

Review

Homogeneous Catalytic Dehydrogenation of Formic Acid: Progress Towards a Hydrogen-Based Economy

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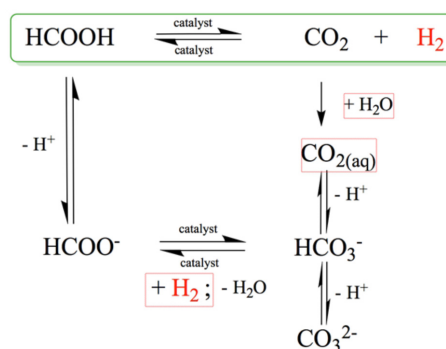
Um dos fatores limitantes de uma economia baseada em hidrogênio está associado à problemas de estocagem de hidrogênio. Muitas abordagens diferentes estão sendo avaliadas e uma abordagem ótima não será a mesma para todas as aplicações, i.e., necessidades estática, móvel, pequena e grande escala, etc. Neste artigo, foca-se no ácido fórmico como molécula promissora para o estoque de hidrogênio, que, em certas condições catalíticas, pode ser desidrogenado gerando hidrogênio altamente puro e dióxido de carbono, com níveis extremamente baixos de monóxido de carbônico gasoso produzido. Vários catalisadores homogêneos disponíveis que geralmente operam em soluções aquosas de ácido fórmico são descritos. Também é descrita brevemente a reação reversa que pode contribuir para tornar o uso de ácido fórmico em estoque de hidrogênio ainda mais atrativo.

One of the limiting factors to a hydrogen-based economy is associated with the problems storing hydrogen. Many different approaches are under evaluation and the optimum approach will not be the same for all applications, i.e., static, mobile, small and large scale needs, etc. In this article we focus on formic acid as a promising molecule for hydrogen storage that, under certain catalytic conditions, can be dehydrogenated to give highly pure hydrogen and carbon dioxide with only extremely low levels of carbon monoxide gas produced. We describe the various homogeneous catalysts available that usually operate in aqueous formic acid solutions. We also briefly describe the reverse reaction that would contribute to making the use of formic acid in hydrogen storage even more attractive.

Keywords: hydrogen economy, hydrogen storage, homogeneous catalysis, formic acid, sustainable chemistry, ruthenium, carbon dioxide

1. Introduction

A cyclic process involving formic acid and carbon dioxide/hydrogen has been proposed as an efficient way to store and generate hydrogen when it is needed (Scheme 1).¹ Indeed, in the last few years, research on the use of formic acid as a hydrogen storage vector has grown rapidly.² The reason for this interest is threefold. First, formic acid contains 4.4 wt.% of H₂, which is equivalent to 53 g hydrogen *per* litre and has a flash point of 69 °C, much higher than that of the gasoline (−40 °C) and methanol (12 °C). Second, carbon dioxide and carbonates can be



Scheme 1. The carbon dioxide-formic acid cycle.

hydrogenated to afford formic acid and formates in water and, due to the abundance of CO₂ in the atmosphere, it is an ideal C₁ building block (formic acid has other industrial uses and is therefore an interesting product beyond being a hydrogen storage molecule).^{3,4} Third, the reverse reaction,

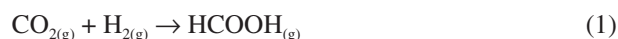
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Dedicated to honor the memory of Prof Roberto F. de Souza, whose sudden death brought to an end an exceptional scientific career well before expected.

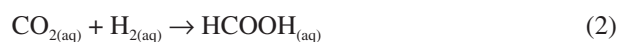
i.e., the dehydrogenation of formic acid to give CO₂ and hydrogen is fast and controllable and would be ideal not only for static applications, but also potentially for mobile applications.³

2. Research on Hydrogenation of Carbon Dioxide

The hydrogenation carbon dioxide and carbonates to formic acid/formates is still a challenging reaction to catalyse in an efficient manner.⁴ While the reaction can be catalysed with heterogeneous catalysts,⁵ more effort is devoted to heterogeneous methanation catalysts instead of catalysts that give formic acid. Hence, the direct hydrogenation of carbon dioxide to formic acid/formates is usually catalysed by homogeneous catalysts in aqueous solution.⁴ Irrespective of the type of catalyst used the rate of this reaction depends strongly on the pH of the solution, with basic solutions resulting in highest reaction rates and conversions. The first product of the stepwise reduction of CO₂ with H₂ is the formic acid, but in gas phase this reaction does not take place,⁶ as $\Delta G_{298}^{\circ} = +32.9 \text{ kJ mol}^{-1}$ (equation 1):



