A Rechargeable Hydrogen Battery Based on Ru Catalysis

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S1. General Remarks.

All high pressure reactions were performed in a 100 mL stainless-steel autoclave (Berghoff, BR-100) that was suitable for pressure of up to 200 bar. NMR spectra were recorded on a Bruker AV300 spectrometer at 300 MHz (1H NMR) at 25 °C unless otherwise noted. Chemical shifts were reported in ppm down field using tetramethylsilane as an internal standard. 1,8-Diazabicycloundec-7-ene (DBU) was purchased from TCI (Tokyo Chemical Industry Co., Ltd). Toluene was purchased from Sigma Aldrich. Hydrogen gas (99,999 %) was purchased from Air Liquide. Carbon dioxide gas was purchased from Kraiss & Friz. All reagents were used without further purification. The PNNP-ligated ruthenium(II) catalyst was prepared according to literature.[1]

S2. General procedure for the hydrogenation of CO2 to DBU-formate.

The catalytic hydrogenation of CO2 was performed in a stainless-steel 100 mL autoclave. A Teflon inlet containing DBU (10.0021 g, 65.7 mmol), toluene (11 mL, 6 M), pentafluorophenol (151.3 mg, 1.25 mol% or 30 mg, 0.25 mol%, if necessary), catalyst (54.8 mg, 0.075 mol% or 10.9 mg, 0.015 mol%) and a stirrer bar was precooled in a liquid nitrogen bath under normal atmosphere. After introducing fresh prepared solid carbon dioxide (20 g) into the Teflon inlet, the liquid nitrogen bath was removed and H2 was introduced under 70 bar pressure. The autoclave was sealed and placed in a preheated aluminum block (100 °C). After 4 hours, the autoclave was cooled down to 5 °C in an ice bath and depressurized. The reaction mixture was degassed by stirring for 10 min at room temperature and solidified within 10 min. Afterwards the yield was analyzed by 1H-NMR to quantify the ratio of formic acid to DBU (NMR sample was taken under a stream of N2).


The catalytic decomposition of DBU-formate was performed in a flame-dried 10 mL Schlenk tube under an atmosphere of N2 and charged with DBU (5 mmol), formic acid (5 mmol), pentafluorophenol (11.5 mg, 1.25 mol% or none), and catalyst (4.2 mg, 0.075 mol%) in toluene (1.67 mL, 3 M). The system was connected to a volumetric cylinder and heated at 100 °C until gas evolution ceased. After full conversion the system was cooled down to 5 °C in an ice bath. GC samples were selectively taken from the gas mixture. No CO was observable.
**Figure S1.** The setup for collecting gas from the decomposition of DBU-formate.

**Figure S2.** The volumetric cylinder.

**Figure S3.** Concentration effects in the catalytic decomposition of DBU-formate. Reactions were performed with DBU-formate (1:1) mixture (5 mmol), catalyst (0.075 mol%) in toluene at 100 °C.
S4. The Investigation of the long-term storage stability. (Figure 4 in manuscript)

As described above in the procedure for the hydrogenation of CO₂ to DBU-formate adducts (S2), the reaction was performed with DBU (68.58 mmol) and catalyst (57.2 mg, 0.075 mol%) in toluene (11.4 mL, 6 M) for 1 hour. After depressurizing and degassing for 10 min at room temperature, the resulting 119% (the mole ratio of formic acid to DBU is 1.19 in ¹H-NMR) DBU-formate adduct was flushed with a nitrogen flow for 10 minutes and then kept in the autoclave at room temperature for 5 days (closed vessel). The reaction mixture was analyzed by ¹H NMR every day and NMR samples were taken under a stream of N₂. After storing for 5 days, the reaction mixture was decomposed to H₂ and CO₂ following the general procedure S3. The evolved gases were collected within 160 min and no CO was observable.

S5. General procedure for the CO₂-based H₂-battery: charging and discharging.

The charging/discharging experiments were performed in a stainless-steel 100 mL autoclave. 1ˢᵗ cycle: A Teflon inlet containing DBU (68.15 mmol), toluene (11.4 mL, 6 M), catalyst (56.8 mg, 0.075 mol%) and a stirrer bar was precooled in a liquid nitrogen bath under a normal atmosphere. After introducing fresh prepared solid carbon dioxide (20 g) into the Teflon inlet, the liquid nitrogen bath was removed and H₂ was introduced under 70 bar pressure. The autoclave was sealed and placed in a preheated aluminum block (100 °C). After the reaction time was over (1 hour), the autoclave was cooled down to 5 °C in an ice bath and depressurized. The reaction mixture was degassed by stirring for 10 min at room temperature and solidified within 10 min. Afterwards the yield was analyzed by ¹H-NMR to quantify the ratio of formic acid to DBU (NMR samples were taken under a stream of N₂). For the decomposition of DBU-formate, the autoclave was placed in a preheated aluminum block (100 °C) and connected to a volumetric cylinder (Figure S1). When the gas evolution was not observed, the autoclave was cooled down to 5 °C in an ice bath and the conversion was analyzed by ¹H-NMR (the NMR sample was taken under a stream of N₂). GC samples were selectively taken from the gas mixture. No CO was observable.

