp)(OH_2)][SO_4]$ catalyst **(1)** (dhbp = 4,4'-dihydroxy-2,2'bipyridine, Cp* = pentamethylcyclopentadienyl) (Figure S4) in bicarbonate hydrogenation to formate (i.e. in basic media) and formic acid dehydrogenation.^[18] Herein we report that complex **(1)** catalyzes direct CO₂ hydrogenation to formic acid in acidic media without additives, as well as FA disproportionation (98% conversion) into methanol (96% selectivity), notably in aqueous acidified solution and at ambient temperature (Equation 2).

$$H_{2(aq)} + CO_{2(aq)} \rightarrow HCOOH_{(aq)}, \Delta G^{\circ}_{298} = -4 \text{ kJ mol}^{-1}$$
(1)

$$3\text{HCOOH}_{(1)} \rightarrow \text{CH}_{3}\text{OH}_{(1)} + \text{H}_{2}\text{O}_{(1)} + 2\text{CO}_{2(g)}, \Delta\text{G}^{\circ}_{298} = -105 \text{ kJ mol}^{-1}$$
(2)

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Pressurization of an aqueous 8 mm (millimolal, i.e. mmol per kg_{H20}) solution of **(1)** with 20 bar ¹³CO₂ and 60 bar H₂, in the absence of organic solvents and additives, afforded a 0.05 m FA solution after 1.5 h at 60 °C (Figure 1, blue squares). Decreasing the temperature to 25 °C, favored FA formation due to the exothermic nature of this reaction, yielding a 0.1 m FA solution (Figure 1, grey squares and Scheme 1a). When the reaction was repeated in the presence of 2.5 m sulfuric acid (H₂SO₄) under 20 bar ¹³CO₂ and 60 bar H₂ pressure at 70 °C, concomitant production of MeOH occurred (Figure 1, green circles). Monitoring the reaction by ¹³C NMR spectroscopy revealed that formic acid formation preceded that of methanol, indicative of the latter originating from formic acid disproportionation and not direct CO₂ hydrogenation (Scheme 1b).



Figure 1. Time course of FA and MeOH formation from CO₂ hydrogenation with **(1)**. $P(^{13}CO_2) = 20$ bar, $P(H_2) = 60$ bar, $n_{cat} = 15.9 \mu mol$, $m_{H2O} = 2.0$ g. FA concentrations obtained at $60 \degree C$ (), at $25 \degree C$ () and in 2.5 m H₂SO₄ at 70 °C (). MeOH () concentrations were detected in the presence of H₂SO₄ at 70 °C, under these conditions. Dashed curve indicates the observable decrease in FA concentration due to continuous MeOH formation (for explanation see Figure S1). The trend lines are shown as a guide and are not a mathematical fit of the data.



Scheme 1. Direct CO₂ transformation to FA and MeOH with complex **(1)**. $P(^{13}CO_2) = 20$ bar, $P(H_2) = 60$ bar, $n_{cat} = 15.9 \mu mol$, $m_{H2O} = 2.0$ g. ¹³C NMR spectra recorded every 3 h, showing a) the increase of the FA doublet at 25 °C, b) the increase of the FA doublet and the MeOH quartet in 2.5 m H₂SO₄ at 70 °C.

Even though sulfuric acid favored MeOH production, it was not indispensable; MeOH was also detected after 20 h at 50 °C or 6 d at 25 °C in the absence of H_2SO_4 under otherwise identical reaction conditions. When an aqueous solution containing 8 mm (1) was left to equilibrate at 20 °C under 20 bar ¹³CO₂ and 60 bar H_2 in the absence of H_2SO_4 , 0.16 m FA and 0.013 m MeOH were obtained. These results constitute the first demonstration of direct CO₂ transformation to MeOH in a "one-pot" homogeneous reaction, in aqueous solution without additives and at ambient temperature. In addition, this FA concentration is comparable to the only reported yield for FA synthesis under similar conditions (i.e. in the absence of base).^[19]

We subsequently aimed at optimizing the formic acid disproportionation reaction, by directly utilizing FA as substrate. Heating a 5 m aqueous H¹³COOH solution at 50 °C in the presence of 8 mm catalyst **(1)** under isochoric conditions (i.e. at constant volume, resulting in a pressure build-up due to

FA dehydrogenation), resulted in the formation of H₂ and ¹³CO₂ as the main products (Figure S2). Simultaneously ¹³CH₃OH with a selectivity of 1.2% was also detected in solution by ¹³C NMR spectroscopy (Table 1, Entry 1). No carbon monoxide (¹³CO) was observed, indicating that formic acid decarbonylation did not occur. No further products were detected. Increasing the reaction temperature obviously favored formic acid dehydrogenation and lowered the methanol selectivity ($\Delta H^{\circ}_{dehyd.} = +31.5 \text{ kJ mol}^{-1} \text{ vs } \Delta H^{\circ}_{disprop.} = -35.6 \text{ kJ mol}^{-1})^{[2,15]}$ (Table S1). Methanol formation always started without an activation period and its concentration increased nearly linearly for the first 15 h at 20 °C (Figure S3).

