Supporting Information

Manganese promoted (bi)carbonate hydrogenation and formate dehydrogenation: Towards a circular carbon and hydrogen economy

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Materials and methods

Unless otherwise stated, all reactions were conducted under an argon atmosphere and all reagents were purchased from commercial suppliers and used without further purification, including \textit{L}-lysine (fluorochem, 97\%), \textit{L}-arginine (Alfa Aesar, >98\%), \textit{L}-glutamic acid (TCI, >99\%), \textit{L}-aspartic acid (Sigma-Aldrich, >99\%), \textit{L}-histidine (Sigma-Aldrich, >99\%), glycine (Sigma-Aldrich, >99\%), succinic acid (Alfa Aesar, >99\%), propionic acid (Sigma-Aldrich, ≥99.5\%), sodium bicarbonate (Merck, >99\%), potassium bicarbonate (Sigma-Aldrich, ≥99.5\%), cesium bicarbonate (Alfa Aesar, >99\%), ammonium bicarbonate (Alfa Aesar, 98\%), lithium carbonate (thermo scientific, 99\%), sodium carbonate (Acros Organics, 99.8\%), potassium carbonates (Sigma-Aldrich, >99\%), rubidium carbonate (Strem, ≥99.8\%), cesium carbonate (Sigma-Aldrich, 99\%), ammonium carbonate (Fisher Scientific, ≥30\%), magnesium carbonate (thermo scientific, >99\%), calcium carbonate (fluorochem, 99\%), barium carbonate (Sigma-Aldrich, >99\%), lithium formate monohydrate (Acros Organics, 98\%), sodium formate (Acros Organics, 99\%), potassium formate (Sigma-Aldrich, >99\%), cesium formate (Sigma-Aldrich, 99\%), ammonium formate (thermo scientific, 97\%), Magnesium formate dihydrate (Fluka, ≥98\%), calcium formate (Sigma-Aldrich, ≥99\%), deuterium oxide (Deutero, D-99.9\%), H\textsubscript{2} (Air Liquide, grade 5.0) were used without further purification. Organic solvents were collected from an SPS machine and stored under argon with molecular sieve. THF without stabilizer and deionized (DI) water were used for hydrogenation and dehydrogenation reactions. Organometallic complexes \textit{Mn-1, Mn-2, Mn-3, Mn-4, Mn-5, Mn-6, Mn-7, Mn-8, Fe-1, Co-1} were synthesized according to the corresponding publications and stored under argon with light exclusion. No unexpected or unusually high safety hazards were encountered.

\textit{H} and \textit{C}\textsubscript{13}\{\textit{H}\} spectroscopy was recorded using Bruker AV 300 MHz and Bruker AV 400 MHz spectrometers. All NMR data in the experimental section are expressed as chemical shift in parts per million (ppm). \textit{H} and \textit{C}\textsubscript{13}\{\textit{H}\} chemical shifts were determined relative to the internal standard DMF at 7.92 ppm and 165.53 ppm in D\textsubscript{2}O, respectively. NMR spectra were interpreted and processed using MestReNova (version 14.0.1-23559). Gas chromatography (Agilent Technologies 7890A GC system, Carboxen / TCD) was used to analyze the content of the gas phase with a CO quantification limit of 10 ppm.
Standard procedure for catalytic hydrogenation of potassium bicarbonate

Potassium bicarbonate (KHCO$_3$, 10 mmol), Mn-2 (0.1 mg, 0.18 μmol), THF (5 mL) and H$_2$O (5 mL) were added to a 100 mL autoclave equipped with a magnetic stir bar. After pressurizing the reactor with H$_2$ (60 bar), the reaction mixture was heated and stirred on a pre-heated oil bath for 12 h. Then the reactor was cooled to r.t. and the inside pressure was carefully released. A biphasic reaction mixture was obtained containing a transparent organic upper layer and an aqueous yellow lower layer. Addition of DI water (ca. 3 mL) to the above mentioned mixture resulted in a homogeneous solution.$^{11}$ DMF (500 μL, 6.48 mmol) was added as an NMR internal standard to the reaction mixture, which was then analyzed by $^1$H NMR with ca. 0.1 mL D$_2$O to lock the signals.$^{12}$ Yield of formate is calculated by (mmol formate)/(mmol KHCO$_3$)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%).
Figure S1. Typical $^1$H NMR in D$_2$O after hydrogenation of KHCO$_3$ to formate catalyzed by Mn-2. DMF (500 μL, 6.48 mmol) as internal standard.

