

Leibniz-Institut für Katalyse e.V. an der Universität Rostock

# Hydrogen Generation from Renewable Resources

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|                                       |  |
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“ ...

Il faut l'espérer, répondit Gédéon Spilett, car enfin sans charbon, plus de machines, et sans machines, plus de chemins de fer, plus de bateaux à vapeur, plus d'usines, plus rien de ce qu'exige le progrès de la vie moderne !

– Mais que trouvera-t-on ? demanda Pencroff. L'imaginez-vous, Monsieur Cyrus ?

– À peu près, mon ami.

– Et qu'est-ce qu'on brûlera à la place du charbon ?

– L'eau, répondit Cyrus Smith.

– L'eau, s'écria Pencroff, l'eau pour chauffer les bateaux à vapeur et les locomotives, l'eau pour chauffer l'eau !

– Oui, mais l'eau décomposée en ses éléments constitutifs, répondit Cyrus Smith, et décomposée, sans doute, par l'électricité, qui sera devenue alors une force puissante et maniable, car toutes les grandes découvertes, par une loi inexplicable, semblent concorder et se compléter au même moment. Oui, mes amis, je crois que l'eau sera un jour employée comme combustible, que l'hydrogène et l'oxygène, qui la constituent, utilisés isolément ou simultanément, fourniront une source de chaleur et de lumière inépuisables et d'une intensité que la houille ne saurait avoir. Un jour, les soutes des steamers et les tenders des locomotives, au lieu de charbon, seront chargés de ces deux gaz comprimés, qui brûleront dans les foyers avec une énorme puissance calorifique. Ainsi donc, rien à craindre. Tant que cette terre sera habitée, elle fournira aux besoins de ses habitants, et ils ne manqueront jamais ni de lumière ni de chaleur, pas plus qu'ils ne manqueront des productions des règnes végétal, minéral ou animal. Je crois donc que lorsque les gisements de houille seront épuisés, on chauffera et on se chauffera avec de l'eau. L'eau est le charbon de l'avenir.

– Je voudrais voir cela, dit le marin.

– Tu t'es levé trop tôt, Pencroff », répondit Nab, qui n'intervint que par ces mots dans la discussion.

...”

- Jules Vernes, *L'île mystérieuse*, 1874

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# Abbreviations

|       |   |
|-------|---|
| Ac    | acetyl  |
| AFC   | alkaline fuel cell  |
| BINAP | 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl                             |
| bpy   | 2,2'-bipyridine   |
| Bu    | 1-butyl   |
| cat.  | catalyst  |
| cod   | 1,5-cyclooctadiene  |
| cp    | cyclopentadienyl C <sub>5</sub> H <sub>5</sub>                          |
| cp*   | pentamethylcyclopentadienyl C <sub>5</sub> Me <sub>5</sub>              |
| Cy    | cyclohexyl  |
| dbu   | diazabicyclo[5,4,0]undecene   |
| DFAFC | direct formic acid fuel cell  |
| dmf   | dimethylformamide   |
| DMFC  | direct methanol fuel cell   |
| dmso  | dimethylsulfoxide   |
| DOE   | Department of Energy  |
| dpen  | 1,2-diphenylethyldiamin   |
| dppb  | 1,4-bis(diphenylphosphino)butane  |
| dppe  | 1,2-bis(diphenylphosphino)ethane  |
| dppf  | 1,1'-bis(diphenylphosphino)ferrocene                                    |
| dppm  | bis(diphenylphosphino)methane   |
| dppp  | 1,3-bis(diphenylphosphino)propane                                       |
| ee    | enantiomeric excess   |
| en    | ethyldiamine  |
| Et    | ethyl   |
| L     | ligand  |
| M     | metal   |
| Me    | methyl  |
| m.p.  | melting point   |
| MAK   | maximale Arbeitsplatzkonzentration – workplace exposure limit (Germany) |
| MCFC  | molten carbonate fuel cell  |
| n.a.  | not available   |
| NMR   | nuclear magnetic resonance  |
| PAFC  | phosphoric acid fuel cell   |
| PEMFC | polymer electrolyte membrane fuel cell                                  |
| Ph    | phenyl  |

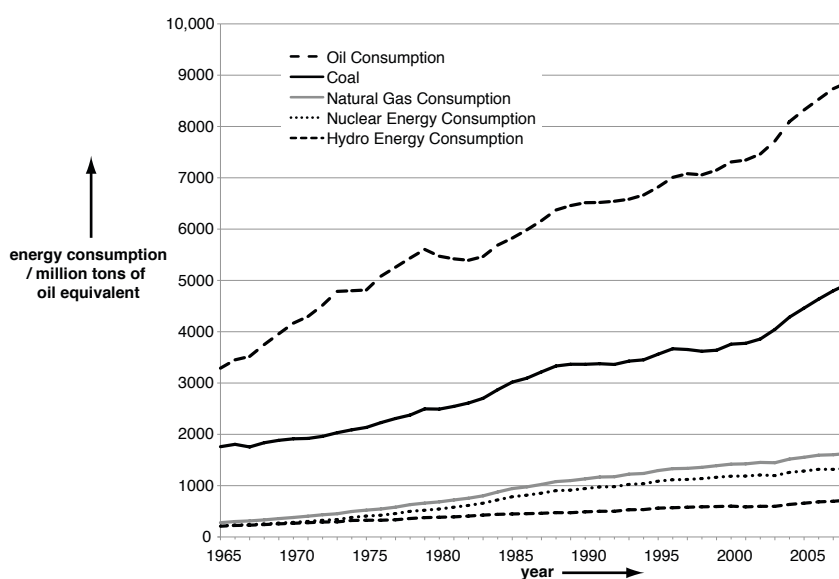
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|                  |  |
|------------------|--|
| Pr               | 1-propyl   |
| 2-Pr             | 2-propyl   |
| ppm              | parts per million  |
| pta              | 1,3,5-triaza-7-phosphadamantane  |
| R                | hydrogen or organic rest   |
| r.t.             | room temperature   |
| R <sub>F</sub>   | perfluorinated organic rest  |
| SOFC             | solid oxide fuel cell  |
| TEAF             | triethylammonium formate (5HCO <sub>2</sub> H·2NEt <sub>3</sub> )  |
| Tf               | trifluoromethylsulfonyl  |
| TOF              | turnover frequency   |
| TON              | turnover number  |
| tpms             | mono- <i>m</i> -sulfonated triphenylphosphine sodium salt, or 3-(diphenylphosphino)-benzenesulfonic acid sodium salt               |
| tppts            | tris- <i>m</i> -sulfonated triphenylphosphine trisodium salt, or 3,3',3''-phosphinidynetris-(benzenesulfonic acid) trisodium salt, |
| X                | leaving group, (pseudo) halide   |
| WGS              | water gas shift  |
| $\Delta G^\circ$ | difference of standard Gibbs' free enthalpy  |
| $\Delta H^\circ$ | difference of standard enthalpy  |
| $\Delta S^\circ$ | difference of standard entropy   |



# 1 Introduction

The supply of energy is one of the most important challenges for the future of the human society. Hydrogen could play an important role in the development of a new, clean, and sustainable energy supply.<sup>1-3</sup> With a growing population, continuous technological progress, and increasing wealth in many parts of this world, the demand for energy has been raising throughout history. According to the projections of energy agencies and private investigators, this increase will even speed up more in the near future.<sup>4-7</sup> Our current energy supply, which largely relies on fossil fuels (Figure 1), cannot keep up with this growing demand – the “Terawatt Challenge” arises, as this gap in energy supply has been called by the 1996 nobel laureate in chemistry Richard E. Smalley.<sup>8</sup> He points out the two main problems of a fossil fuel based energy supply: First, our resources are not infinite, and will deplete in the nearer future. Second, carbon dioxide is released to the atmosphere that had long been bound underneath the earth, causing global warming.<sup>8</sup>



**Figure 1:** World primary energy consumption 1965-2008<sup>9</sup>

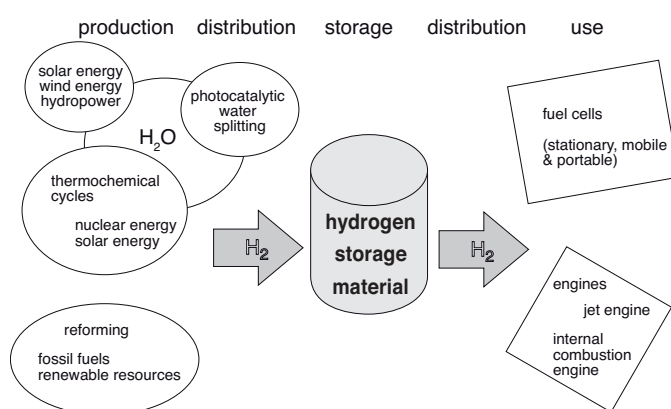
In order to meet the Terawatt Challenge, it is essential to re-think the current way of distributing and using energy, as well as a different source of energy is needed. Within the chemical community, leading scientists have been emphasizing the importance of this challenge, and called chemists to contribute solutions.<sup>3, 8, 10-18</sup>

The only source of energy available that can satisfy current and future sustainable energy demand is the sun. For human use, the sun is a nearly everlasting energy source, and it currently provides 10,000 times more energy than consumed by humans.<sup>3, 14</sup> Interesting options for solar energy conversion and storage in the field of chemistry are photovoltaics, which provide electrical energy,<sup>14, 19</sup> and photocatalytic hydrogen generation. Direct solar water splitting has been achieved with heterogeneous inorganic catalysts.<sup>20, 21</sup> In homogeneous catalysis, mainly photocatalytic hydrogen production from water by proton reduction with a sacrificial donor has been studied, as well as hydrogen generation from other substrates such as alcohols or alkanes.<sup>22-24</sup>

Considering the second task, re-thinking our way of storing and distributing energy, some alternative “energy economies” have been proposed. This means that a newly introduced energy carrier will replace the current ones, like coal, gasoline, natural gas, or electricity. Probably, the hydrogen economy is the most well known, it will be discussed further along. Likewise, a methanol economy<sup>25</sup> and a formic acid economy<sup>26</sup> have been suggested.

## 1.1 A Hydrogen Economy

By definition, in a hydrogen economy, hydrogen is used as an energy carrier that must be produced, stored, transported, and made readily available to the end user (Figure 2). The term has been coined in the early 1970s, a draft of a hydrogen economy was published by Bockris in 1972.<sup>1</sup> While in the 1970s, nuclear power was suggested as major energy source for hydrogen production, priorities have changed since, and Bockris links the concept closely to renewable energy sources in a more recent survey.<sup>27</sup>

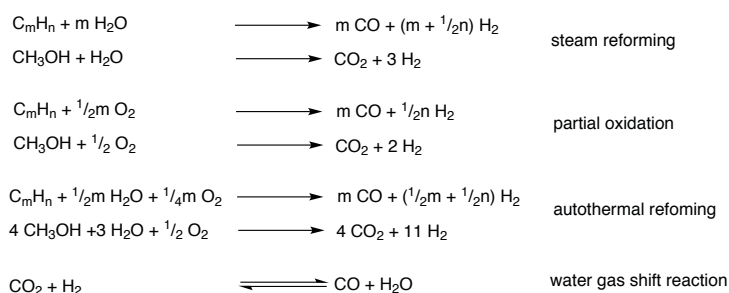


**Figure 2:** Schematic representation of a hydrogen economy<sup>2</sup>

Discussing a hydrogen economy, it is essential to remember that hydrogen is not available on earth in elementary form. It is therefore not a source of energy, unlike coal, or oil. Being an energy carrier only, hydrogen has to be produced, which is an energy-consuming process.