Entry	T (°C)	H_2SO_4 conc. (<i>m</i>)	FA conv. (%)	t (h)	MeOH sel. (%)
1	50	-	98 ± 1	3.5	1.2 ± 0.1
2	50	0.35	98 ± 1	8	10 ± 1
3	50	1.25	98 ± 1	30	21 ± 1
4	50	1.75	98 ± 1	30	29 ± 3
5	50	2.50	98 ± 1	72	59 ± 1
6	50	3.70	98 ± 1	90	59 ± 2
7 ^[b]	50	1.75	96 ± 3	40	3 ± 1
8 ^[c]	20	2.50	60 ± 4	312	97 ± 2
9 ^[d]	50	2.50	98 ± 1	72	96 ± 1

Table 1. Results for FA disproportionation reaction with complex (1) under isochoric conditions^[a]

[a] 10.0 mmol H¹³COOH, $n_{cat} = 15.9 \mu$ mol, $m_{H2O} = 2.0 \text{ g}$. FA conversions and MeOH selectivities were calculated by quantitative ¹³C NMR spectroscopy,^[20] unless otherwise stated. The difference between these values corresponds to FA dehydrogenation (apart from MeOH, H₂/CO₂ and traces of CH₃OOCH were produced). [b] Reaction performed under atmospheric pressure under a N₂ atmosphere. [c] Pre-pressurization with 100 bar H₂. [d] Pre-pressurization with 50 bar H₂, MeOH and FA were detected by GC and HPLC, respectively, n_{FA} = 21.6 mmol, n_{cat} = 32.2 µmol, m_{H2O} = 4.0 g.

Addition of H_2SO_4 to an aqueous 5 *m* H¹³COOH solution containing 8 m*m* (1), significantly enhanced MeOH formation and catalyzed the esterification reaction between FA and MeOH towards methyl formate (CH₃OOCH), with the latter, however, being readily reversible (selectivity for CH₃OOCH was

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always below 2% under optimized conditions). The best MeOH selectivities were obtained with complex (1) in the presence of H_2SO_4 , as demonstrated by screening tests of various catalysts and acid additives (Figure S4, Tables S3 and S4). Optimization of the sulfuric acid concentration (Table 1, entries 2-6) resulted in a MeOH selectivity of 59% for 98% FA conversion, in an aqueous 2.5 m H_2SO_4 solution at 50 °C (Table 1, entry 5 and Scheme 2). The only products detected by ${}^{1}H/{}^{13}C$ NMR spectroscopy, HPLC and GC were methanol, methyl formate, H_2 and CO_2 . Sulfuric acid concentrations above 2.5 m did not further promote FA disproportionation (Table S5). Under these reaction conditions complex (1) provided a cumulative MeOH concentration of 3.2 m after three recyclings (addition of 10.0 mmol $H^{13}COOH$ per cycle) with 99% FA conversion. In a single catalytic cycle, doubling the initial FA and H_2SO_4 concentrations (20 m FA and 5 m H_2SO_4) produced a 2 m MeOH solution, corresponding to a selectivity of 60% (Table S6, entry 2).



Scheme 2. Time course of a FA disproportionation reaction. a) 100 MHz ¹³C NMR spectra recorded every 1.5 h, showing the decrease of the FA doublet and the increase of the MeOH quartet in the presence of complex (1) and $2.5 m H_2SO_4$ under isochoric conditions, b) concentrations of decomposed FA and formed MeOH derived from (a). Experimental conditions: 10.0 mmol H¹³COOH, $n_{cat} = 15.9 \mu$ mol, $m_{H2O} = 2.0 \text{ g}$, T = 50 °C.

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Monitoring pressure evolution in the presence of H_2SO_4 revealed decreased gas production with increasing solution acidity, in agreement with confined FA dehydrogenation and enhanced disproportionation (Figure 2). In addition, the CO₂ concentration in the produced gas mixture rose to 64% in the presence of 2.5 m H₂SO₄ from 50% in the absence of H₂SO₄ (originating only from formic acid dehydrogenation). These results corroborated the occurrence of the FA disproportionation reaction. Control experiments were also performed; heating a 3.6 m aqueous FA/sulfuric acid mixture (1/0.75) at 70 °C for 48 h in the absence of iridium catalyst resulted in no pressure increase.