Dissolution of the gases decreases the entropy term; in aqueous solution, this reaction becomes slightly exergonic with $\Delta G_{298}^{\circ} = -4 \text{ kJ mol}^{-1}$ (equation 2):



Addition of a base improves the enthalpy of the reaction ($\Delta G_{298}^{\circ} = -35.4 \text{ kJ mol}^{-1}$; $\Delta H_{298}^{\circ} = -59.8 \text{ kJ mol}^{-1}$; $\Delta S_{298}^{\circ} = -81 \text{ J mol}^{-1} \text{ K}^{-1}$), making this reaction largely available (equation 3):



A particularly well-studied class of catalyst comprises ruthenium(II) complexes with water soluble phosphine ligands (see Table 1). The most recent ruthenium(II) catalytic system reported comprises [RuCl₂(PTA)₄] (PTA = 1,3,5-triaza-7-phosphaadamantane) in dimethyl sulfoxide (DMSO) and operates in the absence of any base, any additives to afford 1.9 mol L⁻¹ formic acid solutions.⁷ This concentration is unprecedented and corresponds to more than two orders of magnitude higher concentration than other catalysts without base. Moreover, the catalyst is highly stable and can be recycled and reused multiple times without loss of activity.

Although water-soluble ruthenium(II) catalysts have been most extensively studied or this reaction other systems have also been investigated (see Table 2). Indeed, the highest turnover number (TON) reported for CO₂ hydrogenation in basic solution, a staggering 3.5 million, was obtained with an Ir(III) complex with a pincer-ligand.¹⁹

Despite of the important goal in catalysis is to replace noble metal-based catalysts with cheap and earth abundant metals, few reports are available. The first row transition metal based catalytic systems in general have with very low activity. An interesting development in the field is

Table 1. Bicarbonate, carbonate and carbon dioxide hydrogenation into formic acid/formate or formic acid derivatives with ruthenium(II) pre-catalysts

Catalyst	Solvent	Base	PCO ₂ /H ₂ / bar	TON	TOF / h ⁻¹	Ref.
[RuH ₂ (PPh ₃) ₄]	Benzene	NEt ₃ /H ₂ O	25/25	87	4	8
[RuH ₂ (PPh ₃) ₄]	scCO ₂	NEt ₃ , H ₂ O	120/80	1'400	1'400	9
[RuCl ₂ (PMe ₃) ₄]	scCO ₂	NEt ₃ , H ₂ O	120/80	7'200	–	6
[RuCl(OAc)(PMe ₃) ₄]	scCO ₂	NEt ₃ /C ₆ F ₅ OH	120/70	32'000	95'000	10
[Ru(6,6'-Cl ₂ bpy) ₂ (H ₂ O) ₂]/(CF ₃ SO ₃) ₂	EtOH	NEt ₃	30/30	5'000	–	11
[RuHCl(CO)(PNP)]	DMF	DBU	10/30	–	1'100'000	12
[TpRu(PPh ₃)(CH ₃ CN)H]	THF	NEt ₃ , H ₂ O	25/25	760	48	13
[TpRu(PPh ₃)(CH ₃ CN)H]	THF	NEt ₃ , CF ₃ CH ₂ OH	25/25	1'815	113	14
[RuCl ₂ (TPPMS) ₂]	H ₂ O	NaHCO ₃	–	320	9'600	15
[Ru(η ⁶ -C ₆ Me ₆)(4,4'-OMe-bpy)(OH ₂)](SO ₄)	H ₂ O	Citrate buffer	–	55	–	16
[(η ⁶ -C ₆ Me ₆)Ru(bis-NHC)Cl]	H ₂ O	KOH	–	23'000	–	17
[Ru(η ⁶ -C ₆ Me ₆)(DHPT)Cl]Cl	H ₂ O	KOH	–	15'400	3'600	18
[Ru(η ⁶ -C ₆ Me ₆)(DHBP)Cl]Cl	H ₂ O	KOH	–	13'620	4'400	18
[RuCl ₂ (PTA) ₄]	H ₂ O	–	50/150	204	–	7
[RuCl ₂ (PTA) ₄]	DMSO	–	50/150	749	–	7

TON: turnover number; TOF: turnover frequency.