Figure S2. Typical $^{13}$C($^1$H) NMR in D$_2$O after hydrogenation of KHCO$_3$ to formate catalyzed by Mn-2. DMF (500 μL, 6.48 mmol) as internal standard.
Figure S3. Hydrogenation of potassium bicarbonate catalyzed by Mn-2: solvent screening. General conditions: KHCO₃ (10 mmol), Mn-2 (0.1 mg, 0.18 μmol), H₂O/organic solvent (5/5 mL), H₂ (60 bar), 90 °C, 12 h. Amount of formate is determined by ¹H NMR with DMF (500 μL, 6.48 mmol) as internal standard. Yield of formate is calculated by (mmol formate)/(mmol KHCO₃)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%).
Figure S4. Hydrogenation of various bicarbonate salts catalyzed by Mn-2. General conditions: bicarbonate salt (10 mmol), Mn-2 (0.1 mg, 0.18 μmol), H₂O/THF (5/5 mL), H₂ (60 bar), 90 °C, 12 h. Amount of formate is determined by ¹H NMR with DMF (500 μL, 6.48 mmol) as internal standard. Yield of formate is calculated by (mmol formate)/(mmol bicarbonate salt)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%).
Standard procedure for catalytic hydrogenation of potassium carbonate

Potassium carbonate (K₂CO₃, 10 mmol), Mn-2 (0.1 mg, 0.18 µmol), glutamic acid (10 mmol), THF (5 mL) and H₂O (5 mL) were added to a 100 mL autoclave equipped with a magnetic stir bar. After pressurizing the reactor with H₂ (60 bar), the reaction mixture was heated and stirred on a pre-heated oil bath for 12 h. Then the reactor was cooled to r.t. and the inside pressure was carefully released. A biphasic reaction mixture was obtained containing a transparent organic upper layer and an aqueous yellow lower layer. Addition of DI water (ca. 3 mL) to the above mentioned mixture resulted in a homogeneous solution. DMF (500 µL, 6.48 mmol) was added as an internal standard to the reaction mixture. The reaction mixture was then analyzed by ¹H NMR with ca. 0.1 mL D₂O to lock the signals. Yield of formate is calculated by (mmol formate)/(mmol KHCO₃)×100%.
**Figure S5.** Typical $^1$H NMR in D$_2$O after hydrogenation of K$_2$CO$_3$ to formate in the presence of glutamic acid (Glu) catalyzed by Mn-2. DMF (500 μL, 6.48 mmol) as internal standard.
Figure S6. Hydrogenation of potassium carbonates catalyzed by Mn-2 in the presence of various amount of glutamic acid. General conditions: potassium carbonate (K$_2$CO$_3$, 10 mmol), Mn-2 (0.1 mg, 0.18 μmol), glutamic acid (0-150 mol%), H$_2$O/THF (5/5 mL), H$_2$ (60 bar), 90 °C, 12 h. Amount of formate is determined by $^1$H NMR with DMF (500 μL, 6.48 mmol) as internal standard. Yield of formate is calculated by (mmol formate)/(mmol potassium carbonate)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%). The dotted lines serve as guides to the eye.
Figure S7. Mn-2 catalyzed hydrogenation of various carbonate salt in the presence of glutamic acid. General conditions: carbonate salt (10 mmol), Mn-2 (0.1 mg, 0.18 μmol), H₂O/THF (5/5 mL), H₂ (60 bar), glutamic acid (7.5 mmol), 90 °C, 12 h. Amount of formate is determined by ¹H NMR with DMF (500 μL, 6.48 mmol) as internal standard. Yield of formate is calculated by (mmol formate)/(mmol carbonate salt)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%). The dotted lines serve as guides to the eye.
Figure S8. Hydrogenation of various carbonate salts catalyzed by 5 μmol Mn-2 in the presence of Glu. General conditions: carbonate salt (10 mmol), Mn-2 (2.7 mg, 5 μmol), H₂O/THF (5/5 mL), H₂ (60 bar), Glu (75 mol%), 90 °C, 12 h. Amount of formate is determined by ¹H NMR with DMF (500 μL, 6.48 mmol) as internal standard. Yield of formate is calculated by (mmol formate)/(mmol carbonate salt)×100%. All experiments were performed at least twice; average values are shown (St. Dev.<10%).
**Table S1.** Effect of different acids on the formation of bicarbonate, CO$_2$, and carbamate starting from potassium carbonate.\[^a\]