2ⁿᵈ (3ʳᵈ, 4ᵗʰ and 5ᵗʰ) cycles: The reaction mixture from 1ˢᵗ cycle was flushed with nitrogen flow for 10 minutes and kept in the autoclave at room temperature overnight (closed vessel). The autoclave was precooled down to 5 °C in an ice bath before slowly introducing fresh prepared solid carbon dioxide (22 g) into Teflon inlet under a stream of N₂. The liquid nitrogen bath was removed and H₂ was introduced under 70 bar pressure. The autoclave was sealed and placed in a preheated aluminum block (100 °C). Subsequently, the autoclave was placed in a preheated aluminum block (100 °C) and pressured with hydrogen (70 bar). After the reaction time was over (2.5 hour), the autoclave was cooled down to 5 °C in an ice bath and depressurized. The reaction mixture was degassed by stirring for 10 min at room
temperature and solidified within 30 min. Afterwards the yield was analyzed by $^1$H-NMR to
quantify the ratio of formic acid to DBU (the NMR sample was taken under a stream of $N_2$).
For the decomposition of DBU-formate to $H_2$ and $CO_2$, the procedure is as described above in
1$^{\text{st}}$ cycle.

**Caution**: For the 2$^{\text{nd}}$ to 5$^{\text{th}}$ cycle, solid carbon dioxide should be carefully introduced into the
teflon inlet. The reaction mixture bubbles vigorously because the autoclave was only
 precooled down to 5 °C in an ice bath.

![Figure S4. Representative $^1$H-NMR spectrum for the reduction of CO$_2$ to DBU-formate.](image-url)
Figure S5. Representative $^1$H-NMR spectrum after the decomposition of DBU-formate.

Table S1. List of experiments for 5 cycles of charging and discharging (Figure 3 in manuscript).\[^{[a]}\]

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Charging time [h]</th>
<th>Charging yield [%][^{[b]}]</th>
<th>Discharging time [h]</th>
<th>Gas volume [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st})</td>
<td>1</td>
<td>118</td>
<td>2.6</td>
<td>4130</td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>2.5</td>
<td>99</td>
<td>2</td>
<td>3434</td>
</tr>
<tr>
<td>3(^{rd})</td>
<td>2.5</td>
<td>98</td>
<td>1.85</td>
<td>3381</td>
</tr>
<tr>
<td>4(^{th})</td>
<td>2.5</td>
<td>104</td>
<td>2.4</td>
<td>3484</td>
</tr>
<tr>
<td>5(^{th})</td>
<td>2.5</td>
<td>105</td>
<td>2.5</td>
<td>3544</td>
</tr>
</tbody>
</table>

\[^{[a]}\] Reactions were conducted with DBU (68.15 mmol) and catalyst (56.8 mg, 0.075 mol-%) in toluene (11.4 mL, 6 M). \[^{[b]}\] The yield is based on DBU.

S6. General procedure for the generation of H$_2$/CO$_2$ pressure in a closed system. (Figure 5 [A] in manuscript)

As described above in the procedure of the hydrogenation of CO$_2$ to DBU-formate (S2), the reaction was performed with DBU (65.7 mmol) and catalyst (54.8 mg, 0.075 mol%) in toluene (11 mL, 6 M) for 4 h. The resulting 139 % (the mole ratio of formic acid to DBU is 1.39 in $^1$H-NMR) DBU-formate adducts were formed and subsequently the autoclave was sealed and placed in a preheated aluminum block (100 °C). Within three hours an internal pressure of 21 bar was build up. After 18 hours, the autoclave was cooled down to 5 °C in an ice bath and depressurized. The reaction mixture was analyzed by $^1$H-NMR to give 80 % of DBU-formate after 1\(^{st}\) run of decomposition. Heating up the closed vessel again allowed for another 10 bar pressure within 7 hours. After 18 hours, the reaction mixture was analyzed by $^1$H-NMR to give 46 % of DBU-formate after 2\(^{nd}\) run of decomposition.

S7. Gas evolution in the temperature-controlled system. (Figure 5 [B] in manuscript)

As described above in the procedure of the hydrogenation of CO$_2$ to DBU-formate adducts (S2), the reaction was performed with DBU (65.62 mmol) and catalyst (54.7 mg, 0.075 mol%) in toluene (10.9 mL, 6 M) for 3 h. The resulting 134 % (the mole ratio of formic acid to DBU is 1.34 in $^1$H-NMR) DBU-formate were formed and degassed by stirring for 10 min at room
temperature. Heat and cool the autoclave alternatively by placing in an aluminum block at 100 °C and an ice bath, respectively.

Note: During the cooling process, water was sucked back into the buffer flask from can. The volume of gas samples doesn’t change.

Figure S6. The setup for the temperature control system.

S8. Gas Determination.

Gas samples were measured by Agilent 7890A GC and the software EZChrom Elite 3.3.2 version was used. The GC was connected with a FID and TCD. Similar GC systems have been described in literature. In general, a ratio of carbon dioxide and hydrogen of 1:1 (±5%) was detected. The settings of TCD, inlet and columns are shown below:

**TCD** (T = 220 °C), reference flow: 20 mL/min He, makeup flow: 1 mL/min He, **Inlet** (T = 250 °C), pressure: 1 bar, septum purge: 3 mL/min He, split: 2 → 5.3244 mL/min He, **Columns**

- The first column (Gaspro 30 m x 0.320 µm) is used to separate CO₂ from the rest and the second one (molsieve 30 m x 0.320 µm) is used to separate the remaining gases.

S9. References.