Table 2. Bicarbonate, carbonate and carbon dioxide hydrogenation into formic acid/formate or formic acid derivatives with other metal based catalysts

Catalyst	Solvent	Base	PCO ₂ /H ₂ / bar	TON	TOF / h ⁻¹	Ref.
[RhCl(TPPTS) ₃]	H ₂ O	NHMe ₂	–	3'400	7'300	20
[Ir(η ⁵ -C ₃ Me ₅)(DHPT)Cl]Cl	H ₂ O	KOH	–	222'000	33'000	21
[IrI ₂ (AcO)(bis-NHC ²)]	H ₂ O	KOH	–	190'000	2'500	22
[IrCp*(DHBP)Cl]Cl	H ₂ O	KOH	–	190'000	42'000	18
[{IrCp*Cl} ₂ (thbpy)] ²⁺	H ₂ O	KHCO ₃	–	153'000	53'800	23
[Ir(PNP ¹)H ₃]	H ₂ O	KOH/THF	–	3'500'000	150'000	19
[(PNP ²)Fe(H) ₂ (CO)]	H ₂ O	NaOH/THF	–	788	156	24
[Rh(cod)Cl] ₂ /dppb	DMSO	NEt ₃	20/20	1'150	–	25
[Rh(cod)(μ-H) ₄ / PPh ₂ (CH ₂) ₄ PPh ₂	DMSO	NEt ₃	20/20	2'200	375	26
[Rh(hfacac)(dcpb)]	DMSO	NEt ₃	20/20	–	1'335	27
[RhCl(PPh ₃) ₃]	MeOH	NEt ₃ /PPh ₃	40/20	2'700	125	28
Fe(BF ₄)*6H ₂ O/PP ₃	MeOH	NaHCO ₃	0/60	610	30	29
Co(BF ₄)*6H ₂ O/PP ₃	MeOH	NaHCO ₃	0/60	2'877	200	30
FeCl ₃ /dcpe	DMSO	DBU	60/40	113	15.1	31
NiCl ₂ /dcpe	DMSO	DBU	160/40	4'400	20	31
MoCl ₃ /dcpe	DMSO	DBU	60/40	63	8.4	31

TON: turnover number; TOF: turnover frequency.

the re-discovery of a stable iron-based catalyst for the hydrogenation of CO₂ in basic solutions, as well as the formic acid cleavage to CO₂ and H₂. The catalyst, first synthesized and published by Bianchini *et al.* in 1988,³² an iron(II)-tris[(2-diphenylphosphino)-ethyl]phosphine (PP₃) complex, contains a tetradentate phosphine ligand that provides stability to the more reactive (unstable) iron(II) centre. *In situ* multinuclear nuclear magnetic resonance (NMR) spectroscopy was used to study the iron(II)-catalysed reactions for both bicarbonate reduction

and formic acid dehydrogenation and several intermediate species, notable metal-hydride species, were detected allowing catalytic cycles to be postulated (Figure 1).^{29,33}

3. Research on Dehydrogenation of Formic Acid

The most important feature of a formic acid dehydrogenation catalyst is that it must be highly selective for this reaction (equation 4), and not catalyse the

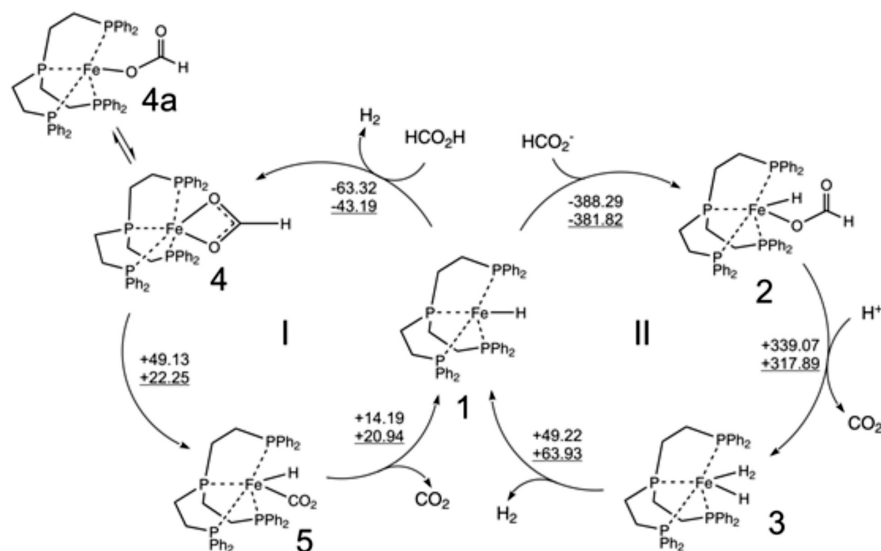


Figure 1. Proposed mechanism for the selective iron-catalyzed hydrogen generation from formic acid with calculated relative energies of complexes (kJ mol⁻¹).^{29,33} Reproduced with permission of The American Association for the Advancement of Science (3470280610808).

dehydration of formic acid that results in the formation of water and carbon monoxide (equation 5).



