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Ru Catalysis

A Rechargeable Hydrogen Battery Based on Ru Catalysis

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***Abstract:** Apart from energy generation, the storage and liberation of energy are among the major problems in establishing a sustainable energy supply chain. Herein we report the development of a rechargeable H_2 battery which is based on the principle of the Ru-catalyzed hydrogenation of CO_2 to formic acid (charging process) and the Ru-catalyzed decomposition of formic acid to CO_2 and H_2 (discharging process). Both processes are driven by the same catalyst at elevated temperature either under pressure (charging process) or pressure-free conditions (discharging process). Up to five charging–discharging cycles were performed without decrease of storage capacity. The resulting CO_2/H_2 mixture is free of CO and can be employed directly in fuel-cell technology.*

The installation of a sustainable energy supply chain is one of the greatest challenges to be addressed in this century.[1,2] The focus of discussions in this field has shifted within the past years from the generation of energy from regenerative sources toward energy storage and liberation. Among the manifold reasons for this change, the most prominent is the fact that energy generation from regenerative sources is not constant and depends on unpredictable climatic factors (like wind, temperature, duration of sunshine, etc). Today the development of efficient energy-storage media that allow efficient energy regeneration is generally considered to be decisive. Within this context, hydrogen as an energy carrier is recognized to be of particular importance.[3] It can be employed in fuel cells for energy generation with formation of water. In the past years the field of fuel-cell technology has reached a sophisticated state of development;[4] however, it is still hampered by the lack of efficient hydrogen-storage systems. Due to the inherent chemical properties of hydrogen, some of these problems (diffusion through metal layers, storage capacity, etc.) can be addressed only with significant technical investment.[5,6] For these reasons the development of practical hydrogen-storage devices plays a key role in sustainable-energy politics. Two general main strategies for tackling this problem have evolved during the past years. Important advances were made in the field of adsorptive H_2 storage.[5–7] More recently, H_2 storage in chemical bonds is considered as a complementary approach.[8] In particular H_2 storage through the reduction of carbon dioxide to formic acid, methanol, or methane opens up new perspectives.[9–20] Furthermore, important studies in the field of H_2 liberation by the dehydrogenation of ammonia–borane adducts,[21] metal hydrides,[22] and alcohols[23] have been reported.

Apart from the development of pilot plants for the separate storage and liberation of hydrogen, systems that allow the reversible storage and liberation of hydrogen gas using an identical catalyst system (i.e. a hydrogen battery) are also of interest. These systems are particularly interesting in the context of autarkic energy supplies (e.g. island solutions, automotive industry, etc.). In order to reach the goal of a hydrogen-driven battery, the charged storage medium must also promote the reverse reaction, that is, the liberation of hydrogen, with full regeneration of the storage medium. In this regard, *N*-ethylhexahydrocarbazol[8] and formic acid present significant advantages since the storage medium (i.e. *N*-ethylcarbazol or CO_2) is completely regenerated, and hence both hydrogen storage and liberation are possible.[8,24–28] Due to its abundance CO_2 might have advantages as an environmentally benign storage medium.

Since the ground-breaking work of Laurenczy et al. in the field of CO_2 reduction/formic acid decomposition, in which an aqueous bicarbonate solution was reduced to the corresponding formate solution, important contributions from the Beller and Fujita groups have been published in which either the temperature or the pH value was used as a switch for the discharging process.[29–32] These systems are based on the reduction of an aqueous bicarbonate solution, but recently Beller et al. reported a reversible hydrogen-storage and -liberation system employing amines as bases.[33] Whereas the increased storage capacity is advantageous, the liberated CO_2/H_2 gas mixture is disadvantageous since CO_2 must be recovered from the gas phase or the gas mixture can directly be employed in fuel-cell technology.[34] However, this type of battery must be stored at temperatures below room temperature after the charging process.

Herein we report a prototype system for the reversible storage and liberation of H_2 based on the amine/CO_2 technology (Figure 1). At elevated temperature both the fast storage and the release of H_2 gas is possible. Several charging and discharging cycles can be performed without the need to change the storage container (an autoclave) or the catalyst. Moreover, the charged system can be stored for days without loss of efficiency.

