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

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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). Indeed, in the last few years, research on the use of formic acid as a hydrogen storage vector has grown rapidly. 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 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). Third, the reverse reaction,
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.⁶ 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,⁷ as ΔG°298=+32.9 kJ mol⁻¹ (equation 1):

\[
\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{HCOOH}(g) \quad (1)
\]

Dissolution of the gases decreases the entropy term; in aqueous solution, this reaction becomes slightly exergonic with ΔG°298=−4 kJ mol⁻¹ (equation 2):

\[
\text{CO}_2(aq) + \text{H}_2(aq) \rightarrow \text{HCOOH}_2(aq) \quad (2)
\]

Addition of a base improves the enthalpy of the reaction (ΔG°298 =−35.4 kJ mol⁻¹; ΔH°298 =−59.8 kJ mol⁻¹; ΔS°298 =−81 J mol⁻¹ K⁻¹), making this reaction largely available (equation 3):

\[
\text{CO}_2(aq) + \text{H}_2(aq) + \text{NH}_3(aq) \rightarrow \text{HCOO}^-(aq) + \text{NH}_4^+(aq) \quad (3)
\]

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 [RuCl₃(PTA)₄] (PTA = 1,3,5-triazapolysphinaadamantane) 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.

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Base</th>
<th>PCO/H₂ bar</th>
<th>TON</th>
<th>TOF/h⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuH₂(PPh₃)₂]</td>
<td>Benzene</td>
<td>NEt₃/H₂O</td>
<td>25/25</td>
<td>87</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>[RuH₂(PPh₃)₃]</td>
<td>scCO₂</td>
<td>NEt₃, H₂O</td>
<td>120/80</td>
<td>1'400</td>
<td>1'400</td>
<td>9</td>
</tr>
<tr>
<td>[RuCl₂(PMe₃)₄]</td>
<td>scCO₂</td>
<td>NEt₃, H₂O</td>
<td>120/80</td>
<td>7'200</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>[RuCl₂(OAc)(PMe₃)₄]</td>
<td>scCO₂</td>
<td>NEt₃/C₆F₅OH</td>
<td>120/70</td>
<td>32'000</td>
<td>95'000</td>
<td>10</td>
</tr>
<tr>
<td>[Ru(6,6′-Cl₂bpy)(H₂O)₂][P(CF₃SO₂)₂]</td>
<td>EtOH</td>
<td>NEt₃</td>
<td>30/30</td>
<td>5'000</td>
<td>–</td>
<td>11</td>
</tr>
<tr>
<td>[RuH₂(CO)(PPh₃)₃]</td>
<td>DMF</td>
<td>DBU</td>
<td>10/30</td>
<td>–</td>
<td>1'100'000</td>
<td>12</td>
</tr>
<tr>
<td>[TpRu(PPh₃)₂(CH₃CN)H]</td>
<td>THF</td>
<td>NEt₃, H₂O</td>
<td>25/25</td>
<td>760</td>
<td>48</td>
<td>13</td>
</tr>
<tr>
<td>[TpRu(PPh₃)(CH₃CN)H]</td>
<td>THF</td>
<td>NEt₃, CF₃CH₂OH</td>
<td>25/25</td>
<td>1'815</td>
<td>113</td>
<td>14</td>
</tr>
<tr>
<td>[RuCl₂(TPPMS)]</td>
<td>H₂O</td>
<td>NaHCO₃</td>
<td>–</td>
<td>320</td>
<td>9'600</td>
<td>15</td>
</tr>
<tr>
<td>[Ru(n⁴=C₅Me₅)(4,4′-OMe-bpy)(OH₂)₂][SO₄]</td>
<td>H₂O</td>
<td>Citrate buffer</td>
<td>–</td>
<td>55</td>
<td>–</td>
<td>16</td>
</tr>
<tr>
<td>[(n⁴=C₅Me₅)Ru(bis-NHC)Cl]</td>
<td>H₂O</td>
<td>KOH</td>
<td>–</td>
<td>23'000</td>
<td>–</td>
<td>17</td>
</tr>
<tr>
<td>[Ru(n⁴=C₅Me₅)(DHPT)Cl]</td>
<td>H₂O</td>
<td>KOH</td>
<td>–</td>
<td>15'400</td>
<td>3'600</td>
<td>18</td>
</tr>
<tr>
<td>[Ru(n⁴=C₅Me₅)(DHBP)Cl]</td>
<td>H₂O</td>
<td>KOH</td>
<td>–</td>
<td>13'620</td>
<td>4'400</td>
<td>18</td>
</tr>
<tr>
<td>[RuCl₂(PTA)]</td>
<td>H₂O</td>
<td>–</td>
<td>50/150</td>
<td>204</td>
<td>–</td>
<td>7</td>
</tr>
<tr>
<td>[RuCl₂(PTA)]</td>
<td>DMSO</td>
<td>–</td>
<td>50/150</td>
<td>749</td>
<td>–</td>
<td>7</td>
</tr>
</tbody>
</table>