In an ideal hydrogen economy, hydrogen would be generated using sunlight, distributed via a safe infrastructure, and readily available for different applications like providing electricity for mobile phones, powering fuel cell vehicles and fuelling large ships, as well as satisfying the energy needs of industry.<sup>2</sup> In order to approach this vision, there are challenges for chemists in three main areas: The production of hydrogen, the use of hydrogen, and hydrogen storage as well as distribution.<sup>28-30</sup>

In 2007, hydrogen was produced mainly from fossil fuels, accounting for 96% of the total volume (48% from natural gas, 30% from refinery/chemical off-gases, 18% from coal).<sup>31</sup> The remaining 4% were obtained mainly by electrolysis. The three most common processes for hydrogen production from fossil fuels are steam reforming, partial oxidation, and autothermal reforming. The carbon monoxide produced in these processes may be converted in a water gas shift reactor (Scheme 1).<sup>32</sup>



**Scheme 1:** Processes for hydrogen formation from hydrocarbons  $C_mH_n$  and methanol<sup>32</sup>

Based on its actual production, hydrogen is currently neither a solution for a shift from fossil fuels, nor is it possible to proclaim the hydrogen economy as a climate saver. But there are other, smaller benefits: Hydrogen fuelled vehicles or fixed power supply units may relieve cities from polluted air, and important knowledge is gained in pilot projects under realistic conditions. In parallel, there is ongoing research for alternative methods to produce hydrogen.<sup>28, 29, 32-35</sup> These methods include electrolysis with sustainable electricity, reforming of biomass, (photo-)biological hydrogen generation from biomass, photoelectrochemical and photocatalytic water splitting, and thermochemical hydrogen generation with solar energy.

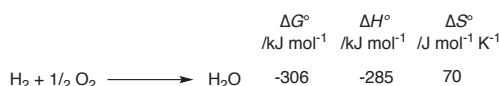
The second challenge is the usage of hydrogen in fuel cells, which convert chemical energy to electrical energy needed for most applications. As the process of energy conversion is purely electrochemical, a fuel cell can be more efficient than a combustion engine, which is limited by the Carnot efficiency.<sup>28, 29</sup> There are several fuel cell types known that work with hydrogen as a fuel (Table 1). Among them, the polymer electrolyte membrane fuel cell (PEMFC, entry 5) is a versatile choice, and, in fact, the direct methanol fuel cell (DMFC, entry 6) and direct formic acid fuel cells (DFAFC, entry 7) are PEMFC optimized for fuels other than hydrogen.

**Table 1:** Selected common types of fuel cells<sup>28, 29</sup>

|   | name                                       | abbrev. | fuel                | oxidant                                    | operating temp. /°C |
|---|--|---------|---------------------|--|---------------------|
| 1 | solid oxide fuel cell                      | SOFC    | H <sub>2</sub> / CO | O <sub>2</sub> / air                       | > 800               |
| 2 | molten carbonate fuel cell                 | MCFC    | H <sub>2</sub> / CO | O <sub>2</sub> / air                       | 600 – 700           |
| 3 | phosphoric acid fuel cell                  | PAFC    | H <sub>2</sub>      | O <sub>2</sub> / air                       | 150 – 220           |
| 4 | alkaline fuel cell                         | AFC     | H <sub>2</sub>      | O <sub>2</sub> / CO <sub>2</sub> -free air | 60 – 90             |
| 5 | polymer electrolyte membrane fuel cell     | PEMFC   | H <sub>2</sub>      | O <sub>2</sub> / air                       | 40 – 90             |
| 6 | direct methanol fuel cell                  | DMFC    | CH <sub>3</sub> OH  | O <sub>2</sub> / air                       | 60 – 120            |
| 7 | direct formic acid fuel cell <sup>36</sup> | DFAFC   | HCO <sub>2</sub> H  | O <sub>2</sub> / air                       | r.t. – >100         |

Prominent advantages of a PEMFC are its low operating temperature, the high power density and the option of operating it with air.<sup>37</sup> They are also easily scalable to compact size, and may be mass-produced at low cost. For PEM fuel cells, the quality of the hydrogen fuel gas is an important issue. Carbon monoxide is a poison for the noble metal (generally platinum) catalyst, and currently between 10 and 0.2 ppm is accepted for fuel cell hydrogen.<sup>38-41</sup> Hydrogen sulfide also acts as a catalyst poison. Other possible impurities are gases such as carbon dioxide, or methane. Depending on their concentration, the operating conditions of the fuel cell, and the fuel cell catalyst employed, these gases can react to form carbon monoxide: methane by oxidation, and carbon dioxide via the water gas shift reaction. It is still disputed, however, to which extent these side-reactions occur, and if this causes irreversible poisoning of the fuel cell.<sup>42-46</sup> Inert gases such as argon or nitrogen do not cause irreversible chemical deactivation of fuel cell catalysts, but any impurity in the hydrogen gas decreases the fuel cell's performance due to mass transport limitations and competition for adsorption sites.<sup>38</sup>

The third challenge is hydrogen storage, which is linked hydrogen distribution.<sup>47-49</sup> The energy content of hydrogen, the lightest of all elements, per mole or per mass unit is very high (Scheme 2), but unfortunately, its density is also very low, even in condensed phase (0.0899 kg m<sup>-3</sup> for the gas at 273.15 K and 1 atm; 70.78 kg m<sup>-3</sup> for the liquid at the normal boiling point 21.2 K).<sup>29</sup>



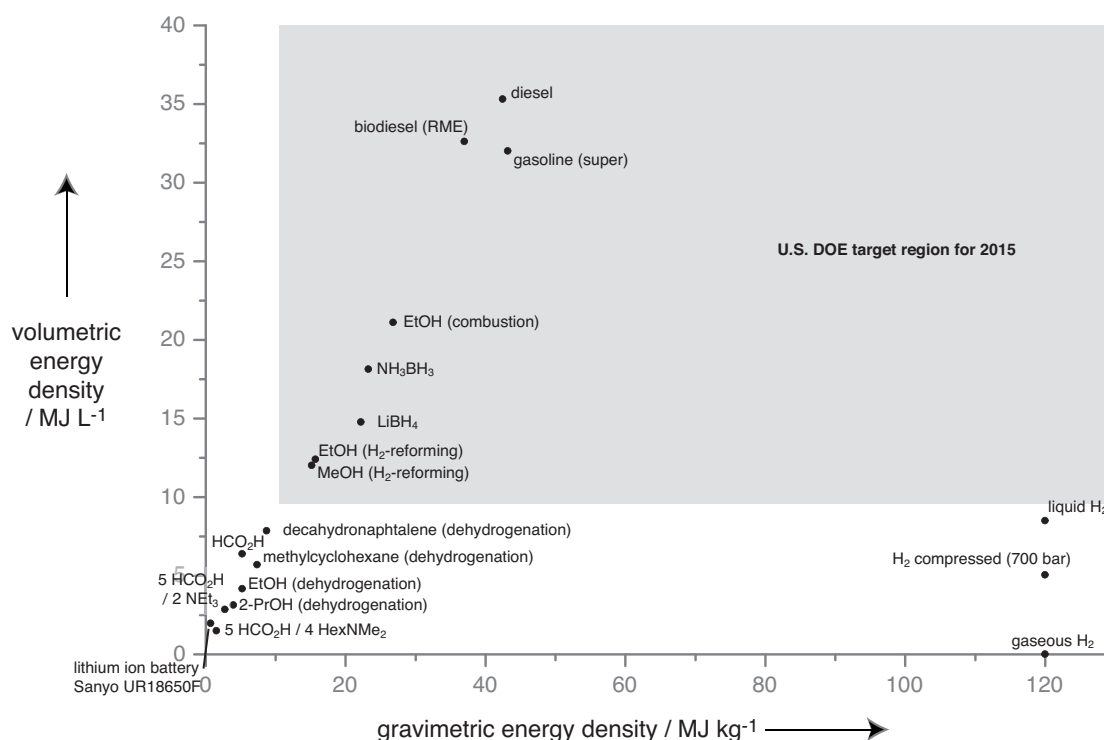
**Scheme 2:** The combustion of a hydrogen molecule<sup>29</sup>

For this reason, it is important to find storage methods where hydrogen is stored in a dense form. An often quoted target for hydrogen storage in vehicles has been set by the U.S. Department of Energy (DOE) in 2005, requiring 90 g H<sub>2</sub> per kilogram storage system and 81 g H<sub>2</sub> per liter storage system by 2015.<sup>50</sup> The hydrogen storage methods investigated to reach this target can be of physical or chemical nature: In physical storage, pure hydrogen is stored in compressed and liquid form,<sup>47, 49</sup> or by adsorption on porous materials e.g. zeolites or molecular organic frameworks.<sup>51-53</sup> In chemical hydrogen storage, hydrogen is chemically bound to other compounds. Mostly hydrides have been explored, including covalent hydrides such as boranes, salts such as magnesium hydride, metallic hydrides of the MH<sub>x</sub> type, and complex hydrides such as Li(AlH<sub>4</sub>).<sup>49, 52, 54-61</sup> In recent years, some organic materials have emerged for covalent hydrogen storage, and especially liquid compounds appear to be very practical.<sup>62</sup>

## 1.2 Liquid Organic Compounds for Hydrogen Storage

Liquid organic compounds have received considerable attention for hydrogen storage recently.<sup>55, 56, 62</sup> In general, they feature the hydrogenation of a carrier compound for hydrogen storage, which is dehydrogenated at the time of hydrogen usage. Examples for hydrogenated carriers are alcohols, especially methanol, formic acid, cycloalkanes and hydrogen saturated heterocyclic compounds. Alcohols are also available from biomass, which is an indirect way of solar energy storage.<sup>63, 64</sup> The main advantages of these systems are that they are relatively easy to handle, and stable to air and moisture in most cases. Due to the covalent nature of hydrogen fixation in these systems, and the limited amount of covalent bonds formed with carbon and other non-metals, the storage capacity remains rather limited, but compounds offer a well-balanced ratio of volumetric vs.

gravimetric hydrogen density. In Figure 3, this ratio is depicted for several hydrogen storage systems. Some hydrogen storage systems other than organics have been included for comparison, as well as some common fuels.



**Figure 3:** Nominal energy content of different hydrogen carriers – other fuels given for comparison. For hydrogen storage materials, the energy content was calculated from the mass% hydrogen released by each compound, its density lower, and the lower heating value of H<sub>2</sub> (242 kJ mol<sup>-1</sup>) assuming 100% conversion without any loss. For data, see refs<sup>65-67</sup>

Evidently, some organic hydrogen carriers fall short of the DOE target, but they offer a higher energy density than a high capacity battery. This might be useful for portable devices. It is however essential to state that for Figure 3 only the nominal theoretical energy densities of the substrates have been concerned, and periphery as well as potential losses have been neglected. In consequence Figure 3 can only serve as a rough guide to estimate the actual energy output of the respective systems.

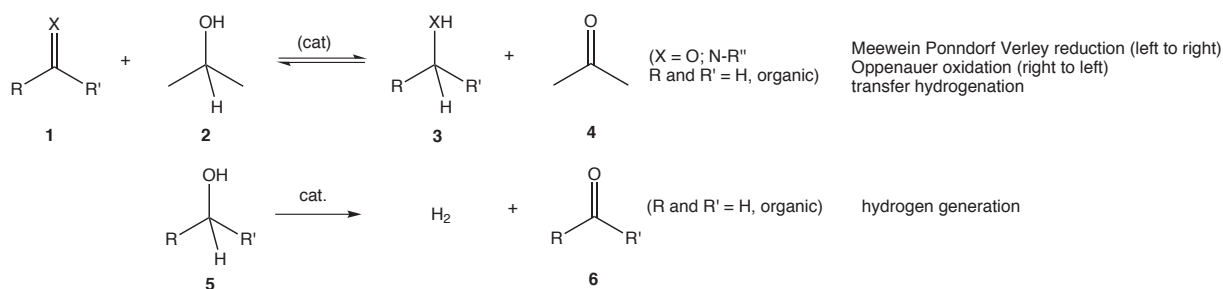
Additionally direct fuel cells for hydrogen carriers like methanol (DMFC)<sup>68, 69</sup> or formic acid (DFAFC)<sup>36</sup> have been proposed. These fuel cells eliminate the hydrogen generation step, which is traded in for other challenges such as cross-over of the fuel through the membrane and undesired side reactions at the fuel cell catalyst.<sup>70-72</sup>

In the following, selected methods for hydrogen generation and hydrogen storage using liquid organic compounds with particular importance for this thesis will be discussed.

### 1.2.1 Hydrogen Generation from Alcohols

Alcohols are largely available from renewable resources such as plants, and they are an attractive raw material for energy generation. The most prominent example certainly is ethanol, but also glycerol is available in large quantities. Other alcohols like methanol, 2-propanol, or glycol may also be obtained from biomass.<sup>63, 64</sup> Though they are technically no alcohols, sugars and other carbohydrates also belong to this group of compounds, from which hydrogen can be obtained in different ways. The steam reforming of alcohols is similar to processes used for hydrocarbons, and aqueous phase reforming occurs at temperatures higher than 200 °C.<sup>32</sup> These conditions are generally too drastic for small, portable applications. Milder conditions are possible for the homogeneously catalyzed dehydrogenation of alcohols.