Recently our group reported the preparation and application of the (PNNP)(acetonitrile)Ru^{II} complex **1** for selective C–H oxidation.[35] With regard to the catalyst structure

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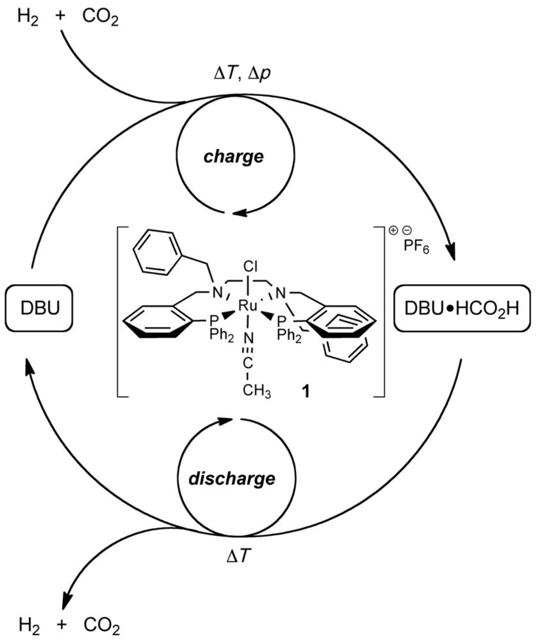


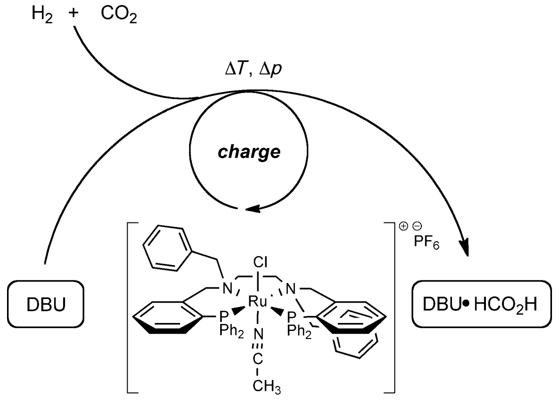
Figure 1. Prototype of a Ru-driven hydrogen battery.

we speculated that the same complex could also be active in hydrogenations. Based on the fundamental reports from the Jessop group[36] in the field of CO_2 reduction, we performed initial experiments using amine bases and catalytic amounts of complex **1** in the hydrogenation of CO_2. Gratifyingly, the reduction of CO_2 to the corresponding DBU formate salt (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) was possible with only 0.015 mol% of **1** within 4 h at 100 °C (entry 8, Table 1).

At higher catalyst loadings under otherwise identical conditions the bis-formic acid DBU product, and hence a significantly increased storage capacity (entries 1–4, Table 1), was observed. Although no solvent is required for the reduction process, the addition of a small amount of toluene reduces the undesired crystallization of the salt and suppresses some problems that were encountered with the neat system (bad miscibility, catalyst deactivation through formation of inclusion products, problematic reactivation of the charged battery after a couple of days; entries 1, 3–6, Table 1). Further optimization of the system showed that the addition of pentafluorophenol had no beneficial influence on the reactivity (entries 3 and 4, Table 1). This observation is in strong contrast to previously reported systems[33,36] and might indicate a different activation–reduction mechanism.

Knowing that complex **1** shows good activity in the CO_2 reduction we subsequently investigated its activity in the decomposition of formic acid (Figure 2). Under pressure-free conditions the DBU formate salt decomposed at 100 °C in the presence of 0.075 mol% **1** within 70 min (Figure 2C). Lowering the temperature resulted in a significant decrease of the decomposition rate. Furthermore, we investigated the influence of pentafluorophenol and toluene on the decomposition rate (Figure 2B). We were pleased to find that the addition of toluene led to an increase of the decomposition rate, whereas the addition of pentafluorophenol had almost no effect.

Table 1: Reduction of CO_2.[a]



1 [*x* mol-%]

Entry	1 [mol%]	C_6F_5OH [mol%]	toluene [M]	*t* [h]	Yield [%]	TON[b]
1	0.075	–	6	1	119	1587
2	0.075	–	–	4	135	1800
3	0.075	1.25	6	4	137	1827
4	0.075	–	6	4	141	1880
5	0.015	0.25	6	4	62	4133
6	0.015	–	6	4	60	4000
7	0.015	0.25	–	4	83	5533
8	0.015	–	–	4	84	5600

[a] Conditions: 65.7 mmol DBU, 100 °C, 70 bar H_2, 20 g dry ice (freshly prepared). [b] Calculated as mole of DBU formate salt per mole of catalyst).

Moreover, CO impurities were not detectable in the gas mixture down to 10 ppm.[37] A further decrease of the catalyst concentration slowed down the reaction significantly.