TON: turnover number; TOF: turnover frequency.
the re-discovery of a stable iron-based catalyst for the hydrogenation of CO<sub>2</sub> in basic solutions, as well as the formic acid cleavage to CO<sub>2</sub> and H<sub>2</sub>. The catalyst, first synthetized and published by Bianchini <i>et al.</i> in 1988,<sup>32</sup> an iron(II)-tris(2-diphenylphosphino)-ethyl]phosphine (PP<sub>3</sub>) complex, contains a tetradentate phosphine ligand that provides stability to the more reactive (unstable) iron(II) centre. In <i> situ</i> 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).<sup>29,33</sup>  

### 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<sup>-1</sup>).]<sup>29,33</sup> 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).

\[
\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4) \\
\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad (5)
\]

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 phosphate 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 (mTPPTS) ligand. 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. 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)-mTPPTS dimer and MCM41 silica functionalized with diphenylphosphine groups via alkyl chains. The catalytic system based on MCM41-Si-(CH₂)₃PPh₂/Ru-mTPPTS 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.

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 the water-soluble m-trisulfonated triphenylphosphine (mTPPTS) ligand. 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. 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)-mTPPTS dimer and MCM41 silica functionalized with diphenylphosphine groups via alkyl chains. The catalytic system based on MCM41-Si-(CH₂)₃PPh₂/Ru-mTPPTS 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.