The dehydrogenation of alcohols has been known in organic chemistry for a long time. It is one half reaction of two well known stoichiometric reactions: The Meerwein Ponndorf Verley reduction and the Oppenauer oxidation.<sup>73</sup> In both reactions, two hydrogen atoms are abstracted from an alcohol or amine **3** and transferred in a base-assisted process to an acceptor, which can be a carbonyl group or an imine **1**. In the Meerwein Ponndorf Verley reduction, 2-propanol **2** is the main hydrogen donor, whereas in the Oppenauer oxidation, acetone **4** acts as hydrogen acceptor. An alternative catalytic reaction is the transfer hydrogenation.<sup>74, 75</sup> It involves the elimination of hydrogen from a donor, generally by a transition metal catalyst. Inspired by these reactions it has been tried to perform the dehydrogenation of an alcohol **5** to an aldehyde or ketone **6** without a hydrogen acceptor in order to generate molecular hydrogen. On one hand, this is a promising approach for a simple selective oxidation in organic synthesis without by-products other than hydrogen gas. On the other hand, it can be used for hydrogen generation from alcohols derived from renewable resources, though not every hydrogen atom in the alcohol is released (e.g. only two of eight in 2-propanol).<sup>76</sup>



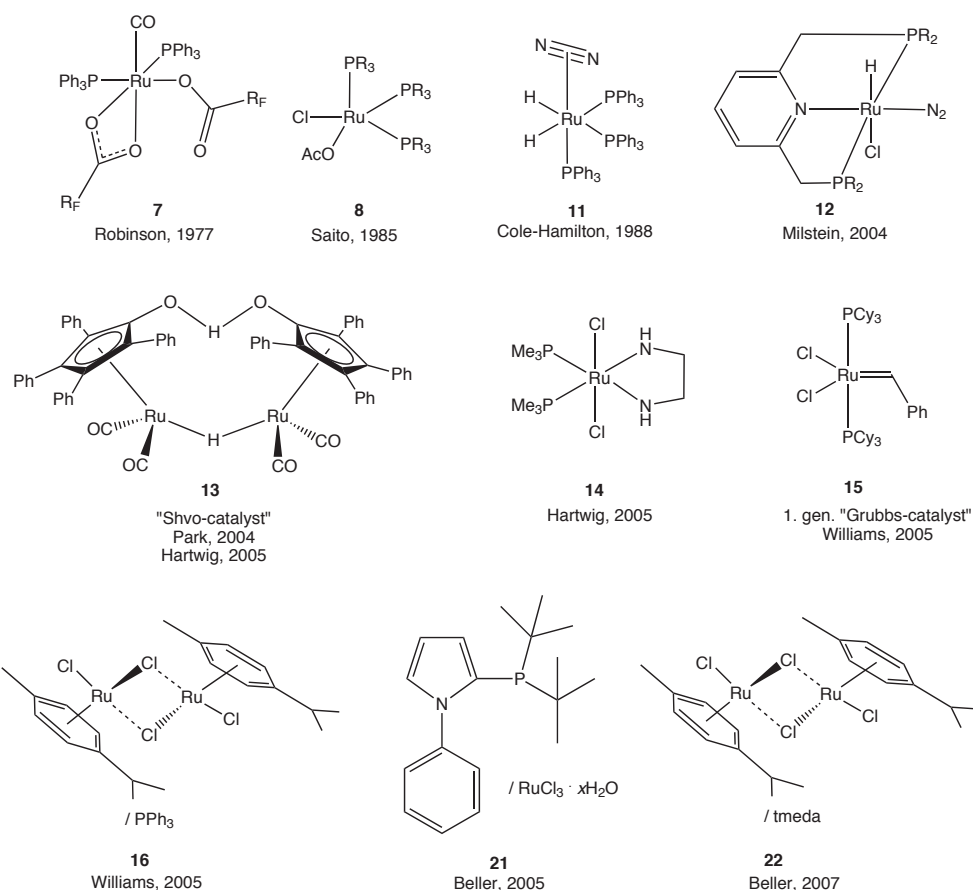
**Scheme 3:** Hydrogen transfer and hydrogen generation reactions

Here, the development of alcohol dehydrogenation will be briefly summarized, a more detailed review can be found in the introduction of the publication in chapter 3.3. In 1967, Charman presented the decomposition of 2-propanol with rhodium(III) chloride in the presence of lithium chloride and hydrochloric acid.<sup>77</sup> The ruthenium-catalyzed dehydrogenation of alcohols with a fluorinated organic acid as co-catalyst was reported by Dobson and Robinson in 1977.<sup>78</sup> Alcohols such as ethanol, 2-propanol, benzyl alcohol or cyclohexanol were dehydrogenated with catalysts of the  $[M(OCOR_F)_2(CO)(PPh_3)_3]$  ( $M = Os, Ru$ ;

$R_F = CF_3, C_2F_5, C_6F_5$ ) **7** type at turnover frequencies (TOFs) between 10 and 20  $h^{-1}$ , with the exception of benzyl alcohol (TOF = 8172  $h^{-1}$ ). However, their results for primary alcohols have been subject of controversy, as they could not be reproduced later.<sup>79, 80</sup> In contrast, the results for secondary alcohols were improved.<sup>81</sup> Other ruthenium catalysts like  $[Ru_2(OAc)_4Cl]$  **8** / phosphine,<sup>82</sup>  $RuCl_3 \cdot x H_2O$ ,<sup>83</sup> or  $RuCl_2(PR_3)_3$ <sup>84</sup> are less active. In the dehydrogenation of cyclohexanol, the initial rate for  $[Ru(OCOCF_3)(CO)(dppe)]$  **9** was TOF = 252  $h^{-1}$  under reflux in the presence of trifluoroacetic acid in a 15 minute reaction.<sup>85</sup>

Approximately at the same time, Cole-Hamilton et al. investigated the base-assisted catalytic alcohol dehydrogenation and photo-dehydrogenation for hydrogen generation. In 1982 they reported that upon irradiation of  $[RhH(CO)(P(2-Pr)_3)_2]$  **10** in 2-propanol hydrogen is evolved.<sup>86</sup> Under non-irradiation conditions, they achieved TOFs up to around 120  $h^{-1}$  for 2-propanol with rhodium bipyridyl and phosphine complexes. The alcohols include methanol, ethanol, 2-propanol, glycol, glycerine, and 2,3-butanediol.<sup>87, 88</sup> Working with ruthenium phosphine complexes at 150 °C, the TOF could be increased to around 200  $h^{-1}$  for 2-propanol, and around 500  $h^{-1}$  for other alcohols. For ruthenium hydride complexes such as  $[RuN_2H_2(PPh_3)_3]$  **11** they observed again that the reaction is significantly accelerated by illumination.<sup>89, 90</sup>





**Scheme 4:** Selected catalyst precursors for the dehydrogenation of alcohols

Ruthenium complexes like the Shvo-catalyst **13**, or Milstein's ruthenium complex **12** with a PNP pincer ligand have also been used in the base assisted alcohol dehydrogenation.<sup>5, 91</sup> For application in organic synthesis, Williams et al. reported the approach of oxidant free oxidation of secondary alcohols to ketones with a  $[\text{RuCl}_2(p\text{-cymene})]_2/\text{PPh}_3$  **15** catalyst or a 1<sup>st</sup> generation Grubbs-catalyst **16**. For benzylic alcohols, up to 90 % conversion were obtained.<sup>92</sup> Coupling the dehydrogenation of alcohols with subsequent enantioselective hydrogenation of the carbonyl compound, the deracemization of benzylic alcohols was reported with up to 74 % enantiomeric excess (ee). The reaction was performed with  $[\text{RuH}_2(\text{PPh}_3)_4]$  **17**, (*R*)-BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) **18**, and (*R,R*)-dpen (1,2-diphenylethylendiamin) **19** und 10 bar hydrogen pressure.<sup>93</sup> The neat cyclization of 1,4-butanediol to  $\gamma$ -butyrolactone with different ruthenium catalysts has been reported by Hartwig et al. with up to quantitative yields. Using  $[\text{RuCl}_2(\text{en})(\text{PMe}_3)_2]$  **20** in 1,4-butanediol, 17,000 turnovers (99 % conversion) were achieved at 205 °C within 48 hours.<sup>94</sup>

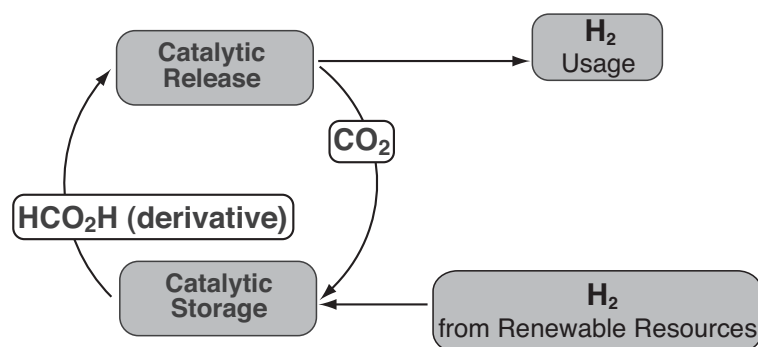
In our research group, we have developed ruthenium phosphine catalysts for the decomposition of 2-propanol.<sup>95</sup> After two hours of reaction, the highest activity for

hydrogen generation from 2-propanol was achieved with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ /di-*tert*-butylphosphinyl-1-phenyl-1*H*-pyrrole **21** at 90 °C (TOF = 155 h<sup>-1</sup>), but systems have not been fully optimized.<sup>96</sup> Later, we developed a catalyst system consisting of  $[\text{RuCl}_2(p\text{-cymene})]_2$  and nitrogen containing ligands.<sup>97</sup> An optimized system with  $[\text{RuCl}_2(p\text{-cymene})]_2$  /tmeda **22** was active for more than 250 h, with a TOF of 519 h<sup>-1</sup> after 2 h. In order to prove the applicability of our approach, we also investigated the purity of the produced hydrogen. No CO was detected throughout the experiments, and traces of 2-propanol and reaction products, mainly acetone, could be removed by simple filtering of the gas stream through a bed of activated charcoal. Additionally, by-products formed in the dehydrogenation other than acetone were identified, which are due to base-catalyzed aldol-type or Guerbet reactions of acetone.<sup>98</sup>

After all, the dehydrogenation of alcohols provides relatively clean hydrogen, and this hydrogen can be used in small fuel cells as a proof of principle. Catalyst performance has been improved substantially since the early days, but so far unfavorable reaction conditions and the availability of more efficient alternatives for energy generation from this feedstock, especially the direct methanol fuel cell,<sup>69</sup> prevent the application for hydrogen generation. Dehydrogenation of compounds containing more than one hydroxyl group, like glycerol or sugars, is still an interesting challenge. The analogy of alcohol dehydrogenations to transfer hydrogenation, especially considering 2-propanol, may lead to the use of another common hydrogen donor in transfer hydrogenations for hydrogen generations - formic acid.

### 1.2.2 Formic Acid and Formate Salts

Based on formic acid and carbon dioxide a sustainable cycle for energy storage may be conceived (Figure 4). Energy is stored by conversion of carbon dioxide to formic acid or a formate derivative, which may occur electrochemically or by catalytic hydrogenation. The resulting material is normally a liquid, either pure formic acid, an adduct containing formic acid, or an inorganic formate in aqueous solution, and can thus be handled and stored easily. Energy is released either in a direct formic acid fuel cell, or through decomposition into carbon dioxide or hydrogen. This gas mixture can be used directly in an appropriate hydrogen oxygen fuel cell. The hydrogen content of pure formic acid is 43 g/kg or 52 g/L, its release from formic acid is thermodynamically downhill by  $\Delta G^\circ = -32.8$  kJ/mol at room temperature, so the hydrogen storage process is uphill.<sup>99</sup>



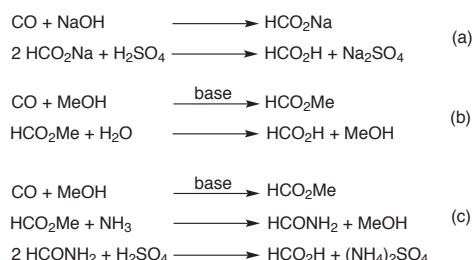
**Figure 4:** A catalytic cycle for hydrogen storage in formic acid

Historically, the electrochemical reduction of carbon dioxide to formic acid and its subsequent decomposition on Pd/C for energy storage have been proposed by Williams, Crandall, and Bloom as early as 1978.<sup>100</sup> A system for solar energy conversion by reduction of aqueous carbonate was proposed by Halmann in 1983.<sup>101</sup> In 1986, a similar concept has been laid out by Wiener, Sasson, and Blum. They also specify a Pd/C catalyst to decompose aqueous formate solutions to obtain hydrogen.<sup>102-104</sup> Both approaches apparently have not led to application. Recently, the use of carbon dioxide for energy storage has been re-discovered.<sup>105-107</sup> While the actual energy storage cycle implies that formic acid is produced in the energy or hydrogen storage process, and subsequently decomposed for hydrogen release, most research groups have focused on only one of these two steps in recent years.