In subsequent experiments the two catalytic transformations were coupled to form a cyclic process. The autoclave was filled with DBU and 0.075 mol% complex **1** since at this catalyst concentration the 2:1 adduct of formate and DBU adduct was formed and yields higher than 100% were observed. The autoclave was charged with dry ice and pressurized with hydrogen gas (70 bar). The system was closed and heated to 100 °C with the pressure approaching about 140 bar. After 2.5 h a pressure drop to about 100 bar was observed. The autoclave was cooled to room temperature and the gas atmosphere was flushed with N_2 gas. The autoclave was subsequently heated up under pressure-free conditions and the released gas was collected in an inverted gas burette. After 2 h gas evolution ceased and the crude product gas was analyzed. The autoclave was cooled to room temperature under an N_2 atmosphere, charged again with dry ice and hydrogen gas (70 bar), closed, and heated up again. This algorithm of charging and discharging was repeated five times (Figure 3). As shown in Figure 3 the H_2 yields equilibrated to about 100% (or a corresponding gas volume of about 3.4 L) after the first cycle. The analysis of the gas mixture showed that apart from traces of N_2 (from flushing the autoclave) equimolar amounts of CO_2 and H_2 were formed. CO impurities were not detectable.[37]

In order to get insight into an undesired decomposition of the formic acid DBU adduct in the presence of the catalyst at