The dehydration reaction not only reduces the amount of hydrogen produced, but the CO by-product is a poison to fuel cells and in general, the concentration of CO should remain below 10 ppm. A large number of heterogeneous catalysts have been evaluated for this reaction, but lack of selectivity tends to be a problem. Thus, there has been much recent interest in homogeneous catalysts and well-defined, immobilized heterogeneous catalysts derived from them.

Key examples of homogeneous catalysts used for the selective dehydrogenation of formic acid to CO₂ and H₂ are listed in Table 3.

In keeping with catalysts for the reverse reaction, Ru(II) complexes with water-soluble phosphine ligands have been widely explored although iron, iridium and rhodium complexes also selectively catalyse the dehydrogenation reaction. Notably, several catalysts that meet the stringent requirements for industrial applications have been developed. A high stable and selective Ru(II) catalyst is readily generated from the *in situ* reaction of RuCl₃ with

the water-soluble *m*-trisulfonated triphenylphosphine (*m*TPPTS) ligand.⁵⁰ The resulting catalyst selectively decomposes formic acid into carbon monoxide, free hydrogen and carbon dioxide in a very wide pressure range and it is undergoing commercialisation.⁴⁶ The catalytic cycle has also been elucidated from *in situ* NMR spectroscopic studies (Figure 2). Heterogeneous catalysts based on immobilisation, have been prepared by the reaction of the ruthenium(II)-*m*TPPTS dimer and MCM41 silica functionalized with diphenylphosphine groups via alkyl chains. The catalytic system based on MCM41-Si-(CH₂)₂PPh₂/Ru-*m*TPPTS demonstrated an activity and stability comparable to those of the homogeneous catalyst: a turnover frequency of 2780 h⁻¹ was obtained at 110 °C, and no ruthenium leaching was detected after turnover numbers of 71000.⁵¹

4. Conclusions

Hydrogen is definitely among the most promising candidates as the energy carrier in the future, though its generation from renewable sources and storage in a safe and reversible way is still challenging. Formic acid is a promising molecule for hydrogen storage and delivery. HCOOH can be generated via catalytic hydrogenation of

Table 3. Selective catalytic cleavage of the formic acid into carbon dioxide and hydrogen

Catalyst	Substrate	Solvent	Temperature / °C	TON	TOF / h ⁻¹	Ref.
[Ir(PPh ₃)H ₃]	HCOOH	AcOH	118	11'000	8'900	34
[RuCl ₂ (benzene)] ₂ /DPPE	HCOOH	Me ₂ NHex	25	260'000	900	35
[RuCl ₂ (PPh ₃) ₃]	HCOOH	NEt ₃	40	891	2'700	36
[Ru(k ³ -triphos)(MeCN) ₃](OTf) ₂	HCOOH	NMe ₂ Oct	80	10'000	–	37
[Ir(PNP ¹)H ₃]	HCOOH/BUOH	Et ₃ N/THF	80	5'000 ^b	120'000 ^c	19
[RuHCl(CO)(PNP ²)]	HCOOH	DMF/NHex ₃	90	706'500	256'000	38
[Cp*IrCl(N [^] C)]	HCOOH	NEt ₃	40	–	147'000	39
[RuCl ₂ (DMSO) ₄]	HCOOH	NEt ₃	–	25'000	18'000	40
[Fe ₃ (CO) ₁₂]/PPh ₃ /tpy	HCOOH/NEt ₃	DMF	40	200	–	41
[Fe ₃ (CO) ₁₂]/PBn ₃ /tpy	HCOOH/NEt ₃	DMF	40	1'266	–	42
[Fe(BF ₄) ₂]*6H ₂ O/PP ₃	HCOOH	Prop. carb.	80	92'417	9'425	33
[(PNP ²)Fe(H) ₂ (CO)]	HCOOH	THF/NEt ₃	40	–	836	43
[IrH ₃ (PNP ¹)]	HCOOH/HCOONa	H ₂ O/THF	60	890	–	19
[Cp*Ir(DHBP)(H ₂ O)](SO ₄)	HCOOH	H ₂ O	90	10'000	14'000	44
[Cp*Rh(DHBP)(H ₂ O)](SO ₄)	HCOOH	H ₂ O	80	83'000	7'700	45
RuCl ₃ /TPPTS	HCOOH	H ₂ O	120	40'000	670	46
RuCl ₃ /cationic phosphines	HCOOH	H ₂ O	120	10'000 ^a	1'950	47
[Ir(Cp*)(H ₂ O)(bpm)Ru(bpy) ₂](SO ₄) ₂	HCOOH/HCOONa	H ₂ O	25	142	426	48
[(Cp*Ir) ₂ (thpbym)Cl ₂]	HCOOH/HCOONa	H ₂ O	80	308'000	–	23
[Ir(Cp*)(TH4BPM)(H ₂ O)](SO ₄)	HCOOH/HCOONa	H ₂ O	80	11'000	39'500	49