The first step is the synthesis of formic acid. In nature, formic acid is present in ants and other insects, and also in stinging nettles and some other plants. Originally distilled from chopped ants, formic acid was first synthesized by Gay-Lussac. In 1855 Berthelot invented the first process that would eventually be used in industrial formic acid production.<sup>108</sup> He used sodium hydroxide and carbon monoxide to obtain sodium formate, which gives formic acid and sodium sulfate upon treatment with sulfuric acid. Currently, the main industrial producers of formic acid are BASF SE (255,000 metric tons/year)<sup>109</sup> and Kemira Oyj (> 100,000 metric tons/year).<sup>110</sup>

Industrial processes today still rely on a method similar to Berthelot's (Scheme 5): Formic acid is generally produced by the two step methyl formate process, where first methanol is carbonylated to form methyl formate in a base catalyzed reaction.<sup>111, 112</sup> Methyl formate is then hydrolyzed to formic acid and methanol, formic acid acts as an auto-catalyst in this reaction. At BASF formic acid is then purified by liquid-liquid extraction from the aqueous phase.<sup>113</sup> In 1982 this process replaced an older one where methyl formate was first converted to formamide, which is then hydrolyzed with sulfuric acid (70 %) to form formic

acid and ammonium sulfate. This detour was necessary in order to circumvent the re-esterification in the direct hydrolysis of methyl formate. The process was hazardous to workers, and has finally been substituted with respect to falling demand for the co-product ammonium sulfate.<sup>113</sup> Formic acid is also formed as an undesired by-product in non-selective oxidation reactions, but its separation is inefficient in most cases.<sup>112</sup>



**Scheme 5:** Formic acid synthesis via formates: a) carbonylation of sodium hydroxide and hydrolysis of sodium formate b) methyl formate process c) methyl formate via formamide and hydrolysis

As these processes rely largely on fossil resources, a more sustainable process is required for the above-mentioned cycle for hydrogen storage involving formic acid. One option is the synthesis of formic acid by hydrogenation of carbon dioxide, which depends on the availability of “green” hydrogen and “green” energy. Another option, the electrochemical reduction of carbon dioxide in water, can also be performed with renewable resources.<sup>114, 115</sup> As already mentioned above, both processes could rely on sunlight as a source of energy.<sup>100-106, 115</sup> For this work the hydrogenation of carbon dioxide is of particular interest, as it is the reverse reaction of formic acid decomposition to hydrogen and carbon dioxide studied.

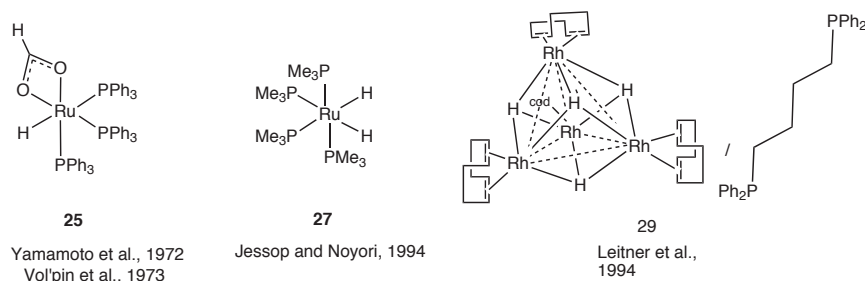
A major challenge in the hydrogenation of carbon dioxide to formic acid is the unfavorable thermodynamics, and fast kinetics with most catalysts complicate the isolation of formic acid. While the separation of a catalyst is a challenge for almost every reaction in homogeneous catalysis, it is especially difficult for formic acid due to its acidity, polarity and relative thermal instability. For this reason in most cases a formic acid derivative is targeted in the hydrogenation of carbon dioxide. Inorganic formate salts are formed in the presence of hydroxides, formate esters in the presence of an alcohol. Secondary amines lead to the formation of formamide, whereas tertiary amines form formic acid amine adducts. In Scheme 6 standard enthalpies and entropies for some reactions are given. The use of carbon dioxide and the different hydrogenation reactions have been reviewed repeatedly.<sup>99, 116-121</sup> Some selected examples of transition metal catalyzed homogeneous

hydrogenations of carbon dioxide will be shown, including early examples and recent developments.

|  |   | $\Delta G^\circ$<br>/kJ mol <sup>-1</sup> | $\Delta H^\circ$<br>/kJ mol <sup>-1</sup> | $\Delta S^\circ$<br>/J mol <sup>-1</sup> K <sup>-1</sup> |
|--|---|---|---|--|
| CO <sub>2</sub> (g) + H <sub>2</sub> (g)                           | $\rightleftharpoons$ HCO <sub>2</sub> H (l)   | 32.9                                      | -31.2                                     | -215   |
| CO <sub>2</sub> (g) + H <sub>2</sub> (g) + NH <sub>3</sub> (aq)    | $\rightleftharpoons$ HCO <sub>2</sub> <sup>-</sup> (aq) + NH <sub>4</sub> <sup>+</sup> (aq) | -9.5                                      | -84.3                                     | -250   |
| CO <sub>2</sub> (g) + H <sub>2</sub> (g) + NHMe <sub>2</sub> (liq) | $\rightleftharpoons$ HC(O)NMe <sub>2</sub> (liq) + H <sub>2</sub> O (l)                     | n.a.                                      | -239                                      | n.a.   |
| CO <sub>2</sub> (g) + 3 H <sub>2</sub> (g)                         | $\rightleftharpoons$ H <sub>3</sub> COH (l) + H <sub>2</sub> O                              | -9.5                                      | -131                                      | -409   |

**Scheme 6:** Thermodynamics of hydrogenation of CO<sub>2</sub> to formic acid and derivatives at 298 K<sup>99</sup>

Scientists first focused on the homogeneous hydrogenation of carbon dioxide with transition metal catalysts in the early 1970s. Formamides were synthesized by Kohnle et al. in 1970, achieving 1200 turnovers with [Ir(CO)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] **23**,<sup>122</sup> and Behr reported that two years later Vol'pin et al. obtained formate esters with [IrH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] **24** in the presence of tetrafluoroborate.<sup>118, 123</sup> Complexes of ruthenium and rhodium with phosphine, hydride, and formate ligands have been synthesized by Vol'pin et al. as well as by Yamamoto et al., most notably the [RuH(HCO<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] complex **25** (Scheme 7).<sup>124, 125</sup> The unusual behavior of this complex in solution – e.g. that no methyl formate is formed upon addition of esterifying agents such as methyl iodide – has led to the assumption of an equilibrium between the hydride formate complex and the dihydride carbon dioxide complex [RuH<sub>2</sub>(CO<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] **26**.<sup>126</sup> With triethylamine as base, a turnover number (TON) of 87 was achieved within 20 h in water with [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **17** at room temperature and pressures of hydrogen and carbon dioxide of 25 bar each.<sup>127</sup> According to reviewers,<sup>99, 118</sup> Takezaki's palladium chloride-catalyzed formic acid hydrogenation in water with potassium hydroxide as base had been the only system achieving a TON > 1,000 for a formate until the early 1990s, which has only been published in Japanese.<sup>128</sup> Additionally, at least one patent has been granted for the ruthenium-catalyzed production of formic acid.<sup>129</sup>



**Scheme 7:** Transition metal complexes used in the development of carbon dioxide hydrogenation

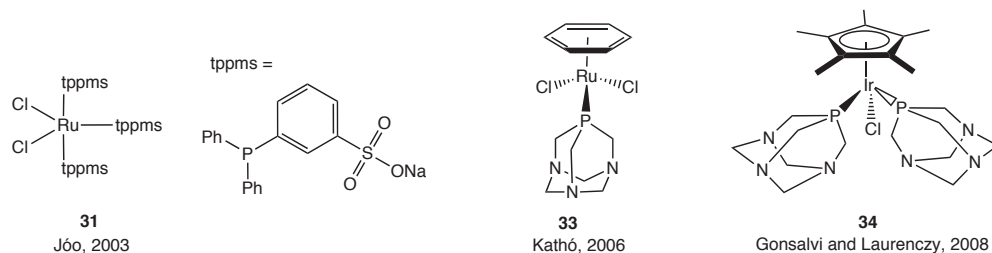
In the 1990s, with the work on hydrogenation of supercritical carbon dioxide by e.g. Jessop and Noyori, or Leitner, new emphasis was given to this field. Jessop and Noyori first

reported this reaction in the presence of triethylamine. With  $[\text{RuH}_2(\text{PMe}_3)_4]$  **27** (Scheme 7) at 50 °C, TOFs are up to 1400 h<sup>-1</sup> within the first hour. The product is an approximately 3:2 mixture of formic acid and triethylamine.<sup>130</sup> By optimization of reaction parameters and the addition of a solvent, these results were improved to TOF > 4,000 h<sup>-1</sup> adding methanol or dimethylsulfoxide (dmsO) as a co-solvent. Concerning the supercritical state of carbon dioxide in the reaction, it was crucial to closely monitor the phase behavior as the addition of the other reactants has a strong effect. While phase separation is not desired for reactants, it is beneficial if a product phase separates assisted by a co-solvent. Other products obtained by this approach are methyl formate and formamides. For *N,N*-dimethylformamide (dmf), a TON of 420,000 was achieved within 70 h.<sup>131</sup> Further studying additives, a TOF of 95,000 h<sup>-1</sup> was achieved using  $[\text{RuCl}(\text{OAc})(\text{PMe}_3)_4]$  **28** with triethylamine and pentafluorophenol in supercritical carbon dioxide at 50 °C, 80 bar hydrogen pressure and 120 bar carbon dioxide pressure. The product was isolated as a 3:2 mixture of formic acid and triethylamine. According to the authors, even higher activities can be achieved using 1,8-diazabicyclo[5,4,0]undecene (dbu) as amine, and triflic acid as additive, but this would have surpassed their infrastructure.<sup>132</sup>

In parallel, Leitner et al. have investigated the hydrogenation of carbon dioxide in solvent media with an auxiliary base. An in situ catalyst prepared of the tetranuclear rhodium complex  $[\text{Rh}_4(\mu\text{-H})_4(\text{cod})_4]$  **29** with 1.2 equivalents of dppb (Scheme 7) hydrogenated carbon dioxide at a TOF of 375 h<sup>-1</sup>, and was stable for up to 2200 turnovers. The authors propose that  $[\text{RuH}(\text{dppb})]$  **30** is formed as the actual catalyst. When pressure was reduced to stop the reaction, samples had to be frozen before analyzing them in order to slow down the reverse reaction. Interestingly, Leitner mentions that this spontaneous decomposition occurring after dropping the pressure in the reaction vessel could be useful for hydrogen storage.<sup>133, 134</sup>