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Temperature / °C</th>
<th>TON</th>
<th>TOF / h⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(PPh₃)H]</td>
<td>HCOOH</td>
<td>AcOH</td>
<td>118</td>
<td>11'000</td>
<td>8'900</td>
<td>34</td>
</tr>
<tr>
<td>[RuCl₃(benzene)]/DPPE</td>
<td>HCOOH</td>
<td>Me₂NHex</td>
<td>25</td>
<td>260'000</td>
<td>900</td>
<td>35</td>
</tr>
<tr>
<td>[RuCl₃(PPh₃)]</td>
<td>HCOOH</td>
<td>NEt₃</td>
<td>40</td>
<td>891</td>
<td>2'700</td>
<td>36</td>
</tr>
<tr>
<td>[Ru(k²-triphos)(MeCN)]₄(OTf)₂</td>
<td>HCOOH</td>
<td>NEt₃, Oct</td>
<td>80</td>
<td>10'000</td>
<td>–</td>
<td>37</td>
</tr>
<tr>
<td>[Ir(PNP)₃]H</td>
<td>HCOOH/BUOH</td>
<td>Et₃N/THF</td>
<td>80</td>
<td>5'000⁻⁰</td>
<td>120'000</td>
<td>19</td>
</tr>
<tr>
<td>[RuHCl(CO)(PNP)₂]</td>
<td>HCOOH</td>
<td>DMF/NHex</td>
<td>90</td>
<td>706'500</td>
<td>256'000</td>
<td>38</td>
</tr>
<tr>
<td>[Cp²*IrCl(NOCl)]</td>
<td>HCOOH</td>
<td>NEt₃</td>
<td>40</td>
<td>–</td>
<td>147'000</td>
<td>39</td>
</tr>
<tr>
<td>[RuCl₃(DMSO)₄]</td>
<td>HCOOH</td>
<td>NEt₃</td>
<td>–</td>
<td>25'000</td>
<td>18'000</td>
<td>40</td>
</tr>
<tr>
<td>[Fe₇(CO)₁₉] /PPh₃/tpy</td>
<td>HCOOH</td>
<td>NEt₃, DMF</td>
<td>40</td>
<td>200</td>
<td>–</td>
<td>41</td>
</tr>
<tr>
<td>[Fe₂(CO)₆] /PPh₃ /py</td>
<td>HCOOH</td>
<td>NEt₃, DMF</td>
<td>40</td>
<td>1'266</td>
<td>–</td>
<td>42</td>
</tr>
<tr>
<td>[Fe₂BF₄]·₆H₂O/PP₃</td>
<td>HCOOH</td>
<td>Prop. carb.</td>
<td>80</td>
<td>92'417</td>
<td>9'425</td>
<td>33</td>
</tr>
<tr>
<td>[(PNP)Fe(H₂CO)]</td>
<td>HCOOH</td>
<td>THF/NEt₃</td>
<td>40</td>
<td>–</td>
<td>836</td>
<td>43</td>
</tr>
<tr>
<td>[IrH₃(PNP)₃]</td>
<td>HCOOH/HCOONa</td>
<td>H₂O/THF</td>
<td>60</td>
<td>890</td>
<td>–</td>
<td>19</td>
</tr>
<tr>
<td><a href="SO%E2%82%84">Cp²*Ir(DHBP)(H₂O)</a></td>
<td>HCOOH</td>
<td>H₂O</td>
<td>90</td>
<td>10'000</td>
<td>14'000</td>
<td>44</td>
</tr>
<tr>
<td><a href="SO%E2%82%84">Cp²*Rh(DHBP)(H₂O)</a></td>
<td>HCOOH</td>
<td>H₂O</td>
<td>80</td>
<td>83'000</td>
<td>7'700</td>
<td>45</td>
</tr>
<tr>
<td>RuCl₃/TPPTS</td>
<td>HCOOH</td>
<td>H₂O</td>
<td>120</td>
<td>40'000</td>
<td>670</td>
<td>46</td>
</tr>
<tr>
<td>RuCl₃/cationic phosphines</td>
<td>HCOOH</td>
<td>H₂O</td>
<td>120</td>
<td>10'000⁻⁰</td>
<td>1'950</td>
<td>47</td>
</tr>
<tr>
<td><a href="SO%E2%82%84">Ir(Cp²*)(H₂O)(bpm)Ru(bpy)₂</a>₂</td>
<td>HCOOH/HCOONa</td>
<td>H₂O</td>
<td>25</td>
<td>142</td>
<td>426</td>
<td>48</td>
</tr>
<tr>
<td><a href="thiphyn">Cp²*Ir</a>(Cl₂)</td>
<td>HCOOH/HCOONa</td>
<td>H₂O</td>
<td>80</td>
<td>308'000</td>
<td>–</td>
<td>23</td>
</tr>
<tr>
<td><a href="SO%E2%82%84">Ir(Cp²*)(TH4BPM)(H₂O)</a></td>
<td>HCOOH/HCOONa</td>
<td>H₂O</td>
<td>80</td>
<td>11'000</td>
<td>39'500</td>
<td>49</td>
</tr>
</tbody>
</table>

TON: turnover number; TOF: turnover frequency.
CO₂ 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.

**Acknowledgements**

Swiss National Science Foundation, EPFL, Commission for Technology and Innovation (CTI), EOS Holding, Competence Center Energy and Mobility (CCEM) and Swiss Competence Centers for Energy Research (SCCER) are thanked for financial support.

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Submitted on: August 25, 2014
Published online: October 3, 2014