\[
\text{CO}_3^{2-} + H^+ \xrightarrow{\text{H}_2\text{O (2 mL)}} \text{HCO}_3^- \xrightarrow{\text{H}_2\text{O}} \text{H}^+ + \text{CO}_2 + \text{H}_2\text{O}
\]

| Entry | Acid (H\(^+\))         | Bicarbonate | CO\(_2\) | Carbamate |
|-------|-------------------------|-------------|----------|-----------|
| 1     | Propionic acid          | 71%         | 8%       | 0         |
| 2     | Succinic acid           | 3%          | 95%      | 0         |
| 3     | Glutamic acid           | 51%         | 16%      | 26%       |

\[^a\] Conditions: K$_2$CO$_3$ (5.0 mmol), acid (5.0 mmol), H$_2$O (2 mL), r.t., 0.5 h. Yield of bicarbonate and carbamate were determined by $^{13}$C NMR-quant. Yield of CO$_2$ was determined by manual burette.
Standard procedure for catalytic dehydrogenation of potassium formate

Potassium formate (KHCO\textsubscript{2}, 5.0 mmol), catalyst, THF (5 mL) and H\textsubscript{2}O (5 mL) were added to a 50 mL pressure tube equipped with a magnetic stir bar. The reaction mixture was then heated and stirred on a pre-heated oil bath for 12 h. The mixture was cooled to r.t. and the inside pressure was released carefully to the manual burettes. A 5 mL degassed syringe was used to obtain a gas sample analyzed by gas chromatography (GC). CO is not detectable in all cases (below the CO quantification limit of 10 ppm). Yield of H\textsubscript{2} is calculated by (mmol H\textsubscript{2})/(mmol KHCO\textsubscript{2})×100%. TON of H\textsubscript{2} is calculated by (mmol H\textsubscript{2})/(mmol catalyst).

Calculation of the hydrogen volume, mole, yield, and the TON. The gas evolution was corrected with the blank volume (18 mL) which corresponds to the gas evolution of the same reaction without any catalyst.

H\textsubscript{2} volume \( V_{H_2} \) and CO\textsubscript{2} volume \( V_{CO_2} \) are calculated with the following equation:

\[
V_{H_2} = (V_{obs} - V_{blank}) \times \frac{\% V_{H_2}}{\% V_{H_2} + \% V_{CO_2}}
\]

\[
V_{CO_2} = (V_{obs} - V_{blank}) \times \frac{\% V_{CO_2}}{\% V_{H_2} + \% V_{CO_2}}
\]

Moles of H\textsubscript{2} \( n_{H_2} \) and moles of CO\textsubscript{2} \( n_{CO_2} \) are calculated with the following equation:

\[
n_{H_2} = \frac{V_{H_2}}{V_{m_{H_2}(25^\circ C)}}
\]

\[
n_{CO_2} = \frac{V_{CO_2}}{V_{m_{CO_2(25^\circ C)}}}
\]

Hydrogen yield \( Y_{H_2} \) is calculated with the following equation:

\[
Y_{H_2} = \frac{n_{H_2}}{n_{FA}} \times 100\%
\]

The turnover number (TON) of H\textsubscript{2} is calculated with the following equation:

\[
TON = \frac{n_{H_2}}{n_{cat}}
\]

Where:

- \( V_{obs} \) is the gas evolution volume of catalytic reaction measured in the manual burettes.
• $V_{\text{blank}}$ is the gas evolution volume of the blank reaction measured in the manual burettes.