Figure 2. Effect of sulfuric acid concentration on pressure increase due to H_2 and CO_2 formation from formic acid disproportionation/dehydrogenation reactions in the presence of **(1)** under isochoric conditions. Experimental conditions: $n_{FA} = 10.0 \text{ mmol}$, $n_{cat} = 15.9 \text{ }\mu\text{mol}$, $m_{H2O} = 2.0 \text{ g}$, $T = 50 \text{ }^\circ\text{C}$.

The acidic environment itself was not the only parameter for promoting FA disproportionation; both acidic media and H₂ pressure resulted in higher MeOH selectivities. When a 5 *m* FA solution was heated in the presence of 1.75 *m* H₂SO₄ under atmospheric pressure (i.e. no pressure build-up), methanol selectivity dropped from 29 to 3% (Table 1, entries 4 and 7). Increased methanol selectivities under elevated H₂/CO₂ pressure were also reported by Cantat and co-workers.^[16] Therefore, FA disproportionation reactions with a preceding H₂ pressurization step were performed, resulting in an excellent MeOH selectivity of 97% alongside 60% FA conversion at 20 °C (Table 1, entry 8). Likewise, at 50 °C under 50 bar of initial H₂ gas pressure, practically complete FA conversion (98%) into MeOH was achieved with a methanol selectivity of 96% (Table 1, entry 9). To date, these are the best values obtained for the formic acid disproportionation reaction and constitute a significant improvement in terms of methanol selectivity, reaction temperature and type of solvent.

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The "self-induced" formic acid reduction to methanol (Equation 3) with H₂ gas originating from the formic acid dehydrogenation reaction was excluded because it would be unequivocally accompanied by a "delay" in methanol formation. This delay would be linked to the time necessary to build-up the required H₂ pressure in order to ensure adequate H₂ concentration in the aqueous solution. However, since H₂SO₄ greatly decreased the FA dehydrogenation/H₂ generation rate, MeOH formation without an activation period (Scheme 2 and Figure S3) via Equation 3 was ruled out. Employing isotopically enriched D₂ gas to elucidate the nature of the reactions, resulted in inconclusive results due to much faster H⁺/D⁺ exchange catalyzed by **(1)** (Figure S5).^[21]

$$HCOOH_{(aq)} + 2 H_{2(aq)} \rightarrow CH_3OH_{(aq)} + H_2O_{(aq)}$$
(3)

The decrease in MeOH selectivity under atmospheric pressure can be rationalized through a reaction mechanism operating via multiple non-classical hydride moieties, dependent on equilibria influenced by H₂ pressure. A similar phenomenon has already been reported for the iron-catalyzed formic acid dehydrogenation reaction; elevated H₂ pressure hindered H₂ elimination from an FeH(H₂) complex and therefore the progression of the catalytic cycle.^[22]

The FA-to-MeOH transformation occurring via formaldehyde intermediacy was excluded because the latter was never detected by ¹³C NMR spectroscopy or GC/HPLC techniques during our studies. It was therefore reasonable to assume that the FA-to-MeOH transformation took place in the first coordination sphere of the iridium metal, incorporating a formato moiety, n^2 -H₂ ligand(s) and/or terminal hydride(s), with similar iridium polyhydrides already known.^[23] Rearrangement of the Cp* ligand on (1), i.e. ring-slippage from η^5 -C₅Me₅ to η^3 -C₅Me₅ and/or η^1 -C₅Me₅, could provide the required vacant coordination sites.^[24] Throughout FA dehydrogenation reactions in the absence of H_2SO_4 , a signal for the monohydridic form of (1) at -11.3 ppm, (1'), was present in the ¹H NMR spectrum.^[25] Addition of H₂SO₄ resulted in the disappearance of (1'), thus explaining the reduced catalytic activity for FA dehydrogenation, while multiple new resonances appeared in the hydride region of the ¹H NMR spectrum (Figure S6). Despite several attempts to derive structural information on these signals from quantification and multiplicity resolution studies, we were limited by fluxional behavior, low concentration of the dynamically formed catalytic species as well as low catalyst solubility. In agreement with literature reports, H_2SO_4 can protonate previously formed hydride moleties, yielding species with coordinated η^2 -H₂ ligands, which would then rapidly release H₂ gas.^[25] We reason that the role of H₂ pressure was to stabilize these η^2 -H₂ structures (i.e. shift the equilibria S7), implicated towards complexes **(II)**, Figure which were further in FA reduction/disproportionation.