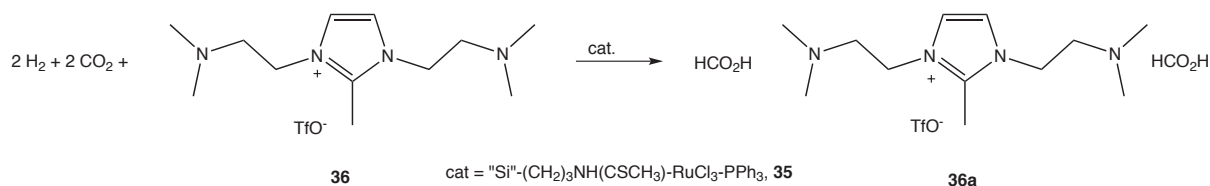
Within the last decade, the development of highly active water soluble transition metal catalysts has been an important development in the hydrogenation of carbon dioxide and carbonates. For example, the groups around Jóo, Kathó, and Laurenczy have developed several water-soluble catalyst systems containing transition metals and tppms (mono-*m*-sulfonated triphenylphosphine sodium salt, or 3-(diphenylphosphino)benzenesulfonic acid sodium salt) or pta (1,3,5-triaza-7-phosphaadamantane) as ligands. With the relatively simple complex  $[\text{RuCl}_2(\text{tppms})_3]$  **31** TOFs up to 9600 h<sup>-1</sup> were achieved at 80 °C and 95 bar,

while at milder conditions (50 °C and 10 bar), 35-50 turnovers per hour were observed.  $[\text{RuH}(\text{HCO}_2)(\text{tppps})_3]$  **32** was found as an intermediate in the reaction.<sup>135</sup> The aqueous hydrogenation of sodium bicarbonate is also catalyzed by  $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}(\text{pta})]$  **33** and two equivalents of excess pta with TOFs up to  $409 \text{ h}^{-1}$ .<sup>136</sup> The reaction is performed at 80 °C and 100 bar hydrogen pressure. As a special property of the pta ligand, the authors propose an interaction between the nitrogen atoms of the ligand, and the substrate. A similar iridium pta complex **34** of Gonsalvi, Laurenczy et al. was less active.<sup>137</sup>



**Scheme 8:** Water-soluble complexes for the hydrogenation of carbon dioxide or carbonate

Very recently, Han et al. reported a method for the hydrogenation of carbon dioxide where the decomposition of formic acid has been prevented, using task specific ionic liquids in combination with a silica-supported ruthenium triphenylphosphine catalyst **35** (Scheme 9). The task specific ionic liquid 1,3-di(*N,N*-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate **36** was employed in a reaction performed at 60 °C, 9 bar hydrogen pressure and 18 bar overall pressure. For work-up the catalyst was filtered off, and formic acid distilled from the ionic liquid. The yield of formic acid is close to two equivalents per molecule of ionic liquid, and TOFs up to  $920 \text{ h}^{-1}$  were achieved.<sup>138, 139</sup>



**Scheme 9:** The hydrogenation of  $\text{CO}_2$  with the help of a task specific ionic liquid

Additionally, the thermodynamic and kinetic parameters of the carbon dioxide hydrogenation to formic acid also make it an ideal candidate for in situ product separation in continuous reactions, as reported e.g. by Cole-Hamilton for hydroformylation.<sup>140</sup> However, first experiments have shown that this approach is not easily transferable.<sup>141</sup>

Summarizing the recent developments in carbon dioxide hydrogenation, an active system for the formation of formic acid has not been achieved yet, but seems to be realistic exploring advanced techniques like those reported in the latest publications. Completing



this task, the first step of the cycle using carbon dioxide/formic acid for hydrogen storage present above (Figure 4) can be accomplished.

In the second step of the cycle for hydrogen storage in formic acid, the latter is selectively decomposed to hydrogen and carbon dioxide. The reaction has been reported by Sabatier already in 1912.<sup>142</sup> Today, it is employed in heterogeneous catalysis, where the decomposition of formic acid vapors on surfaces is a valuable tool for understanding adsorption and desorption processes.<sup>143-147</sup> The reaction may occur via two different pathways, dehydrogenation or decarboxylation and dehydration or decarbonylation (Scheme 10).<sup>148</sup> Both reactions are thermodynamically downhill at standard conditions. As carbon monoxide is a catalyst poison for fuel cell catalysts, only the dehydrogenation/decarboxylation pathway is of interest for hydrogen generation. Only reaction systems that selectively catalyze this reaction will be considered here.

|                    |                                    |                                   | $\Delta G^\circ$<br>/kJ mol <sup>-1</sup> | $\Delta H^\circ$<br>/kJ mol <sup>-1</sup> | $\Delta S^\circ$<br>/J mol <sup>-1</sup> K <sup>-1</sup> |
|--------------------|------------------------------------|-----------------------------------|---|---|--|
| HCO <sub>2</sub> H | → CO <sub>2</sub> + H <sub>2</sub> | dehydrogenation / decarboxylation | -32.9                                     | 31.2                                      | 215  |
|                    | → CO + H <sub>2</sub> O            | dehydration / decarbonylation     | -12.4                                     | 28.7                                      | 138  |

**Scheme 10:** Formic acid decomposition pathways, and their thermodynamic properties (calculated from<sup>149</sup>, see also<sup>99</sup>)

An early example of heterogeneously catalyzed decomposition of formic acid was reported by Rienäcker et al. The reaction is performed with formic acid vapors on surfaces of copper-gold- and silver-gold-alloys.<sup>150</sup> Later working at the “Institut für Katalyseforschung” in Rostock, Rienäcker et al. employed the decomposition of formic acid to measure the activity of many types of heterogeneous catalysts, mainly metals and alloys of transition metals, such as iron, nickel, copper, palladium, silver, platinum or gold.<sup>151-153</sup> Another heterogeneous reaction is the photocatalytic decomposition of formic acid on titanium dioxide or other nanoparticles,<sup>154-156</sup> which is used for wastewater treatment.<sup>157</sup> As an application of catalytic formic acid decomposition, Hyde and Poliakoff et al. have proposed formic acid or formates as hydrogen sources for hydrogenation reactions “without gases”. Formic acid is first decomposed in a pressure reactor on a platinum catalyst, at 450°C, and the resulting supercritical fluid is fed to a second reactor, where the substrate and further solvent are added. The product can be collected downstream after decompression of the supercritical fluid from the reactor. This principle has successfully been shown for hydrogenation of alkenes, alkynes, and carbonyl compounds.<sup>158-160</sup>

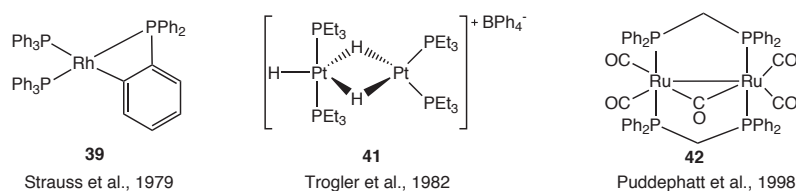


For hydrogen generation, the decomposition of formic acid on Pd/C catalysts has been proposed for hydrogen storage cycles as discussed earlier. In 1978, Williams et al. used Pd/C (1 wt.% Pd) to obtain around 55 mL of hydrogen from 4 mol/L aqueous formic acid within 10 min. The carbon dioxide obtained was trapped in a column filled with potassium hydroxide pellets. In the approach of Wiener, Sasson, and Blum from the mid-1980s, 900 mL of hydrogen are evolved from a 4 mol/L aqueous sodium formate solution during 20 min at 70 °C with a Pd/C catalyst (10 wt.% Pd).<sup>102</sup> They used a barium hydroxide solution as carbon dioxide trap.

After two decades, the heterogeneously catalyzed selective formic acid decomposition has been re-discovered for hydrogen generation recently. Xing et al. have studied the decomposition of formic acid/sodium formate solutions with noble metal catalysts supported on charcoal. They obtained around 1250 mL of gas from a solution of 1 eq. sodium formate in 3 eq. formic acid with a Pd-Au/C catalyst that had been co-deposited with CeO<sub>2</sub> at 92 °C, which corresponds to a TOF of 227 h<sup>-1</sup>.<sup>161</sup> Another example is the report of Iglesia et al., who selectively decomposed formic acid on gold or platinum on alumina at 80 °C at rates of more than 1,000 mol g(Au)<sup>-1</sup> h<sup>-1</sup>, which corresponds to a TOF of about 5 h<sup>-1</sup>. According to the authors, it depends on the size of Au domains whether formic acid dehydrogenation or dehydration, or even WGS occurs.<sup>162</sup> The electrochemical decomposition of formic acid, which is of interest for wastewater treatment, has also been reported. Carbon dioxide and hydrogen are generated separately on different electrodes, and hydrogen can be obtained in high purity (99.999%).<sup>163</sup>

In homogeneous catalysis, an early report of a selective catalyzed decomposition of formic acid to carbon dioxide and hydrogen dates back to the 1960s, when Coffey showed formic acid decomposition with several platinum, ruthenium and iridium phosphine complexes.<sup>164</sup> Since that time, and until today, various catalyst systems mostly containing transition metals and phosphine ligands have been employed in this reaction, often with increasing activities. For some catalysts, mechanistic studies have been performed. Selected examples will be discussed below. Coffey's own most active catalyst is [IrH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] **24** reaching an initial 8890 turnovers per hour in a refluxing solution of formic acid in acetic acid. Though metal carbonyls were formed, no free carbon monoxide could be detected. Four years later, Forster and Beck used rhodium and iridium iodocarbonyl compounds in the presence of hydroiodic acid, achieving a TOF of 4.4 h<sup>-1</sup> in 70% aqueous formic acid at 100 °C.<sup>165</sup> In

1978, Otsuka et al. studied the selective dehydrogenation of formic acid with an approach of finding possible intermediates for the (homogeneously) catalyzed water gas shift reaction. Their platinum(0) complex  $[\text{Pt}(\text{2-Pr}_3\text{P})_3]$  **37** catalyzes the decomposition of formic acid in acetone/water at 20 °C at a rate of 25 turnovers within the initial 15 minutes. A mechanism for the role of this complex in the water gas shift reaction was proposed, involving the decomposition of formic acid via the unstable platinum formate  $[\text{PtH}(\text{HCO}_2)(\text{2-Pr}_3\text{P})_2]$  **38**.<sup>166</sup> The next year, Strauss, Whitmire and Shriver showed that their cyclometalated rhodium triphenylphosphine complex **39** (Scheme 11) is a precursor for  $[\text{Rh}(\text{HCO}_2)(\text{PPh}_3)_3]$  **40**, which could be isolated. The decomposition of formic acid was carried out in a solution of formic acid in toluene at 20 °C, the turnover frequency  $0.06 \text{ h}^{-1}$  of this catalyst is rather low.<sup>167</sup> Trogler et al. report a binuclear platinum triethylphosphine catalyst **41** (Scheme 11) that decomposes an aqueous solution of formic acid in the presence of sodium formate with a TOF of  $3.3 \text{ h}^{-1}$  at 20 °C and at a constant rate for several hundred turnovers in 1982.<sup>168</sup> Rhodium, iridium, ruthenium, and palladium chloride in the presence of sodium nitrite, but without any other ligand, were found to catalyze formic acid decomposition at 90 °C in aqueous solution by King and Bhattacharyya (max. TOF  $126 \text{ h}^{-1}$ ) in 1995.<sup>169</sup>

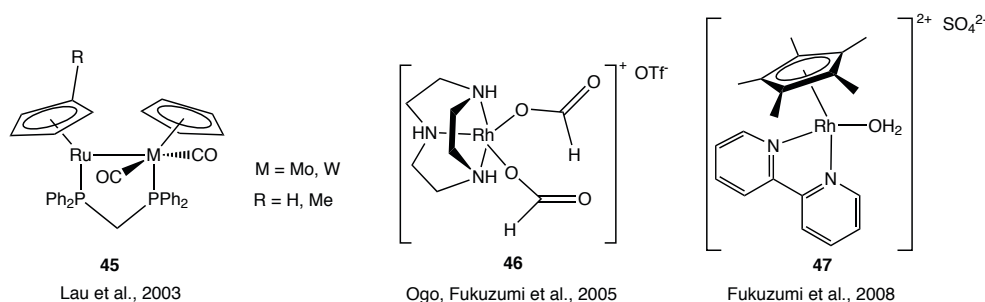


**Scheme 11:** Catalyst precursors for the decomposition of formic acid 1979-1998

The first binuclear complex for formic acid decomposition was presented by Puddephatt et al. in 1998. Their binuclear ruthenium phosphine complex  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  **42** was the most active complex for this reaction at that time, achieving a TOF of  $500 \text{ h}^{-1}$  after quantitative formic acid decomposition (15 min.). The reaction was performed in an NMR tube at room temperature in a solution of formic acid and acetone- $\text{d}_6$ . The authors identified various intermediate hydrides and formate complexes by NMR spectroscopy, and isolated  $[\text{Ru}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]$  **43**. In the presence of triethylamine they successfully performed the reverse reaction, achieving a maximum  $\text{HCO}_2\text{H} : \text{NEt}_3$  ratio of 1.2 : 1.<sup>170, 171</sup>