• $\%V_H_2$ and $\%V_CO_2$ are the volume ratios of H$_2$ and CO$_2$, respectively, determined by GC.

• $n_{FA}$ and $n_{cat}$ are the moles of FA and catalyst, respectively.

• $V_{m_H_2(25^\circC)}$ and $V_{m_CO_2(25^\circC)}$ are the molar volumes of H$_2$ and CO$_2$ at room temperature (25 °C), respectively, calculated with the Van Der Waals equation, see table below:

| Calculation of H$_2$ molar volume $V_{m_H_2(25^\circC)}$ | Calculation of CO$_2$ molar volume $V_{m_CO_2(25^\circC)}$ |
|---------------------------------------------------------|---------------------------------------------------------|
| $V_{m_H_2(25^\circC)} = \frac{R \times T}{p} + b - \frac{a}{R \times T} = 24.48$ | $V_{m_CO_2(25^\circC)} = \frac{R \times T}{p} + b - \frac{a}{R \times T} = 24.36$ |

Where:

- $R = 8.3145 \text{ m}^3\text{·Pa·mol}^{-1}\text{·K}^{-1}$
- $T = 273.15 + \text{room temperature} (\text{°C}) \text{ K}$
- $P = 101325 \text{ Pa}$
- $a = 24.9 \times 10^{-3} \text{ Pa·m}^6\text{·mol}^{-2}$
- $b = 26.7 \times 10^{-6} \text{ m}^3\text{·mol}^{-1}$

- $R = 8.3145 \text{ m}^3\text{·Pa·mol}^{-1}\text{·K}^{-1}$
- $T = 273.15 + \text{room temperature} (\text{°C}) \text{ K}$
- $P = 101325 \text{ Pa}$
- $a = 36.5 \times 10^{-2} \text{ Pa·m}^6\text{·mol}^{-2}$
- $b = 42.7 \times 10^{-6} \text{ m}^3\text{·mol}^{-1}$
Figure S9. Catalytic dehydrogenation of potassium formate: catalysts screening in the absence of additives. General conditions: KHCO$_2$ (5.0 mmol), catalyst (0.1 mg), H$_2$O/THF (5/5 mL), 90 °C, 12 h. Volume and content of the gas phase from manual burettes were analyzed by gas chromatography (GC) after correction by the blank volume. CO is not detectable in all cases (below the CO quantification limit of 10 ppm). Yield of H$_2$ is calculated by (mmol H$_2$)/(mmol KHCO$_2$)×100%. The dotted lines serve as guides to the eye.
Figure S10. Catalytic dehydrogenation of various formate salts in the absence of additives. General conditions: formate salt (5.0 mmol), Mn-2 (2.7 mg, 5 μmol), H₂O/THF (5/5 mL), 90 °C, 12 h. Volume and content of the gas phase from manual burettes were analyzed by gas chromatography (GC) after correction by the blank volume. CO is not detectable in all cases (below the CO quantification limit of 10 ppm). Yield of H₂ is calculated by (mmol H₂)/(mmol KHCO₂)×100%. The dotted lines serve as guides to the eye.
Figure S11. GC chromatogram of blank reaction for the dehydrogenation of FA. Only argon was reported at retention time 8.122 min.
Figure S12. Typical GC chromatogram of potassium formate dehydrogenation in the absence of additives.
Figure S13. Typical GC chromatogram of potassium formate dehydrogenation in the presence of L-lysine (Lys).
Figure S14. Typical GC chromatogram of potassium formate dehydrogenation in the presence of L-glutamic acid (Glu).
Standard procedure for H₂ storage-release cycles starting from formate salts/Lys