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In conclusion, we demonstrated that catalyst **(1)** possesses multiple functionalities that can be "tuned", depending on the process of interest. First of all, it catalyzes the hydrogenation of CO₂ to formic acid in aqueous acidic media without additives, unlike most reported complexes that require forcing basic conditions. In addition, formic acid can undergo complete disproportionation into MeOH with unprecedented selectivities of 96% with the same catalyst in the presence of H₂SO₄, with FA conversions of 98%. The "one-pot" homogeneous production of both FA and MeOH was demonstrated in a single reaction performed at 20 °C, where an aqueous solution of **(1)** without additives was pressurized with 20 bar ¹³CO₂ and 60 bar H₂. The catalyst operating in water, endorses the "green" character of the system. Conveniently, MeOH-H₂O solutions do not form an azeotrope (in contrast to several MeOH-organic solvent mixtures), facilitating their separation via distillation.^[14] The reactions realized by catalyst **(1)** are relevant to various fields of research, such as CO₂ valorization, sustainable H₂ storage and alternative FA/methanol production.

Experimental Section

All experiments were prepared without precluding air, unless otherwise stated. The selectivity for MeOH was calculated according to Equation 2, as three times the moles of MeOH produced divided by the amount of FA consumed. Concentrations are given in terms of molality (*m*), i.e. mol per kg_{solvent}. In a typical CO₂ hydrogenation reaction an aqueous solution of **(1)** was pressurized with ¹³CO₂, completed with H₂ to a given pressure, thermostated and then the reaction was monitored by ¹³C NMR spectroscopy. In a typical FA disproportionation reaction an aqueous FA solution, containing **(1)** and the acid additive was heated in a sapphire NMR tube, Parr autoclave or in a Schlenk tube equipped with a condenser under a N₂ atmosphere. The reaction was followed by monitoring the pressure increase due to gas evolution as a function of time, and/or by ¹³C NMR spectroscopy, and/or by GC/HPLC techniques (see Supporting Information for details).

Acknowledgements

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Figure 1. Time course of FA and MeOH formation from CO₂ hydrogenation with **(1)**. $P(^{13}CO_2) = 20$ bar, $P(H_2) = 60$ bar, $n_{cat} = 15.9 \mu mol$, $m_{H2O} = 2.0$ g. FA concentrations obtained at $60 \ C$ (), at $25 \ C$ () and in 2.5 *m* H₂SO₄ at 70 °C (). MeOH () concentrations were detected in the presence of H₂SO₄ at 70 °C, under these conditions. Dashed curve indicates the observable decrease in FA concentration due to continuous MeOH formation (for explanation see Figure S1). The trend lines are shown as a guide and are not a mathematical fit of the data.

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Scheme 2. Time course of a FA disproportionation reaction. a) 100 MHz ¹³C NMR spectra recorded every 1.5 h, showing the decrease of the FA doublet and the increase of the MeOH quartet in the presence of complex (1) and $2.5 m H_2SO_4$ under isochoric conditions, b) concentrations of decomposed FA and formed MeOH derived from (a). Experimental conditions: 10.0 mmol H¹³COOH, $n_{cat} = 15.9 \mu$ mol, $m_{H2O} = 2.0 \text{ g}$, T = 50 °C.

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Entry	т (°С)	H ₂ SO ₄ conc. (<i>m</i>)	FA conv. (%)	t (h)	MeOH sel. (%)
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Table 1. Result	ts for FA dispro	portionation r	eaction with c	omplex (1)) under	isochoric c	onditions ^[a]
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[a] 10.0 mmol H¹³COOH, $n_{cat} = 15.9 \mu$ mol, $m_{H2O} = 2.0 \text{ g}$. FA conversions and MeOH selectivities were calculated by quantitative ¹³C NMR spectroscopy,^[20] unless otherwise stated. The difference between these values corresponds to FA dehydrogenation (apart from MeOH, H₂/CO₂ and traces of CH₃OOCH were produced). [b] Reaction performed under atmospheric pressure under a N₂ atmosphere. [c] Pre-pressurization with 100 bar H₂. [d] Pre-pressurization with 50 bar H₂, MeOH and FA were detected by GC and HPLC, respectively, n_{FA} = 21.6 mmol, n_{cat} = 32.2 µmol, m_{H2O} = 4.0 g.

Text for Table of Contents

An iridium complex was successfully employed in the direct, homogeneous transformation of carbon dioxide to formic acid and methanol, via formic acid disproportionation, in aqueous solution and at ambient temperature. Unprecedented methanol selectivities of 96% were obtained for complete formic acid conversion in the presence of sulfuric acid under optimized conditions. The reactions reported herein might be beneficial in the fields of CO₂ valorization, sustainable H₂ storage and alternative formic acid/methanol production.



Keywords

carbon dioxide, formic acid, homogeneous, hydrogenation, methanol