The formic acid decomposition with an early transition metal complex,  $[\text{cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}]$  **44**, was reported by Parkin et al. in 2002.<sup>172</sup> Another approach has been followed by Lau et

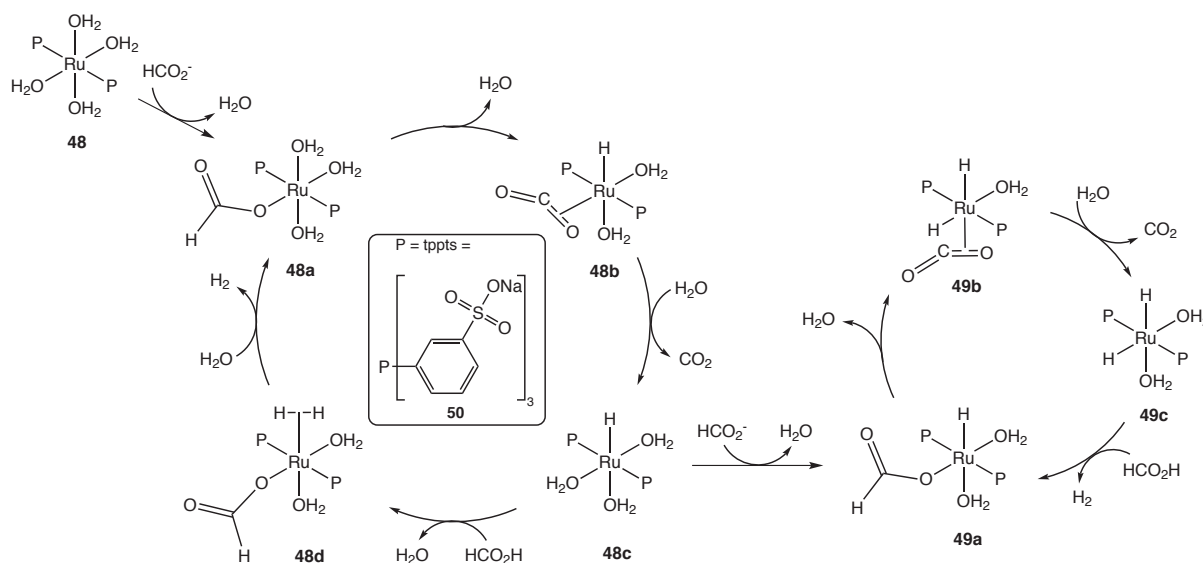
al. in 2003. Attempting to explore different acidities of Ru-H and Mo-H or W-H hydrides, they synthesized heterobinuclear bisphosphine complexes **45** containing ruthenium and molybdenum or tungsten for the interconversion of carbon dioxide/hydrogen and formic acid (Scheme 11). In NMR studies, they identified a complex bearing a bridging hydride, which was not stable as a formate, but could be isolated as a tetrafluoroborate. However, the activity of these complexes does not exceed a TOF of 30 h<sup>-1</sup> for carbon dioxide hydrogenation and 2 h<sup>-1</sup> for formic acid decomposition.<sup>173</sup> Ogo, Fukuzumi et al. observed stoichiometric hydrogen evolution treating [Rh(III)(1,4,7-triazacyclononane)(HCO<sub>2</sub>)<sub>2</sub>](OTf) **46** with sodium formate, and they obtained a dihydride carbonyl complex.<sup>174</sup> Using <sup>1</sup>H NMR and mass spectroscopy together with deuteration experiments and other spectroscopic studies, they concluded that hydrogen is generated from the diformate complex **46** by protonation. They demonstrated that the hydrogen is in fact evolved from the formate ligands, and that a ruthenium carbonyl complex is formed. Based on their former investigations on carbon dioxide hydrogenation,<sup>175, 176</sup> Fukuzumi et al. used [Rh(cp\*)(bipy)(H<sub>2</sub>O)](SO<sub>4</sub>) **47** and similar complexes for the hydrogen generation from aqueous formic acid with a maximal TON of 30 after 2 h at pH = 3.8. Combining spectroscopic studies and DFT calculations, they demonstrated that formic acid decomposition occurs via a formate complex and a hydride complex.<sup>177</sup>



**Scheme 12:** Catalyst precursors for the decomposition of formic acid 2003-2008

In 2008, Laurenczy et al. and our group independently revisited the concept of formic acid as a hydrogen storage material. Based on their expertise in the hydrogenation of carbonate, Laurenczy et al. have developed a water-soluble ruthenium tppts (tris-*m*-sulfonated triphenylphosphine trisodium salt, or 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt, **50**) in situ catalyst system, which supplies hydrogen from aqueous solutions of formic acid / sodium formate (9:1) from room temperature up to 120 °C, and at pressures between 1 and 220 bar. No loss of catalytic activity is observed up to 750 bar.<sup>178-180</sup> Under this rather high pressure, carbon dioxide hydrogenation takes places with the

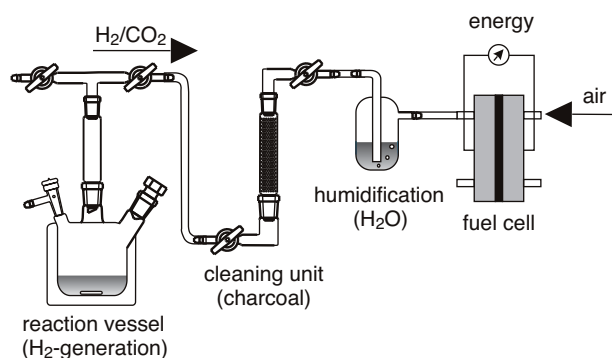
remaining product gases when the reaction turns slightly basic after full conversion of formic acid due to the presence of formate. Remarkably, no carbon monoxide was detected in the gas phase by high pressure infrared spectroscopy. In a continuous setup, where formic acid is fed to the autoclave as product gases are released from it, a TOF of 460 h<sup>-1</sup> was obtained, and the catalyst was stable for more than 90 h, reaching more than 40,000 cycles. High pressure NMR provided information for proposing a mechanism with two competing pathways of formic acid decomposition, one involving a monohydride, the other a dihydride catalyst species (Scheme 13).



**Scheme 13:** Mechanism of formic acid decomposition catalyzed by the Ru/tppts system (P = tppts; charges are omitted for clarity)<sup>180</sup>

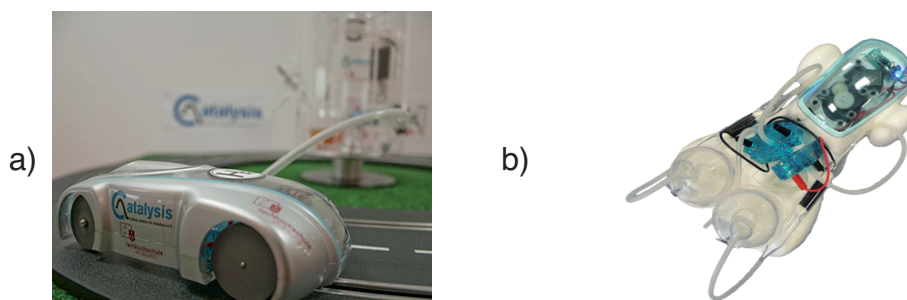
Starting from the bisphosphine tetraqua ruthenium complex **48**, formate replaces a water ligand to form complex **48a**. A second water molecule is lost when β-elimination of a hydrogen atom from formate occurs, forming the carbon dioxide hydride complex **48b**. Carbon dioxide is replaced by water to give the monohydride complex **48c**. Concluding the monohydride mechanism, formic acid replaces a water ligand and protonates the hydride to form dihydrogen in **48d**, which is subsequently displaced by water to reform formate **48a**. Monohydride **48c** is also the starting point for the dihydride mechanism. Instead of formic acid, a formate ion coordinates to give the hydride formate species **49a**. Then β-elimination of hydrogen forms the carbon dioxide complex **49b**, which eliminates carbon dioxide to form **49c**. From this complex, hydrogen is eliminated upon addition of a molecule of formic acid. The authors suggest that the reaction mainly occurs via the faster dihydride mechanism.

In our own work, we have focused on a different approach, initially using the formic acid triethylamine 5:2 adduct also known as triethylammonium formate (TEAF) as substrate/solvent for hydrogen generation.<sup>181</sup> This substrate is also well known as a hydrogen donor from transfer hydrogenation reactions,<sup>74, 75, 182-184</sup> a field in which our group has considerable expertise.<sup>185-189</sup> In ruthenium- or rhodium-catalyzed transfer hydrogenations with formic acid derivatives, hydrogen is sometimes evolved as a by-product, in addition to the expected carbon dioxide.<sup>182, 190</sup> For the selective decomposition of formic acid for hydrogen generation, we have investigated several homogeneous and heterogeneous catalyst precursors. Ruthenium  $\eta_6$ -arene complexes have shown the best activity and stability among phosphine-free catalysts.<sup>191</sup> Interestingly, a Pd/C catalyst, which had been proposed for other systems,<sup>100, 102</sup> was deactivated after an initial phase of high activity. Hydrogen generation also depends on the type and the amount of amine in the substrate solution. The introduction of a phosphine ligand in a ruthenium triphenylphosphine complex increased the activity of the catalyst by one order of magnitude. Exploring this high activity of the ruthenium phosphine catalyst, a procedure for in situ catalysts was established and several phosphine ligands studied. In combination with an optimized substrate, a first application was developed: As a proof of concept, the gas output from 5HCO<sub>2</sub>H/4HexNMe<sub>2</sub> decomposed with [RuCl<sub>2</sub>(benzene)]<sub>2</sub> / 6 PPh<sub>3</sub> **51** at room temperature, an equimolar mixture of carbon dioxide and hydrogen, was coupled to a fuel cell (Figure 5). Until full conversion of formic acid, 26 mW (at 370 V) were obtained for 42 hours.<sup>192</sup> After full conversion of formic acid, the system can be re-activated simply by adding formic acid, which is a proof of the relative robustness of the catalyst. In parallel, having studied a larger number of bases, a relationship between their basicity and the performance of the hydrogen generation system was established, but not all bases are compatible with phosphine containing catalysts. Besides, the use of a higher boiling base is desirable to minimize its loss in the reaction.<sup>193</sup> The actual results of our work are discussed in the publications, chapter 3.



**Figure 5:** A setup coupling hydrogen generation with a fuel cell

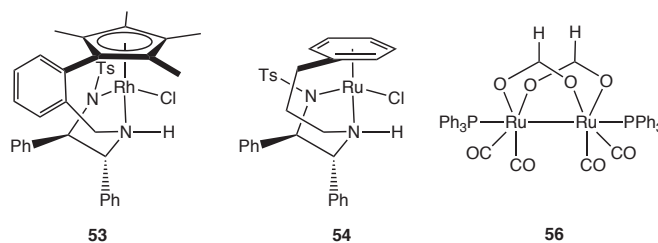
In our most recent communication, we showed that a continuous system for the decomposition of formic acid containing an in situ catalyst **52** prepared with  $[\text{RuCl}_2(\text{benzene})]_2$  and dppe, and dimethylhexylamine as amine was still active after 260,000 cycles, with an average TOF of  $900 \text{ h}^{-1}$ .<sup>194</sup> No carbon monoxide was detected in the gas phase by GC analytics. A batch reaction of a similar system was also coupled to a fuel cell for demonstration purposes, and two small prototype model cars powered by a hydrogen/oxygen fuel cell were designed, one featuring on-board hydrogen generation (Figure 6). As an improvement, a heterogeneous or heterogenized catalyst is desirable for a real world application, but for the formic acid amine system, these still suffer from either low activities or leaching.<sup>195</sup>



**Figure 6:** a) the first prototype model car coupled to a stationary hydrogen generation facility b) the second model car featuring onboard hydrogen generation

The group of Wills have studied the hydrogen generation from TEAF with their tethered half-sandwich complexes of rhodium **53** and ruthenium **54** at r.t., obtaining a TOF of around  $490 \text{ h}^{-1}$ .<sup>196</sup> In the same publication, they also presented studies with different transition metal complexes at  $120^\circ\text{C}$ , among them  $[\text{RuCl}_2(\text{dmsO})_6]$  **55**. This is an active catalyst ( $\text{TOF} = 18,000 \text{ h}^{-1}$ ), which is also stable and recyclable ( $\text{TON} = 25,000$ , after 4 cycles). Addition of one equivalent of phosphine led to deactivation, and the formate-bridged binuclear complex  $[\text{Ru}_2(\text{HCO}_2)_2(\text{CO})_4(\text{PPh}_3)_2]$  **56** was observed. A similar

tetranuclear complex was crystallized. Its properties, especially NMR data, are different from data found for a  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{PPh}_3$  catalyst prepared in a way similar to ours. The data reported for the latter, however, is similar to our own observations.<sup>197</sup> The mechanism, thus, is still subject of investigations.