The H₂ storage-release cycles starts from the dehydrogenation of formate salt (H₂-release): Mn-2 (5 μmol), formate salt (5.0 mmol), Lys, THF (5 mL) and H₂O (5 mL) were added to a 100 mL autoclave equipped with a magnetic stir bar. The reaction mixture was then heated and stirred on a pre-heated oil bath at 90 °C for 12 h. The reactor was cooled to r.t. and the inside pressure was released carefully to the manual burettes and the content of the gas phase was analyzed by gas chromatography (GC). CO is not detectable in all cases (below the CO quantification limit of 10 ppm). The autoclave was then filled with 60 bar of H₂, heated and stirred on a pre-heated oil bath at 90 °C for 12 h (H₂-storage). After the completion of H₂ storage, the reactor was cooled to r.t. and the inside pressure was released carefully. Then the autoclave was subjected to the H₂-release procedure again. Following such process, the H₂ evolution in the H₂ storage-release cycles were implemented with various formate salts.
**Table S2.** H₂ evolution yields in the H₂ storage-release cycles applying formate salt (5.0 mmol).[a]

| Substrate | Cycle | 1ˢᵗ  | 2ⁿᵈ  | 3ʳᵈ  | 4ᵗʰ  | 5ᵗʰ  | Formate salt[b] |
|-----------|-------|------|------|------|------|------|----------------|
| LiHCO₂    | 99    | 75   | 62   | 91   | 20   | 19   |                |
| NaHCO₂    | 99    | 78   | 71   | 58   | 48   | 45   |                |
| KHCO₂     | 96    | 85   | 83   | 80   | 77   | 68   |                |
| CsHCO₂    | 99    | 72   | 68   | 46   | 38   | 32   |                |
| NH₄HCO₂   | 99    | 89   | 57   | 32   | 21   | 19   |                |
| Ca(HCO₂)₂ | 99    | 58   | 48   | 36   | 29   | 21   |                |
| Mg(HCO₂)₂ | 100   | 68   | 58   | 45   | 39   | 30   |                |

[a] H₂ yields of each cycle are calculated based on the initial loading of formate salt (5 mmol). [b] Formate salt yields after the hydrogenation step of the final cycle, calculated based on the initial loading of formate salt (5 mmol).
**Figure S15.** Typical $^1$H NMR in D$_2$O of the H$_2$ cycles starting from formate salt and Lys. DMF (250 μL, 3.24 mmol) as internal standard.

**Figure S16.** Typical $^{13}$C($^1$H) NMR in D$_2$O of the H$_2$ cycles starting from formate salt and Lys. DMF (250 μL, 3.24 mmol) as internal standard.
Standard procedure for H₂ storage-release cycles starting from carbonate salts/Glu

The H₂ storage-release cycles start from the hydrogenation of carbonate salt (H₂ storage): Mn-2 (5 μmol), carbonate salt (5.0 mmol), Glu, THF (5 mL) and H₂O (5 mL) were added to a 100 mL autoclave equipped with a magnetic stir bar. After pressurizing the reactor with H₂ (60 bar), the reaction mixture was heated and stirred on a pre-heated oil bath for 12 h. Afterwards, the reactor was cooled to r.t. and the inside pressure was released carefully. The autoclave was then subjected to H₂ release process at 90 °C for 12 h. After the completion of the H₂ release step, the reactor was cooled to r.t. and the inside pressure was released carefully to the manual burettes and the content of the gas phase was analyzed by gas chromatography (GC). CO is not detectable in all cases (below the CO quantification limit of 10 ppm). Then the autoclave was subjected to the H₂ storage procedure again. Following such process, the H₂ evolution in the H₂ storage-release cycles were tested with various carbonate salts.
Table S3. H$_2$ evolution yields in the H$_2$ storage-release cycles applying carbonate salt (5.0 mmol).[a]