TON: turnover number; TOF: turnover frequency.

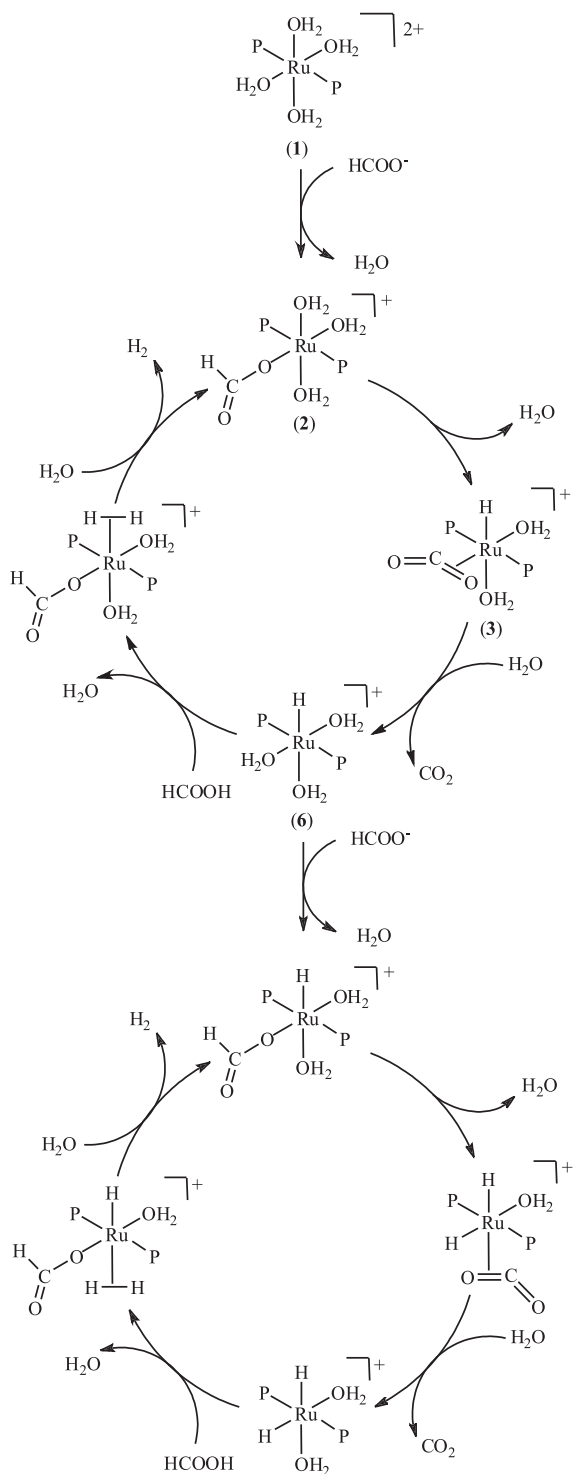


Figure 2. Proposed reaction mechanism involving two competing cycles in the formic acid dehydrogenation reaction using the RuCl_3 pre-catalyst with the water-soluble *m*-trisulfonated triphenylphosphine (*m*TPPTS = P) ligand.⁴⁶ Reproduced with permission of J. Wiley and Sons (3470260322908).

CO_2 or bicarbonate with suitable catalysts. Under mild experimental catalytic conditions, it can be dehydrogenated to give highly pure hydrogen and carbon dioxide. We summarised here the various homogeneous catalysts

available that usually operate both in aqueous and in organic formic acid solutions. The homogeneous catalytic decomposition of formic acid in aqueous solution provides an efficient *in situ* method for hydrogen production that operates over a wide range of pressures, under mild conditions, and at a controllable rate. On the basis of these results one can envisage the practical application of carbon dioxide as hydrogen vector: storage and delivery.

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