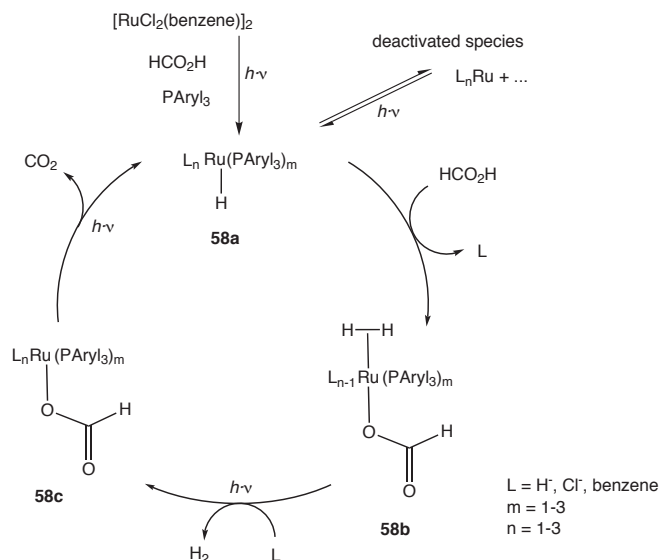
**Scheme 14:** Complexes by Wills et al. for the dehydrogenation of formic acid

Another interesting aspect of the catalytic decomposition of formic acid is its photochemical acceleration. In the early 1990s, there have been two independent reports of light-accelerated reactions of formic acid and transition metal complexes in solution. Onishi reported that irradiation with a 400 W Hg vapor lamp with Pyrex filter accelerates the reaction of formic acid with  $[\text{HCo}(\text{PhP}(\text{Et})_2)_4]$  **57**, performed in THF at 30 °C, from 0.09 turnovers to 1.6 turnovers within three hours, and 3.1 in six hours.<sup>198</sup> They also observed a shift of the hydride signal in  $^1\text{H}$  NMR from a well defined quintet at  $\delta$ -14.76 ppm of the original complex to a broad singlet -12.47 ppm upon the addition of formic acid, which did not change neither after ageing the complex for 6 h, nor after subsequent irradiation. At the same time, King et al. showed that hydrogen is evolved from aqueous formate solutions with chromium hexacarbonyl under irradiation with a TON of 18 after 1 h in a setup similar to Onishi's.<sup>199</sup> They proposed that one carbon monoxide ligand dissociates from the chromium center upon photolysis, which is replaced by a weakly coordinated solvent molecule (methanol). When formate was added, hydrogen was evolved. Interestingly this reaction is inhibited by the addition of pyridine.

While investigating the decomposition of TEAF with ruthenium phosphine catalysts, A. Boddien in our group observed that this process is also accelerated by illumination with sunlight.<sup>200</sup> Though the photochemistry of ruthenium phosphine hydride- and carbonyl complexes<sup>201, 202</sup> and ruthenium  $\eta_6$ -arene complexes<sup>203-206</sup> is well known, this behavior has seldom been explored for catalysis.<sup>89, 90</sup> Hence, when our previous ruthenium phosphine containing catalyst systems were irradiated with visible light gas evolution increased up to 11 times. This effect can also be triggered switching on and off the light source. The best catalyst productivity was observed with a  $[\text{RuCl}_2(\text{benzene})]_2/\text{dppe}$  catalyst **52**, where gas



evolution increased from 407 to 2804 turnovers, which is an almost 7-fold increase. Irradiation first generates an active species, and then accelerates the actual reaction. The first effect was also achieved irradiating the pre-catalyst solution. Based on our observations, and on NMR-spectroscopic investigations, we proposed a mechanism for this light accelerated dehydrogenation of formic acid (Scheme 15).



**Scheme 15:** A mechanism for the light-accelerated decomposition of formic acid by Beller et al.<sup>200</sup>

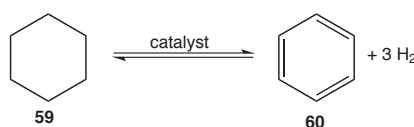
Departing from the  $[RuCl_2(benzene)]_2$  precursor, a ruthenium hydride phosphine complex **58a** is formed, while the  $\eta_6$ -benzene ligand is cleaved under irradiation. Formic acid adds to this complex, possibly via intermediates, and a dihydrogen formate ruthenium complex **58b** is formed. Dihydrogen loss from **58b** is accelerated by light, as it is the subsequent  $\beta$ -elimination of carbon dioxide from the formate **58c** to reform the ruthenium hydride phosphine complex **58a**. Additionally, irradiation prevents the catalyst from being deactivated.

With these latest developments, the generation of hydrogen from formic acid is not far from application, and could make its way into niche markets. A current co-operation of our group with the Fachhochschule Stralsund, University of Applied Sciences, includes the development of a formic acid powered racecar for the prestigious Shell eco marathon. On the other hand, many research groups are currently interested in a better understanding of formic acid decomposition and carbon dioxide hydrogenation mechanisms. Important developments might come up in the next years in this field. Another interesting class of compounds that has been proposed as liquid hydrogen storage materials are cycloalkanes and similar heterocyclic compounds.



### 1.2.3 Cycloalkanes and Heterocyclic Compounds



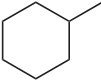
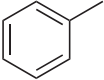


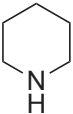
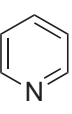
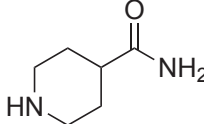
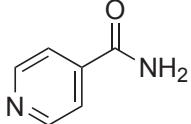
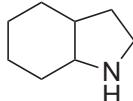
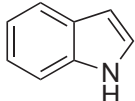
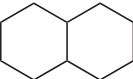
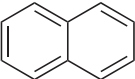
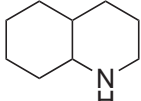
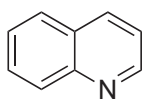
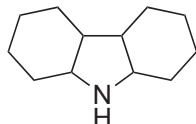
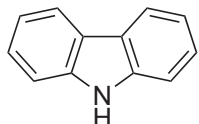
The principle of hydrogen storage in cycloalkanes has been proposed almost forty years ago (Scheme 16),<sup>207</sup> as stated by Jessop et al. in a recent paper.<sup>208</sup> In the need of a hydrogen carrier with high hydrogen content, e.g. for fuel cell powered vehicles, this class of compounds has been suggested as organic hydrides for hydrogen storage, and has been reviewed in this respect several times.<sup>49, 55, 56, 62</sup> The principle is based on the catalytic hydrogenation and dehydrogenation of aromatics and the corresponding hydrogenated compounds such as benzene **60** and cyclohexane **59**, naphtalene/decahydronaphtalene, pyridine/piperidine, indole/octahydroindole, carbazole/dodecahydrocarbazole etc.



**Scheme 16:** Dehydrogenation of cyclohexane to benzene for hydrogen storage<sup>207</sup>

In practice, the hydrogen charged compound would be delivered to the end user, generally for use in vehicles, for example at petrol stations. The dehydrogenated aromatic compound can be collected at the same place, and then be recycled. The systems offer a relatively high storage capacity of up to 7.2 mass% (decalin), and volumetric storage capacities up to 65 g/L.<sup>49</sup> Selected examples are given in Table 2. For hydrogen release, generally a heterogeneous transition metal catalyst is used at temperatures around 100–300 °C. After recollection, the aromatic compound would be re-hydrogenated at specialized plants at elevated hydrogen pressure, depending on the system, and temperatures in the same range as for dehydrogenation.<sup>55</sup> A major drawback of these storage materials are the relatively high enthalpies of dehydrogenation, which means that high temperatures are needed for hydrogen release. In addition, the high melting point of some of the most promising materials could cause serious problems in operation.<sup>49</sup>

**Table 2:** Selected cyclic compounds for hydrogen storage, and energy of dehydrogenation  $\Delta H_{\text{rxn}}$ 

| hydrogenated form   | m.p. / °C <sup>209</sup>            | dehydrogenated form   | m.p. / °C <sup>209</sup> | $\Delta H_{\text{rxn}}$ / kJ mol <sup>-1</sup> of H <sub>2</sub> released | mass% releasable H <sub>2</sub> | ref. |
|---|-------------------------------------|---|--------------------------|---|---------------------------------|------|
| 1    | 7                                   |    | 5.5                      | 68.6  | 7.1                             | 55   |
| 2    | -126                                |    | -93                      | 68.3  | 6.2                             | 55   |
| 3    | 68–69 <sup>210</sup>                |    | 88–91                    | 54.8  | 5.5                             | 62   |
| 4    | -13                                 |    | -42                      | 80.0  | 7.1                             | 62   |
| 5    | 152–153 <sup>211</sup>              |    | 154–155 <sup>212</sup>   | n.a.  | 5.0                             | 208  |
| 6   | liquid at r.t.                      |   | 51–54                    | 57.5  | 6.4                             | 208  |
| 7  | -43 cis<br>-32 trans                |  | 80–82                    | 64.0 cis<br>66.3 trans  | 7.2                             | 55   |
| 8  | 48 cis<br>(4aS, 8aS) <sup>213</sup> |  | -17– -13                 | 69.9  | 7.2                             | 62   |
| 9  | 73 – 74.5 <sup>214</sup>            |  | 246                      | 52.8  | 6.7                             | 208  |

A recent example for this method is the dehydrogenation of 4-substituted piperidines, octahydroindoles (entry 6, Table 1), and dodecahydro-1*H*-carbazoles (entry 9, Table 1) by Jessop et al<sup>208</sup>. According to the authors the most promising experimental results were obtained for 4-piperidinecarboxamide (entry 5, Table 1). This is explained by the decrease of the dehydrogenation enthalpy in comparison to piperidine due to the effect of the substituent in 4-position. 4-Piperidinecarboxamide dehydrogenates to 4-pyridinecarboxamide on Pd/SiO<sub>2</sub> at 170 °C in an open vessel with a half-life time of 16 min. During re-hydrogenation, 4-pyridinecarboxamide is converted quantitatively within max. 24 h at 160 °C on a Rh/C catalyst at 70 bar hydrogen pressure.

Concluding, despite some disadvantages, especially nitrogen-containing heterocycles are another option for hydrogen storage.

### 1.3 Conclusion

It has been shown that alcohols, formic acid, and cyclic organic compounds are interesting materials for hydrogen storage. Important developments and problems in the hydrogen generation from these substrates have been summarized, and recent advances have been reported. While reaction conditions for hydrogen generation from formic acid and alcohols are similar, cyclic organic compounds need higher temperature to release hydrogen. Thus, these storage materials aim at different applications than formic acid and alcohols.

Many alcohols can be obtained in a sustainable way by fermentation, but the homogeneous catalytic dehydrogenation is not competitive with respect to reforming processes, or direct alcohol fuel cells to date. The direct methanol fuel cell is already on the market, and other alcohols are more efficiently used by reforming, or even in combustion engines. The hydrogen production from organic compounds containing multiple hydroxy groups, such as glycerol, sugars, starch, or wood, by homogeneous dehydrogenation or low temperature reformation remains a rewarding challenge so far.

For formic acid, in turn, several methods for hydrogen generation are available awaiting application. Different conditions reported by research groups permit high pressure hydrogen generation as well as systems working at ambient conditions, and at low temperatures. It has been shown that systems invented in the lab can be actually used in real world applications, and that scale-up is viable. Yet a less expensive catalyst system is desirable, and investigations are ongoing. Hydrogen cleaning is easy, but for a prolonged fuel cell lifetime, hydrogen and carbon dioxide should be separated. For the production of formic acid, a sustainable process for the direct catalytic hydrogenation of carbon dioxide to neat formic acid does not seem too distant.