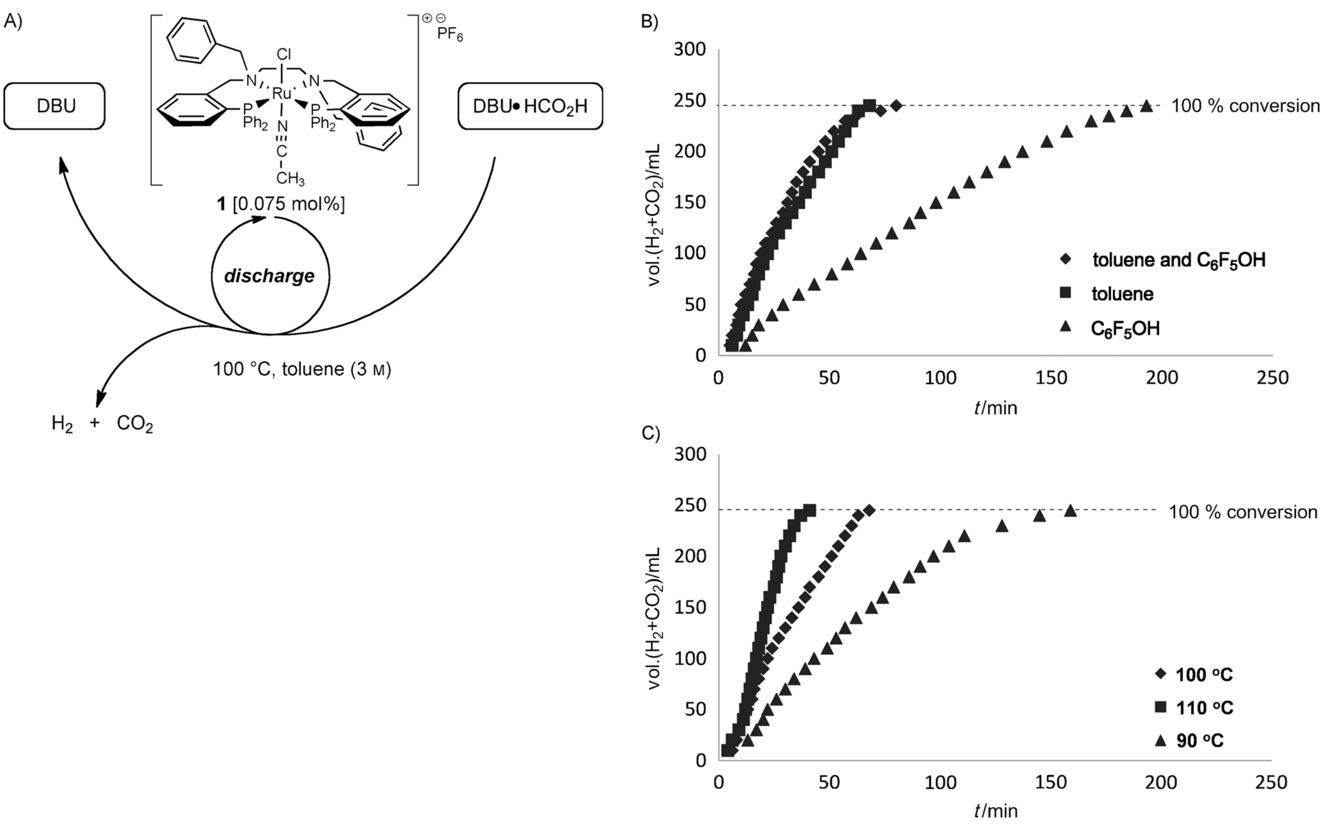


Figure 2. A) Activity of catalyst **1** in the decomposition of formic acid. B) Effects of additives and solvent; reagents and conditions: 1:1 adduct of formic acid and DBU (5 mmol), **1** (0.075 mol%), C_6F_5OH (1.25 mol%, if necessary), toluene (1.66 mL). B) Temperature effects; reagents and conditions: 1:1 adduct of formic acid and DBU (5 mmol), **1** (0.075 mol%), toluene (1.66 mL).

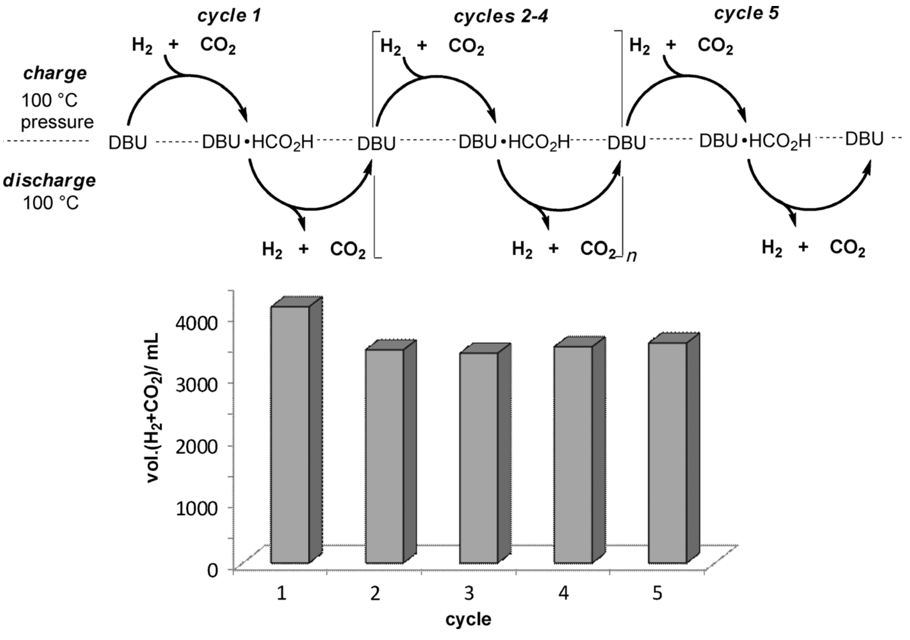


Figure 3. Charging and discharging cycles of the H_2 battery.

room temperature and into the long-term stability of the catalyst in the presence of the formic acid DBU adduct, we investigated the long-term stability of the charged H_2 battery (Figure 4). After the battery had been charged the system was cooled to room temperature and flushed with N_2. The composition of the condensed phase was analyzed by NMR spectroscopy on a daily basis over a period of five days. The composition of the battery content did not change (Figure 4A) and hence heating the system to 100°C after five days resulted in complete H_2 generation (chart (B), Figure 4B). After the discharging process was complete, the system was charged again without loss of efficiency.

Having tested the recyclability and long-term stability of the storage medium and the catalyst, we evaluated the possibilities for removing a defined amount of gas in two final experiments. The charged system was heated to 100°C and the internal pressure was monitored over the time. Within 2.5 h an internal pressure of 22 bar was recorded (Figure 5A). Hence, this battery can also be used in combination with a suitable valve technology for high-performance fuel cells in which defined gas volumes are