| Substrate          | Cycle | 1$^{st}$ | 2$^{nd}$ | 3$^{rd}$ | 4$^{th}$ | Formate salt$^{[b]}$ |
|--------------------|-------|----------|----------|----------|----------|---------------------|
| K$_2$CO$_3$ + Glu [50%] | 34    | -        | -        | -        | 22       |
| K$_2$CO$_3$ + Glu [75%]  | 96    | 58       | -        | -        | 41       |
| K$_2$CO$_3$ + Glu [100%]  | 94    | 87       | 72       | 49       | 36       |
| Li$_2$CO$_3$        | 98    | 89       | 53       | -        | 40       |
| Na$_2$CO$_3$        | 97    | 99       | 78       | 49       | 33       |
| Rb$_2$CO$_3$        | 100   | 76       | 66       | 40       | 25       |
| Cs$_2$CO$_3$        | 100   | 87       | 45       | -        | 29       |
| (NH$_4$)$_2$CO$_3$  | 93    | 53       | -        | -        | 38       |
| MgCO$_3$           | 67    | 53       | 33       | -        | 19       |
| CaCO$_3$           | 28    | -        | -        | -        | 12       |
| BaCO$_3$           | 33    | -        | -        | -        | 10       |

[a] H$_2$ yields of each cycle are calculated based on the initial loading of carbonate salt (5 mmol). [b] Formate salt yields after the hydrogenation step of the final cycle, calculated based on the initial loading of carbonate salt (5 mmol).
Figure S17. Typical $^1$H NMR in D$_2$O of the H$_2$ cycles applying carbonate salt and Glu. DMF (250 μL, 3.24 mmol) as internal standard.

Figure S18. Typical $^{13}$C($^1$H) NMR in D$_2$O of the H$_2$ cycles applying carbonate salt and Glu. DMF (250 μL, 3.24 mmol) as internal standard.
Figure S19. $^1$H NMR in D$_2$O of K$_2$CO$_3$ (10 mmol) hydrogenation applying H$_2$/CO$_2$ (60/10 bar), Mn-2 (0.18 μmol), H$_2$O/THF (5/5 mL), 90 °C, 12 h. Internal standard for NMR: DMF (500 μL, 6.48 mmol). Yield of formate is calculated by (mmol formate)/(mmol K$_2$CO$_3$ ×2)×100%.
Figure S20. $^{13}$C-quant NMR in D$_2$O after the first H$_2$ storage-release cycle applying K$_2$CO$_3$/Glu (5.0/5.0 mmol), Mn-2 (5 μmol), H$_2$O/THF (5/5 mL), 90 °C, 12 h. Internal standard for NMR: DMF (48 μL, 0.625 mmol).
Table S4. Comparison of CO$_2$ capture ability between K$_2$CO$_3$ and Lys.$[^a]$ 

| Entry | Substrate | CO$_2$ in carbamate [mmol] | CO$_2$ in bicarbonate [mmol] | total CO$_2$ captured [mmol]$[^b]$ |
|-------|-----------|-----------------------------|-------------------------------|----------------------------------|
| 1     | K$_2$CO$_3$ | 0                           | 1.8                           | 1.8                              |
| 2     | Lys       | 2.2                         | 0.7                           | 2.9                              |

$[^a]$ Conditions: K$_2$CO$_3$ or Lys (5.0 mmol), H$_2$O (5 mL), CO$_2$ (2 bar), r.t. (24 °C), 0.5 h. The captured CO$_2$ amount were calculated by gravimetric analysis. $[^b]$ Calculated by (mmol CO$_2$ in carbamates)+(mmol CO$_2$ in bicarbonate).

Table S5. Table of pH values.$[^a]$ 

| Compounds | K$_2$CO$_3$ (5.0 mmol) | KHCO$_2$ (5.0 mmol) | Glu (5.0 mmol) | K$_2$CO$_3$ + Glu (5.0 + 5.0 mmol) | KHCO$_2$ + Glu (5.0 + 5.0 mmol) |
|-----------|------------------------|---------------------|----------------|----------------------------------|----------------------------------|
| pH        | 12.1                   | 8.0                 | 3.2            | 7.9                              | 4.7                              |

$[^a]$ Conditions: compound (5.0 mmol), H$_2$O (5 mL), r.t. (24 °C). pH values were measured on a laboratory digital pH meter (Mettler-Toledo AG, SevenEasy pH 8603) at r.t. (24 °C).
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