Alcohols and formic acid obtained from sustainable resources might be of considerable importance as hydrogen storage materials. While, due to their intrinsic properties, it has never been likely that any of them, maybe except methanol, might play a major role for our future energy needs replacing current energy carriers, they can be valuable as an intermediate solution or for niche applications, such as small portable devices.

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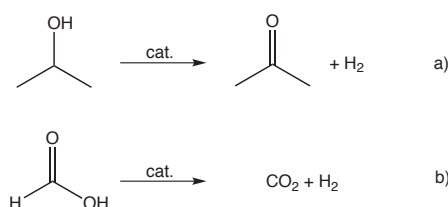
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## 2 Objectives of this Work

Hydrogen generation from renewable resources is important as a short-to-mid-term solution for satisfying the increasing energy demand. If it is performed in a sustainable way, it will help to prevent further climate change, and will not further deplete resources, either fossil or natural.

Liquid organic materials, which can be derived from these renewable resources, are alcohols or formic acid. They are easily handled and stored, and could be used as hydrogen storage materials for portable application, given the fact that a suitable catalyst to release the hydrogen is available. The focus of this dissertation has been the development of such catalysts, which satisfy the requirements for real world applications, e.g. stability, activity and efficiency. As model reactions, the dehydrogenation of 2-propanol to acetone and hydrogen, and the decomposition of formic acid to carbon dioxide and hydrogen have been studied (Scheme 17).



**Scheme 17:** a) the dehydrogenation of 2-propanol b) the decomposition of formic acid

The base-assisted dehydrogenation of 2-propanol at temperatures < 100 °C had been established earlier in our group. In this work, using ruthenium precursors and nitrogen containing ligands, less expensive and less air sensitive catalysts were targeted for this reaction.

Furthermore, a selective catalyst for the decomposition of formic acid to carbon dioxide and hydrogen should be established. As a starting point, the 5 HCO<sub>2</sub>H · 2 NEt<sub>3</sub> adduct was chosen in order to find a suitable catalyst. With modifications of the substrate, and the introduction of phosphine ligands, the properties of the reaction system should be investigated. Based on these observations, it was planned to optimize the performance of the system, especially concerning hydrogen output. Besides, the purity of the generated gas mixture of hydrogen and carbon dioxide was investigated in order to enable fuel cell usage.

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Another aim was to study the influence of light on the decomposition of formic acid with ruthenium phosphine catalysts both quantitatively and mechanistically. Finally, the applicability of our approach was to be demonstrated.

## 3 Publications

### 3.1 Summary

For the generation of hydrogen from renewable resources, two main approaches have been followed in this thesis, the dehydrogenation of 2-propanol as a model system for the dehydrogenation of alcohols, and the decomposition of formic acid to carbon dioxide and hydrogen.

In order to explore the potential of the dehydrogenation of 2-propanol, inexpensive and robust catalysts were targeted. Interestingly, it was established that a ruthenium(II) precursor in combination with a diamine ligand gives an active in situ catalyst. Several diamine ligands have been investigated, and the results were published in publication 3.2, *Chem. Commun.* **2007**, 522-524.

As we have also been interested in the applicability of the above mentioned catalyst system, we have improved it towards hydrogen outcome and long term stability. Furthermore, the quality of the generated hydrogen was assured. Along with a review of former investigations, these improvements have been summarized in publication 3.3, *Chem. Ing. Tech.* **2007**, 79 (6), 741-753.

Subsequently, we have focused on the hydrogen generation from formic acid. Hydrogen can be generated from formic acid by catalytic decomposition in an equimolar mixture with carbon dioxide. A competing reaction is the decomposition of formic acid into carbon monoxide and water. As carbon monoxide is a catalyst poison for fuel cells, it is a priori not acceptable in hydrogen for fuel cell use. Thus, a practicable procedure for the hydrogen generation by selective decomposition of formic acid or its derivatives had been desired.

As a starting point, the formic acid triethylamine 5:2 adduct has been chosen. First, a ligand free model system with a ruthenium catalyst working at 40 °C has been established. Later, this system has been significantly improved using the simple  $[\text{RuCl}_2(\text{PPh}_3)_3]$  complex as catalyst precursor, and sufficient hydrogen was generated to be directly used in a fuel cell. Additionally, a range of different homogeneous and heterogeneous transition metal catalysts has also been investigated for different substrates containing formic acid and an



amine. The influence of the substrate composition has been studied replacing triethylamine with other tertiary amines. For details, see 3.4, *Angew. Chem.* **2008**, 120 (21), 4026-4029, or *Angew. Chem. Int. Ed.* **2008**, 47 (21), 3962-3965.

In order to further explore the activating effect of phosphines, a procedure for in situ generated ruthenium catalysts has been developed. The catalyst activity has been further increased varying the phosphine ligands and ruthenium precursors. With an improved catalyst, long-term and recycling experiments have been performed in order to assess the stability of the catalyst. Electricity has been generated in a fuel cell for almost two days using the hydrogen generated by a room temperature experiment. The reaction itself was investigated by variation of the basic additive and its concentration. This has been published in 3.5, *ChemSusChem* **2008**, 1 (8-9), 751-758.

In parallel, the parameters affecting the decomposition of formic acid have been investigated in more detail. This includes different bases, catalyst precursors, and inorganic salts as additives. A relationship between basicity and activity has been established for the base additives. The results have been published in 3.6, *Tetrahedron Lett.* **2009**, 50 (14), 1603-1606.

Excitingly, we have found that illumination with sunlight significantly accelerates the reaction during experiments with ruthenium phosphine in situ catalysts. A method has been developed in order to study this effect with artificial sunlight, and hydrogen generation has increased by up to one order of magnitude due to illumination. Photo-acceleration can also be triggered switching on and off the light source. Exposition to light in different phases of pre-treatment and reaction has different effects on the reaction. With this knowledge, and having studied the catalyst with  $^1\text{H}$  NMR, a mechanism for the light acceleration has been proposed. Other effects such as temperature have been ruled out. This work has been published in 3.7, *Chem. Commun.* **2009**, 4185-4187.

The hydrogen generation from formic acid amine mixtures with ruthenium phosphine in situ catalysts has been scaled up in order to produce large amounts of hydrogen for a prolonged time, which is important for future applications. Long-term experiments as well as catalyst recycling experiments and continuous experiments have been performed. It has been confirmed that the gas evolved contains only hydrogen and carbon dioxide after a small filter, which is important for using this gas in fuel cells. For the catalytic experiments, the performance and stability of the ruthenium phosphine system have been maximized

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under conditions suitable for application, e.g. using standard commercial reagents. The parameters investigated are catalyst concentration, the (phosphine) ligand, ruthenium to ligand ratio, the auxiliary amine, and the concentration of this amine. An update has been published in *Adv. Synth. & Catal.* **2009**, 351 (14), 2517-2520; see chapter 3.8.

## 3.2 Novel Improved Ruthenium Catalysts for the Generation of Hydrogen from Alcohols

Henrik Junge, Björn Loges, and Matthias Beller\*

*Chemical Communications* **2007**, 522-524.

To this publication, B.L. contributed a significant part of the catalytic experiments, and participated in the evaluation and discussion of the results, as well as in the preparation of the manuscript. His overall contribution is about 40%.

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### **3.3 Herstellung von Wasserstoff aus nachwachsenden Rohstoffen mit molekular definierten Katalysatoren**

Björn Loges, Henrik Junge, Björn Spilker, Christine Fischer, and Matthias Beller\*

*Chemie Ingenieur Technik* **2007**, 79 (6), 741-753.

In this publication, B.L. contributed the larger part of the catalytic experiments, was involved in the discussion of results, and prepared most of the paper, B.L.'s overall contribution is about 40%.

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### 3.4 Kontrollierte Wasserstoffherzeugung aus Ameisensäure-Amin-Addukten bei Raumtemperatur und direkte Nutzung in H<sub>2</sub>/O<sub>2</sub>-Brennstoffzellen

Björn Loges, Albert Boddien, Henrik Junge, and Matthias Beller\*

*Angewandte Chemie* **2008**, 120 (21), 4026-4029.

also published as:

Controlled Generation of Hydrogen from Formic Acid Amine Adducts at Room Temperature and Application in H<sub>2</sub>/O<sub>2</sub> Fuel Cells

*Angewandte Chemie International Edition* **2008**, 47 (21), 3962-3965.

For this paper, B.L. developed and performed most catalytic experiments. He contributed a significant amount to the discussion and the preparation of the manuscript. B.L.'s overall contribution is about 75%.

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### 3.5 Hydrogen Generation at Ambient Conditions: Application in Fuel Cells

Albert Boddien, Björn Loges, Henrik Junge, and Matthias Beller\*

*ChemSusChem* **2008**, 1 (8-9), 751-758.

In this paper, B.L. designed and performed catalytic experiments not involving phosphines. He performed long-term experiments and analyzed the gaseous products. He was involved in the discussion and the preparation of the manuscript. B.L.'s overall contribution is about 30%.

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### 3.6 Improved Hydrogen Generation from Formic Acid

Henrik Junge, Albert Boddien, Francesca Capitta, Björn Loges, James R. Noyes, Serafino Gladiali, and Matthias Beller\*

*Tetrahedron Letters* **2009**, 50 (14), 1603-1606.

B.L. contributed a significant amount in the discussion and the development of experiments. He was also involved in the preparation of the manuscript. The overall contribution is about 15%.

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### 3.7 Hydrogen Generation: Catalytic Acceleration and Control by Light

Björn Loges, Albert Boddien, Henrik Junge, James R. Noyes, Wolfgang Baumann, and Matthias Beller\*

*Chemical Communications* **2009**, 4185-4187.

In this paper, B.L. developed and performed most catalytic experiments, and developed and performed NMR experiments in cooperation with Dr. Wolfgang Baumann. He wrote the paper, and was involved in the discussion and interpretation of the results. His overall contribution is about 70%.



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### 3.8 Continuous Hydrogen Generation from Formic Acid: Highly Active and Stable Ruthenium Catalysts

Albert Boddien, Björn Loges, Henrik Junge, Felix Gärtner, James R. Noyes,  
and Matthias Beller\*

*Advanced Synthesis & Catalysis* **2009**, 351 (14), 2517-2520.

B.L. participated in the design of catalytic experiments, and was involved in the discussion and interpretation of results as well as the preparation of the paper. His overall contribution is about 15 %.

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# Selbständigkeitserklärung

Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe, keine außer den von mir angegebenen Hilfsmitteln und Quellen dazu verwendet habe und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen als solche kenntlich gemacht habe.

Rostock, 04. September 2009

## Abstract

In this thesis, the hydrogen generation by dehydrogenation of 2-propanol and formic acid as model substances for renewable resources have been studied, which is of importance for hydrogen storage. For the base-assisted dehydrogenation of 2-propanol, a ruthenium diamine catalyst system has been investigated. For the selective decomposition of formic acid to hydrogen and carbon dioxide, a system has been established containing ruthenium catalysts and formic acid amine adducts as substrates. The best catalyst activity and productivity have been achieved with in situ generated ruthenium phosphine catalysts, e.g.  $[\text{RuCl}_2(\text{benzene})]_2$  / dppe (TOF =  $900 \text{ h}^{-1}$ , TON = 260,000). The gas evolved has been directly used in fuel cells. Furthermore, the influence of irradiation with visible light has been described for the ruthenium phosphine catalysts.

In dieser Dissertation wurde die Wasserstofferzeugung aus 2-Propanol und Ameisensäure als Modellsubstanzen für erneuerbare Ressourcen untersucht, was für die Wasserstoffspeicherung von Bedeutung ist. Zur Base-unterstützten Dehydrierung von 2-Propanol wurde ein Ruthenium-Diamin-Katalysatorsystem untersucht. Für die selektive Zersetzung von Ameisensäure in Kohlenstoffdioxid und Wasserstoff wurde ein System aus Ruthenium-Katalysatoren und Ameisensäure-Amin-Addukten entwickelt. Die besten Aktivitäten und Produktivitäten wurden mit in situ dargestellten Ruthenium-Phosphin-Katalysatoren erzielt, z.B.  $[\text{RuCl}_2(\text{benzene})]_2$  / dppe (TOF =  $900 \text{ h}^{-1}$ , TON = 260.000). Hieraus entstandenes Gas wurde direkt in einer Brennstoffzelle eingesetzt. Zusätzlich wurde der Einfluss von sichtbarem Licht auf Ruthenium-Phosphin-Systeme beschrieben.