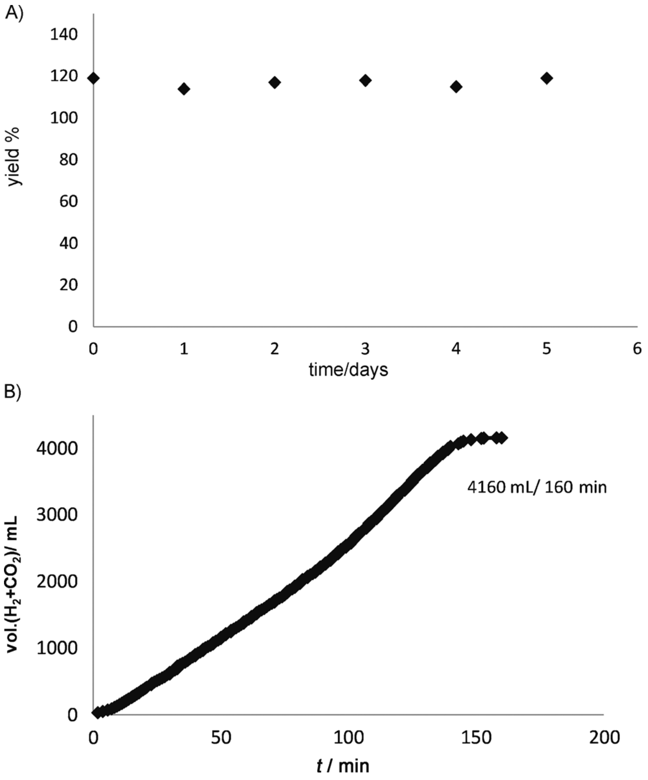


Figure 4. A) Long-term stability of the storage medium (determined by ^{1}H NMR integration). B) Discharging process after the battery had been stored for 5 days at room temperature.

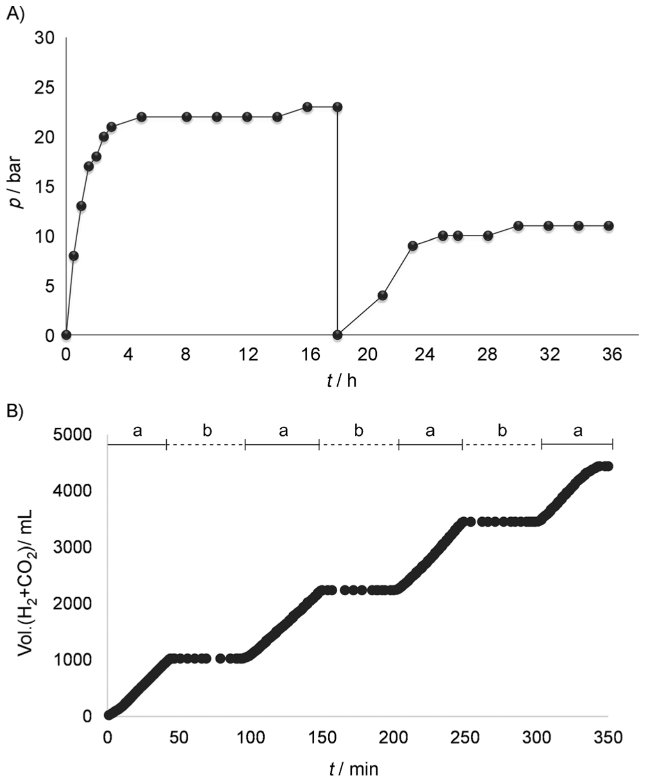


Figure 5. A) Pressure–time course for the decomposition in a closed system. B) Temperature-controlled gas removal [(a) heating to 100 °C; b) cooling to RT].

injected under pressure. Apart from the use of dosing valves the amount of the produced gas can also be directed by means of the temperature. In order to prove this hypothesis the system was subjected to an alternating heating–cooling algorithm. The formation of the CO_2/H_2 gas mixture was followed volumetrically over the time (Figure 5B). As can be seen from this diagram the system is stable and allows the controlled release of a defined amount of H_2 gas either under pressure or pressure-free by adjustment of the respective heating period.

Herein we have reported the use of a readily accessible (PNNP)(acetonitrile)Ru^{II} complex for the efficient and reversible reduction of CO_2 in the presence of DBU as a base. At a catalyst loading of only 0.075 mol % both the reduction using H_2 pressure as well as the decomposition of the formic acid adduct under pressure-free conditions were demonstrated. As compared to the hydrogen storage via reduction of CO_2 to methanol The present system has a lower hydrogen-storage capacity (4.4 wt %) than that achieved for the reduction of CO_2 to methanol (12.5 wt %). However, it possesses the advantage of being a fully reversible hydrogen-storage system that can be used in conventional fuel cells.[38] Technical problems like the addition of solid CO_2 and the recycling of the released CO_2 will be addressed in future work by employing microreactors.

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